BORON REMOVAL FROM AQUEOUS SOLUTIONS VIA POLYMER ENHANCED ULTRAFILTRATION USING NOVEL IMINO-BIS-PROPANE DIOL FUNCTIONAL POLYMERS

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BORON REMOVAL FROM AQUEOUS SOLUTIONS VIA POLYMER ENHANCED ULTRAFILTRATION USING NOVEL IMINO-BIS-PROPANE DIOL FUNCTIONAL POLYMERS

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ABSTRACT

BORON REMOVAL FROM AQUEOUS SOLUTIONS VIA POLYMER ENHANCED ULTRAFILTRATION USING NOVEL IMINO-BIS-PROPANE DIOL FUNCTIONAL POLYMERS

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In this work, newly synthesized poly (vinyl amino-N, N'-bis-propane diol) (GPVA) and copolymer, poly (vinyl amino-N, N'-bis-propane diol-*co*-DADMAC) (GPVA-*co*-DADMAC) were efficiently exploited for boron removal via polymer enhanced ultrafiltration (PEUF). Boron concentration could be reduced from 10ppm down to 0.4ppm using GPVA whereas it could be reduced from 10ppm down to 0.8ppm with copolymer GPVA-*co*-DADMAC at pH 9 and loading (boron-to-polymer mass ratio) 0.001 via continuous polymer enhanced ultrafiltration (PEUF). Experiments revealed that GPVA shows the highest PEUF boron retentions (96% at pH 9.0) reported so far, without precipitation in a wide concentration range. Detailed investigations such as effect of pH, loading and polymer concentration showed that, the boron binding is highly pH dependent and increases with polymer concentration at constant loading for all the synthesized polymers. Furthermore, permeate flux was found as nearly independent of polymer concentration within the range of parameters studied (polymer concentration≤10g/L; pressure drop: 200kPa). High pH and concentration dependency of boron binding makes it possible to have polymer regeneration and boron recovery. In addition, gyration radius of GPVA in solution increases with increasing pH and polymer concentration in the presence of boron as inferred from Dynamic and Static Light Scattering measurements. Furthermore, a two-step equilibrium model was correlated with the experimental boron retention data, to explain the compexation behavior of polymer. Regarding with high efficiency and hydrolytic stability of the synthesized polymers, their use in combination with PEUF would be of interest for large scale and long term use in boron removal.

Key words: Boron removal; polymer enhanced ultrafiltration; binding model; polymer boron complexation; polychelatogen.

ÖZ

İMİNO-BİS-PROPAN DİOL FONKSİYONLU YENİ POLİMERLER KULLANARAK POLİMER KOMPLEKSLEMELİ ULTRAFİLTRASYON YÖNTEMİ İLE SULU ÇÖZELTİLERDEN BOR AYIRIMI

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Bu çalışmada, yeni poli (vinil amino-N, N'-bis-propan diol) (GPVA) ve poli (vinil amino-N, N'-bis-propan diol-*co*-DADMAC) (GPVA-*co*-DADMAC) polimerleri sentezlendi ve bunlardan polimer komplekslemeli ultrafiltrasyon (PKUF) yöntemi ile bor ayırımı için verimli bir şekilde faydalanıldı. Kesiksiz PKUF yöntemi ile pH 9 ve yükleme (bor-polimer kütle oranı) 0.001 için bor konsantrasyonu, GPVA kullanıldığında 10ppm değerinden 0.4ppm değerine GPVA-*co*-DADMAC kullanıldığında ise 10ppm değerinden 0.8ppm değerine düşürülebildi. Yapılan deneylerin sonucunda GPVA' nın geniş bir konsantrasyon aralığında çökelme olmadan şimdiye kadarki en yüksek PKUF bor alıkonmasını (pH 9'da 96%) sağladığı görülmüştür. pH, yükleme ve polimer konsantrasyonunun etkileri gibi detaylı incelemeler, gösterdi ki tüm sentezlenen polimerler için bor bağlanmasının yüksek derecede pH'a bağlı olduğunu ve sabit yüklemede polimer konsantrasyonunun artması ile arttığını göstermiştir. Bunların yanı sıra, süzüntü akısının çalışılan deneysel şartlarda (polimer konsantrasyonu ≤ $10 g.L^{-1}$; basınç düşümü: 200kPa) polimer konsantrasyonundan hemen hemen bağımsız olduğu bulundu. Bor bağlanmasının pH ve konsantrasyona yüksek bağlılığı polimer rejenerasyonu ve bor geri kazanımını mümkün kılabilmektedir. Bunlara ek olarak, Dinamik ve Statik Işık Saçılımı ölçümlerinin gösterdiği üzere, çözeltideki GPVA polimerinin jirasyon çapı bor varlığında pH ve konsantrasyon arttıkça artmaktadır. İki basamaklı bir denge modeli deneysel bor alıkonma verileri ile bağıntılandırılarak polimerin kompleksleşme davranışı açıklanmıştır. Sentezlenen polimerlerin yüksek verim ve hidrolize karşı kararlılığı göz önüne alındığında, PKUF yönteminde kullanılmaları büyük ölçekli ve uzun süreli bor ayırımı için cazip görünmektedir.

Anahtar Kelimeler: Bor ayırımı; polimer komplekslemeli ultrafiltrasyon; bağlanma modeli; polimer bor kompleksleşmesi; polişelatojen.

To my wife Gül Zerze

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AAS	Atomic Absorption Spectrometry
AMPD	2, 2-Azo-bis (2-methyl propionamidine) dihydrochloride
C_i^F	Conentration of species i in the feed (mol.L^{-1})
C_i^P	Conentration of species i in the permeate (mol.L^{-1})
CA	Cellulose acetate
CEUF	Complexation Enhanced Ultrafiltration
CoEUF	Colloid Enhanced Ultrafiltration
Da	Dalton
DADMAC	Diallyl dimethyl ammonium chloride
D&SLS	Dynamic and Static Light Scattering
GPVA	Poly (vinyl amino-N, N’-bis-propane diol)
GPVA-*co*-DADMAC	Poly (vinyl amino-N, N’-bis-propane diol-*co*-DADMAC)
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
K_A	Acid dissociation constant of protonated amine groups
K_B	Acidity constant of boric acid
K_C	Equilibrium constant for boron-polymer complexation
L_{mass}	Loading (g boron / g polymer in feed solution)
L_{molar}	Loading (mol boron / mol polymer in feed solution)

m	Reaction order with respect to repeating units in the polymer chain
MEUF	Micellar Enhanced Ultrafiltration
MF	Microfiltration
M_P	Average molecular weight of repeat units in macromolecular chain ($g.mol^{-1}$)
M_V	Viscosity average polymer molecular weight ($g.mol^{-1}$)
MWCO	Molecular Weight Cut-Off ($g.mol^{-1}$)
NF	Nanofiltration
PA	Polyamide
PEI	Polyethylenimine
PES	Polyethersulfone
PEUF	Polymer Enhanced Ultrafiltration
PNS	Hydroxyethylamino glycerol functioned polyglycidyl methacrylate
PS	Polysulfone
PVDF	Polyvinylidene fluoride
R	Retention
R_B	Retention of boron in the absence of any polymer
RC	Regenerated cellulose
RF	Radio Frequency
R_g	Radius of gyration, (nm)
RO	Reverse Osmosis
RSD	Relative Standard Deviation
TOC	Total Organic Carbon
UF	Ultrafiltration
x_{DADMAC}	Number fraction of DADMAC segments in macromolecular chain

$\left[B(OH)_3\right]$	Molar concentration of non-bound boric acid in the feed (mol.L^{-1})
$\left[B(OH)_4^-\right]$	Molar concentration of non-bound borate anion in the feed (mol.L^{-1})
$\left[H^{\div}\right]$	Molar concentration of hydrogen ions in the feed
$[P]$	Molar concentration of non-bound repeat units in the feed (mol.L^{-1})
$[PB]$	Molar concentration of complexed repeat units in the feed (mol.L^{-1})

Greek Symbols

$\boldsymbol{\alpha}$	The fraction of the total polymer repeating units in non-protonated form
$[\boldsymbol{\eta}]$	Intrinsic viscosity
$\boldsymbol{\eta}_{\mathbf{sp}}$	Specific viscosity

Subscripts

P	Polymer
B	Boron

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CHAPTER 1

INTRODUCTION

Boron is a vital element since it is involved in some metabolic reactions such as carbohydrate metabolism, sugar translocation, pollen germination, hormone action, normal growth and functioning of the apical meristem, nucleic acid synthesis, membrane structure and function and cell wall crosslinking [1]. Moreover, photosynthesis is inhibited by its deficiency which may stunt the plant growth [2].

Despite being an essential micronutrient, its excess contamination in water slightly over the essential levels, may cause detrimental impacts on crops as well as on human health. When allowable boron concentration is exceeded in irrigation water, boron poisoning can occur; which can be recognized by yellow spots on the leaves [2]. Although safe concentration levels may differ from one type of vegetation to another, it is around 1ppm in general. The relevant restrictions in boron concentration of irrigation water were reported in the literature for various plants [3]. Furthermore, it was reported in 2011 WHO (World Health Organization) guidelines that boron concentration of potable water should not be above 2.4ppm level [4].

Boron is an indispensable element and is used in many important industrial areas such as manufacture of glass, ceramics, soap, detergents, pharmaceutics, cosmetics, fire retardants and controlling fission in nuclear reactors [3, 5]. Therefore, its contamination in industrial effluents is usually inevitable. In addition, water can be naturally contaminated by boron since it exists in mines, seas and geothermal water sources [6]. Boron concentration in these sources usually exceeds the permitted levels, especially in Turkey. In order to illustrate this, ranges of some important parameters are given for 41 different water resources in Table 1.1. Moreover, potable and irrigation water demand increases whereas suitable water sources diminish inevitably [7]. Therefore, boron should be removed from wastewater or natural streams in order to prevent its negative impacts on the environment.

Table 1.1. Ranges of some important parameters of water from 41 different resources in Denizli geothermal regions (Extracted from the data set obtained from ORME JEOTERMAL A.Ş. in 09.10.2008)

Temperature (^oC)	**pH**	**Boron Conc. (ppm)**	**SO_4^{2-} Conc. (ppm)**	**Cl^- Conc. (ppm)**
25 - 242	5.8 - 9.4	0.9 – 63.0	32 - 4700	8 - 187

1.1. Membrane Processes

Although traditional separation methods have been extensively used for removal of hazardous compounds, membrane technologies have replaced them in a large number of applications. Suitability for scale-up and integration to other separation processes, minimal energy consumption, moderate separation conditions and existence of a variety of membrane material and properties are among the main profits of membrane separation processes. On the other hand, membrane processes may possess some drawbacks such as concentration polarization, fouling and short membrane lifetimes [8].

Membranes are semipermeable barriers which separate two mediums from each other. They can be either porous or dense. Porous membranes allow the passage of molecules or particles from the voids in the membrane structure while in dense membranes transfering molecules penetrate through the dense molecular network. Performance of a membrane separation is characterized by permeate flux and retention. Permeate flux refers to permeate flow rate per unit membrane area. Percent retention, on the other hand, is expressed by Eqn. 1.

$$\%R = 100\left(1 - \frac{C_i^P}{C_i^F}\right) \qquad \text{(Eqn. 1.)}$$

where C_i^P and C_i^F are concentrations of species *i* in permeate and feed streams, respectively.

The transfer of molecules across the membrane can be induced by different driving forces: they can be driven by difference in pressure, concentration or electric field each being a component of chemical potential [8].

1.2. Pressure Driven Membrane Processes

In pressure-driven membrane processes, a pressure difference in two sides of the membrane is established and separation is achieved according to size exclusion by the membrane. Species which are larger in size (for porous membranes) or which have less solubility and diffusivity inside the membrane (for dense membranes) can more difficultly pass across it. Pressure-driven membrane processes can be classified as below according to the size of the molecule(s) or particle(s) which are to be separated:

- Microfiltration (MF)
- Ultrafiltration (UF)
- Nanofiltration (NF)
- Reverse Osmosis (RO)

General specifications of the four pressure-driven membrane processes are represented in Table 1.2. Both microfiltration and ultrafiltration membranes are porous membranes. Pore size of the microfiltration membranes is in the range between roughly 0.05µm and 4µm. In ultrafiltration, on the other hand, membranes with pore sizes between roughly 0.005µm and 0.05µm are used. Although there is not a clear transition between the pore sizes of ultrafiltration and microfiltration membranes, they are distinguished from each other by the structure of the target species. That is, microfiltration is used for separating particles or microorganisms whereas ultrafiltration is used for separation of macromolecules from solution.

Table 1.2. General specifications of four different pressure-driven membrane processes.

Specifications	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Pore size	0.05-4μm	0.005-0.05μm	Dense	Dense
Pressure difference	Less than 2 bar	1-10 bar	5-35 bar	15-150 bar
Membrane materials	PVDF, CA, RC	PES, PS, CA, PVDF	CA, PA	CA, PA
Target species	Separation of microorganisms and colloids	Separation of macromolecules	Separation of ions with multi-valency	Separation of ions with single valency

Nanofiltration and Reverse osmosis membranes are dense (non-porous) membranes. Separation is achieved due to the differences in solubility and diffusivity of different molecules inside the membrane matrix.

It is worth noting that size of the target molecule determines the type of the membrane process to be employed and required transmembrane pressure difference increses as membrane pore size decreases. This may imply that separation of smaller molecules require higher operating costs. This observation led to the idea that small molecules can be attached to larger species in order to achieve separation with a membrane of large pores and by this way flux can be increased while a much less energy for the same separation becomes adequate. This can also enable selective separation of species with similar sizes. This idea is in the origin of separation techniques called as Complexation Enhanced Ultrafiltration Processes.

1.3. Complexation Enhanced Ultrafiltration Processes

Complexation Enhanced Ultrafiltration (CEUF) is a general term for ultrafiltration processes prior to which a target molecule is attached to a much larger molecule or a colloid. The aim of this process is to separate small molecules by much less transmembrane pressure differences and to have higher fluxes than nanofiltration. This process can be classified according to the complexation agent as Micellar Enhanced Ultrafiltration (MEUF), Colloid Enhanced Ultrafiltration (CoEUF) and Polymer Enhanced Ultrafiltration (PEUF).

In MEUF, surfactant molecules composed of hydrophilic and hydrophobic parts are dissolved in water and they construct large structures known as micelles above a certain concentration called critical micelle concentration. These large structures attract target molecules and attach to them in aqueous solution and the ultrafiltration performed after this complexation provides separation of these complexes. The main disadvantage of this technique is that high amounts of surfactant is needed in order to form micelles.

In CoEUF, colloids are used to bind ions or organic solutes prior to ultrafiltration. Colloids are generally small charged particles of metal oxides. Using charged membranes is an important factor for CoEUF processes [9]. The main disadvantage of CoEUF is that selectivity of a certain ion cannot be achieved against the other ions in the solution [10].

1.4. Polymer Enhanced Ultrafiltration (PEUF)

Polymer Enhanced Ultrafiltration (PEUF) is a new promising membrane separation technique which combines homogeneous polymer complexation with ultrafiltration. Water soluble polymeric ligands having specific functional groups form complexes with target compounds and then these complexes are separated from aqueous solution by ultrafiltration.

This technique is seen as appropriate for dilute aqueous solutions. Moreover, there are a variety of polymers proven to be effective for separation of specific compounds in PEUF studies [11-15]. Selective separation can be achieved by the synthesis of target-specific functional polymers. In the polymer synthesis, functionalities of special adsorbents may be imitated in which their water-soluble counterparts can be obtained to employ in PEUF processes. Thus, the drawbacks of mass-transfer resistance may be avoided by providing a homogeneous complexation medium [16]. Herein, loading ratio refers to target species-to-polymer mass ratio within the feed solution. It is an operational parameter which can be formulated as:

$$L = \frac{C_i^F}{C_P^F} \qquad \text{(Eqn. 2.)}$$

where C_P^F denotes mass concentration of polymer dissolved in feed.

1.5. Functional Polymers

Functional polymers can be synthesized in two ways: either by synthesizing a monomeric ligand and then polymerizing it (a) or by attaching functional groups to an appropriate polymer (b). These two possible ways are illustrated in Figures 1.1.a and 1.1.b respectively.

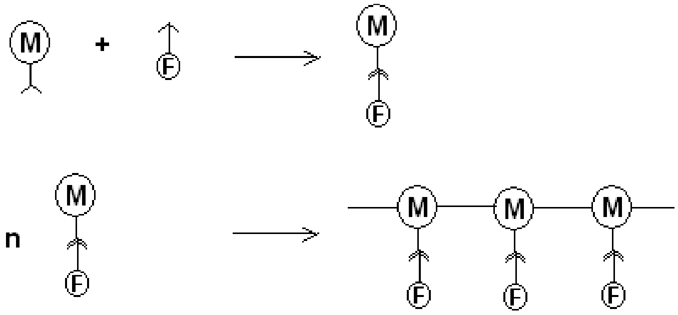


Figure 1.1.a. Representative scheme for the synthesis of monomeric ligand and polymerization of this monomer to obtain a functional polymer. M and F stand for the monomer and the molecule which provides functionality, respectively.

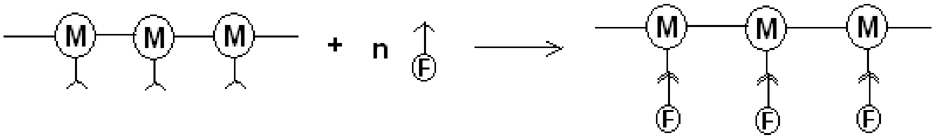


Figure 1.1.b. Representative scheme for the addition of functional unit to an existing polymer to obtain a functional polymer. M and F stand for the monomeric unit and the molecule which provides functionality, respectively.

Polymer-metal complexation can be in two different mechanisms: Polymers may attract ions by ionic interactions or they may form coordination bonds [17].

Polymers of the former case are sorted as polyelectrolytes while the ones of the latter as polychelatogens or chelating polymers [18]. Use of polyelectrolytes in PEUF may be undesirable due to the lack of selectivity. Chelating polymers are generally preferrable since target specific affinity can be achieved by synthesizing polymers with suitable functional groups. Amines, carboxylic acids, amides, alcohols, aminoacids, pyridines, thioureas, iminos are among the most studied chelating ligands [18]. In Figure 1.2, complexatation of polyvinyl alcohol with boric acid is shown as an example for polychelatogen complexation [19].

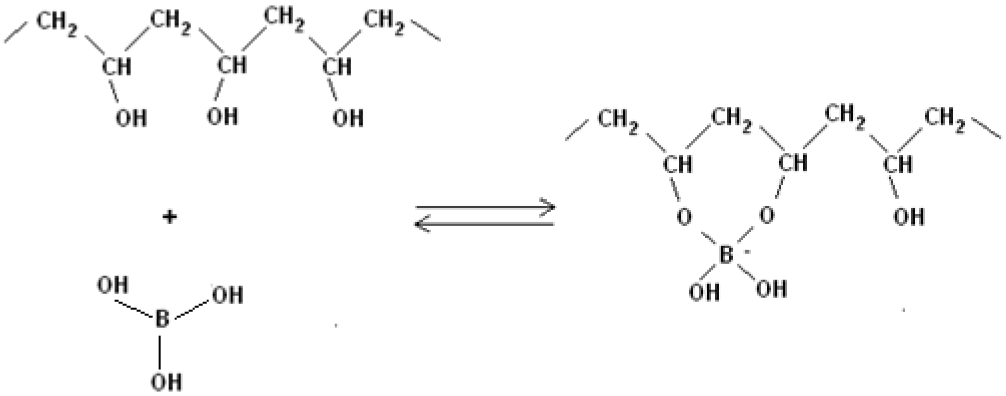


Figure 1.2. Polyvinyl alcohol-boric acid reaction as a representative polychelatogen complexation [19].

As seen in Figure 1.2, hydroxy groups in the polymer are responsible for the selective complexation with boric acid. In order to compare polychelatogens with polyelectrolytes, ionic bond between protonated polyethyleneimine and borate anion [13] is represented in Figure 1.3 as an example to polyelectrolyte complexation. As seen in this figure, attraction of the polyelectrolyte can be towards any anion which brings no selectivity for borate.

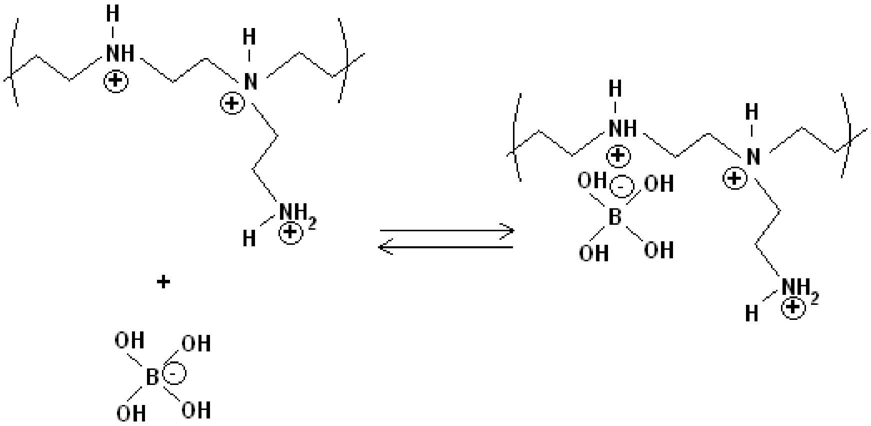


Figure 1.3. Ionic interaction between protonated polyethyleneimine and borate as a representative polyelectrolyte complexation.

Functional polymer is the main issue in the success of PEUF studies. In the design of a functional polymer; there are some important criteria to consider. These criteria are mainly selectivity for a specific ion, solubility, reversibility in complexation reaction, molecular weight and stability of the polymer.

Selectivity is the degree of affinity of the polymer to the target compound in comparison with the other species inside the solution. This is an important criteria in polymer design mainly because the affinity of the polymer to other ions may cause a decrease in the extent of separation of the target ion by blocking the functional groups of the polymer. Selectivity can be achieved by synthesizing suitable polychelatogens as complexation agents. Polymers with high solubility are preferrable since a wide range of loading values can be attainable in that case. Moeover, risk of coagulation can be prevented when highly water-soluble polymers are used. In PEUF, decomplexation of the polymer-ion complex is also important for a suitable polymer recovery. Hence, the reversibility of the complexation is important. The direction of the complexation reaction is adjustable by a parameter such as pH. Polymer molecular weight determines directly the pore size of the ultrafiltration membrane to be used since polymer molecules should always be larger than the pores in order to prevent the passage of them across the membrane. From this perspective, polymers with high molecular weight mean large pores and thus high fluxes. Moreover, in order to prevent the blokage of the pores by macromolecules, there should be a significant difference between the size of the pores and the size of the polymer molecules. However, polymers with high molecular weight have the disadvantage of low solubility. Stability of a polymer is a measure of its lifespan during which it can be used repeatedly. Polymers should be stable against extreme pH. Thus, synthesizing polymers which has non-hydrolizable groups is a requirement for long term usage. Otherwise, there is a risk for the polymer molecules to permeate across the membrane due to decrease in molecular weight.

1.6. Chemistry of Boron

Boron is found mostly in the form of boric acid and borate salts in the environment. There is a chemical equilibrium between these two species [19]:

$$H_3BO_3 + H_2O \overset{K_B=9.14}{\rightleftharpoons} B(OH)^-_4 + H_3O^+$$

This reaction implies that borate concentration is high at high pH values. Figure 1.4 represents the percent boron in the form of boric acid with respect to pH of the solution.

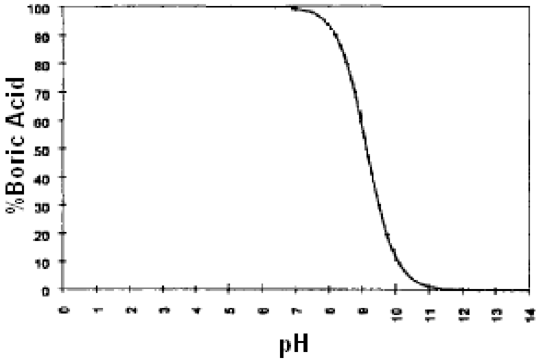


Figure 1.4. Change of boric acid percent with pH of the solution [20].

A very important point is that boric acid has valence orbital that can make coordination bond with a proper functional polymer unlike borate anion. On the other hand, borate anions take part only in the ionic interactions with the charged locations –if any- of the functional polymer. In other words; borate anion form is not able to make coordination bond since it has no valence orbital. However, borate-to-boric acid ratio in the original solution may not affect significantly the complexation through coordination bond formation due to a potential shift to boric acid from borate anion as complexation proceeds. In fact, the effect of pH on complexation is most probably dominated by the change in the conformation of the polymer molecules by pH.

1.7. Aim and Scope of the Study

In the scope of this study, suitable water soluble functional polymers, poly (vinyl amino-N, N'-bis-propane diol) (GPVA) and copolymers, poly (vinyl amino-N, N'-bis-propane diol-*co*-DADMAC) (GPVA-*co*-DADMAC) were synthesized as efficient boron-chelating polymers with high and selective boron affinity. These novel polymers were characterized and used for boron removal from water via

PEUF process, at low concentrations. For the synthesized polymers, effects of operational parameters i.e. pH, loading, polymer concentration at constant loading and molecular weight on boron retention were investigated in order to find the optimum conditions for boron removal by PEUF. In addition, effect of other ions such as chloride and sulfate on boron retention was investigated so as to find the selectivity of the polymers for complexing boron. Thereafter, in an effort to question the real applications of the proposed technique, boron removal studies were conducted with geothermal water samples. As a part of commercial application, decomplexation experiments were conducted also.

CHAPTER 2

LITERATURE SURVEY

Various methods have been studied for boron removal from water such as chemical precipitation, extraction, adsorption, ion exchange, and several membrane processes. A detailed review of the related techniques was elaborated by Jiang (2008) [3].

Chemical precipitation is a separation process based on formation of slightly soluble complexes of the target species by introducing suitable chemicals. Numerous precipitating agents were studied for boron removal [3]. One of those agents is lime by which boron could be diluted down to 400ppm corresponding to the solubility of the precipitating complex [3]. Thus, chemical precipitation may not be suitable for dilute feed solutions since the precipitating species has a certain solubility below which target species cannot be diluted. Metal salts were also used for boron precipitation, which necessitated highly alkaline medium [3]. But excessive use of caustic for this need may bring an additional operational cost. Moreover, handling solid waste and the highly alkaline solution would be a great concern which may limit the application of precipitation for large scale boron removal.

Several boron extractors were prepared by dissolving special boron-binding chemicals in water-immiscible solvents [3, 21-24]. Bicak (2003) presented *N*,*N*-Bis(2,3-dihydroxypropyl) octadecylamine (BPO) in 2-ethyl hexanol as an efficient boron extractor [21]. This process has been considered as an efficient way of boron recovery, but not suitable when removal at low concentrations is targeted [21]. Moreover, in extraction processes, rate is limited to external mass transfer and organic solvents may pose an environmental threat when used in large scale water treatment.

Adsorption is another boron removal process and numerous adsorbents were experimented [25-30]. Bicak et.al. (1998) chemically impregnated sorbitol to a polymeric support as a boron binding ligand [30]. Despite its high boron binding capacity (70% of the theoretical capacity), regeneration procedure was repeated four times by acid treatment for complete boron desorption [30]. 1-(2-hydroxylethylamino)-2,3-propanediol functional resin beads were prepared by Gazi et.al. (2008) and were demonstrated to adsorb boron within 2 min. with a capacity of 3.29 mmol.g^{-1} which corresponds to the maximum theoretical value for that resin [31]. A polymeric boron adsorbent possessing 2-hydroxylethylamino propylene glycol functions was also synthesized and used in boron removal [32]. However in those studies, highly acidic solution (4M HCl) was required for 98% [31] and 95% [32] boron release during the regeneration of these particles.

Strong-base anion exchange resins have widely been studied for boron removal [2, 33-37]. Nadav (1999) embedded N-methyl glucamine on macroporous polystyrene in order to use in further removal of boron from permeate of sea water reverse osmosis [2]. In that study, 5% hydrochloric acid or 5%sulfuric acid was used in the regeneration step. Moreover, ion-exchange may not be suitable for solutions with rich ionic content since anionic contaminants other than borate may also be exchanged by the resin and this may result in an inefficient and uneconomical separation process [33], with low selectivity. Furthermore, application of ion-exchange may have some limitations concerning post-treatment of regeneration effluent [3].

Boron separation from dilute aqueous solutions has been performed also with traditional membrane techniques such as nanofiltration [38], reverse osmosis [6, 38] and electrodialysis [39]. However, these separation techniques may be disadvantageous due to two main reasons: selective separation cannot be achieved and they are expensive processes due to high electrical consumption. Besides, the retention can decrease due to other ions in the solution when electrodialysis is applied [40].

Polymer Enhanced Ultrafiltration (PEUF) is one of the promising alternative boron separation processes [11-14]. PEUF possesses several inherent advantages and may eliminate some of the drawbacks of traditional removal methods. In comparison with RO and NF, higher permeate fluxes are targeted with appreciably lower operational pressure and thus promises lower energy cost [16]. Furthermore, selective separation can be obtained by synthesizing target-specific chelating polymers. Functionalities of special adsorbents may be imitated by the synthesis of their water-soluble counterparts in order to use in PEUF processes. Thus, the drawbacks of mass-transfer resistance may be prevented by providing a homogeneous medium for complexation [16].

Based on those benefits, PEUF has been used successfully for removal of numerous target species [11-16, 18, 41-47] most of which are cations. Also, many studies on boron separation were conducted via PEUF process [11-14, 16, 44].

In a previous study [12], polyvinyl alcohol polymers with different degrees of hydrolysis were used for boron removal via continuous PEUF process and, effects of pH, loading, polymer molecular weight and degree of hydrolysis on boron retention were investigated. Retention values were higher for higher pH values between 7 and 10. Loading values lower than 0.002 could not be studied due to solubility problem of polyvinylalcohol. Maximum boron retention was reported as 28%. Thereafter, specially tailored polymers were synthesized by researchers [11, 13, 16, 44].

Hydroxyethylamino glycerol functioned polyglycidyl methacrylate (PNS) and poly (4-Vinyl-1, 3-dioxalan-2-one-*co*-vinyl acetate) (COP) were synthesized and used previously for boron removal by Doğanay et.al. [16]. Effects of pH, loading, polymer structure and molecular weight on boron retention were investigated. It was found that boron retention rises considerably with increasing pH. Maximum retention was obtained with PNS as 57% (loading: 0.001 and pH: 9.0). However, difficulties in dissolution of polymer at higher concentrations, prevented studies at lower loading values [16].

Bowman et.al. synthesized hyperbranched boron chelating polymers and used those in PEUF studies [11]. However, in the same study, some drawbacks of the functional polymer were reported: polymer gelation was observed upon complexation with boron and approximately one-third of the dendrimeric polymer was lost in four cycles of separation-regeneration due to undesirable acid-hydrolysis of the amide linkages involved.

In Smith B. F. et.al. [13]; three different polymers, which were synthesized from polyethyleneimine functionalized with three different ligands yielding monool, diol and triol groups, were used for boron complexation [13]. It was reported that boron retention decreased with increasing boron concentration for 1% of polymer mass fraction and the process was suggested for recovery of enriched boric acid used in the coolant loop of nuclear reactors rather than its removal [13]. However, the obtained permeate boron concentrations were higher than the boron concentration limits for discharge streams. It was found that boron binding was due to both ionic attraction of protonated amine groups with borate anions and ester formation between hydroxy groups and boron. In complexation with polymer having monool functionals, ester formation did not contribute to boron binding while ester formation is significant for polymers having diol and triol functionals. This may imply that it is essential to synthesize polymers which have at least two hydroxy groups available in each repeated unit for one boron atom.

The studies which are shortly mentioned above on boron separation via PEUF have shown that PEUF can be a suitable technique for boron removal. However, it is needed to design and synthesize more suitable polymers which possess non-hydrolyzable linkages, high water solubility and highly pH dependent reversible boron complexation property. Effect of other ions on the performance of boron separation should be studied and efforts for real boron removal applications should be elaborated. Furthermore, enhacement of polymer conformation and solubility during the synthesis has never been addressed.

CHAPTER 3

MODELING OF PEUF EXPERIMENTS

Boron retention results were exploited in order to find a useful model for equilibrium constant of boron-polymer complexation. The relevant reactions are assumed to be as depicted in Figure 3.1. In this study, two-competitive-interaction of boric acid was proposed, in the first, boric acid dissociates in water, while in the second it forms neutral chelate with imino-bis-propane diol functions of the polymer.

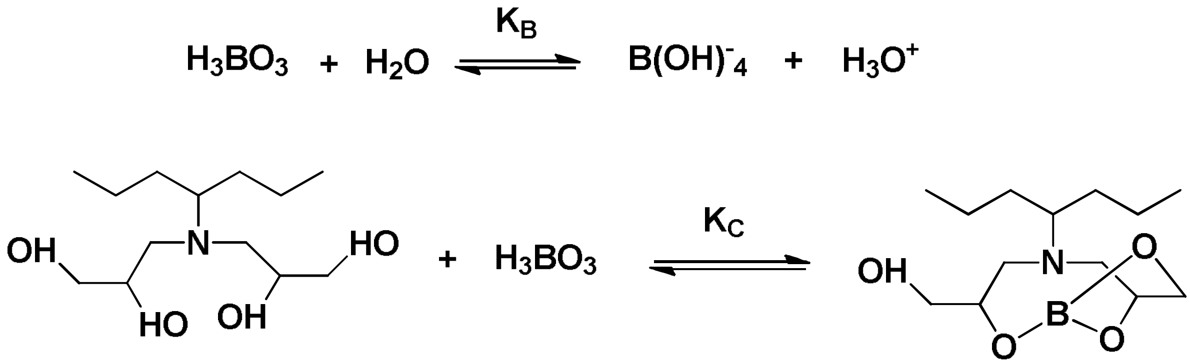


Figure 3.1. Boric acid-borate equilibrium and boron chelation with imino-bis-propane diol functional polymer.

Boric acid-borate equilibrium is already well-known from literature and expressed as (Eqn. 3.1) [19, 20]:

$$K_B = \frac{\left[B(OH)_4^-\right]\left[H^+\right]}{\left[B(OH)_3\right]} \qquad \text{(Eqn. 3.1)}$$

As reported by Belcher (1970), complexation reaction was assumed to be first order with respect to boric acid and mth order with respect to free complexation sites (denoted as P) on polymer whereas decomplexation reaction was assumed to be first order with respect to boron-complexing sites (denoted as PB) on the macromolecule (Eqn. 3.2) [48].

$$K_C = \frac{[PB]}{[P]^m\left[B(OH_3)\right]} \qquad \text{(Eqn. 3.2)}$$

Mole balances for boron (Eqn. 3.3) and complexation sites (Eqn. 3.4) can be formulated as follows:

$$C_B^F = \left[B(OH)_4^-\right] + \left[B(OH_3)\right] + [PB] \qquad \text{(Eqn. 3.3)}$$

$$C_P^F\left(1 - x_{DADMAC}\right) = [P] + [PB] = \left(1 - x_{DADMAC}\right) \times \frac{C_B^F}{L_{molar}} \qquad \text{(Eqn. 3.4)}$$

Where C_B^F (Eqn. 3.3) is total molar concentration of boron in feed, C_P^F is molar concentration of repeating units, L_{molar} denotes molar loading which is expressed by $L_{molar} = C_B^F / C_P^F$, and x_{DADMAC} (Eqn. 3.4) represents ratio of DADMAC repeating units which are assumed not to complex boron. Since experimental loading values are reported as mass ratio (L_{mass}) in this study, they are converted to molar loading, L_{molar} by using molecular weight of boron (M_B=10.8 g/mole) and average molecular weight of polymer repeating unit (M_P) by Eqn. 3.5. Average molecular weight of polymer repeating unit, M_P can be calculated by molecular weight of DADMAC and imino-bis-propane diol groups as shown in Eqn. 3.6.

$$L_{molar} = \frac{M_P}{M_B} \times L_{mass} \qquad \text{(Eqn. 3.5)}$$

$$M_p = 191\left(1 - x_{DADMAC}\right) + 162 x_{DADMAC} \qquad \text{(Eqn. 3.6)}$$

It is important to note that concentrations of all species on the feed-side of the membrane surface are assumed to be the same as the feed concentrations, since concentration polarization is negligible and operation is carried out at total recycle mode.

Boron retention values in the presence of polymer are found experimentally and expressed as:

$$R = 100\left(1 - \frac{C_B^P}{C_B^F}\right) \qquad \text{(Eqn. 3.7)}$$

Where C_B^P denotes molar concentration of boron in permeate. Possibility of free boron retention, R_M by membrane itself, is not omitted in this model and thus concentration of non-complexed boron species may differ from boron concentration in the permeate solution. The corresponding equation which relates free boron concentration in feed to the one in permeate (Eqn. 3.9), can be derived from the definition of R_M (Eqn. 3.8) which can be determined experimentally in the absence of the polymer. In the model, R_M is assumed to be independent from the presence of macromolecules.

$$R_M = 100\left(1-\frac{C_B^P}{\left[B(OH)_4^-\right]+\left[B(OH)_3\right]}\right) \qquad \text{(Eqn. 3.8)}$$

$$\left[B(OH)_4^-\right]+\left[B(OH)_3\right]=\left(\frac{100-R}{100-R_M}\right)C_B^F \qquad \text{(Eqn. 3.9)}$$

Since boric acid and borate anion are in equilibrium in aqueous solution with an acidity constant K_B, the ratio of the fractions of two species can be related to pH and K_B:

$$pK_B = -\log\left(\frac{\left[B(OH)_4^-\right]}{\left[B(OH)_3\right]}\right)+pH \qquad \text{(Eqn. 3.10)}$$

$$\frac{\left[B(OH)_4^-\right]}{\left[B(OH)_3\right]}=10^{pH-pK_B} \qquad \text{(Eqn. 3.11)}$$

Combining Eqn. 3.9 and Eqn. 3.11, one can obtain the equations expressing concentrations of borate anion (Eqn. 3.12) and boric acid (Eqn. 3.13).

$$\left[B(OH)_4^-\right]=\frac{10^{pH-pK_B}}{1+10^{pH-pK_B}}\left(\frac{100-R}{100-R_M}\right)C_B^F \qquad \text{(Eqn. 3.12)}$$

$$\left[B(OH)_3\right] = \frac{1}{1+10^{pH-pK_B}}\left(\frac{100-R}{100-R_M}\right)C_B^F \qquad \text{(Eqn. 3.13)}$$

The value, [PB] (Eqn. 3.14) can be found by solving Eqn. 3.3 and Eqn. 3.9, simultaneously.

$$\left[PB\right] = \left(\frac{R-R_M}{100-R_M}\right)C_B^F \qquad \text{(Eqn. 14)}$$

Knowing [PB], values of [P] can easily be calculated by Eqn. 3.4. Hence, all the unknowns except m in the expression for the complexation constant defined in Eqn. 3.2 can be calculated at a given pH value knowing R_M and R. In order to find out the value of K_C and m, logarithms of both sides of the Eqn. 3.2 is taken:

$$\log K_C = \log\left(\frac{[PB]}{\left[B(OH_3)\right]}\right) - m\log[P] \qquad \text{(Eqn. 3.15)}$$

$$\log\left(\frac{[PB]}{\left[B(OH)_3\right]}\right) = \log K_C + m\log[P] \qquad \text{(Eqn. 3.16)}$$

Therefore, if one plots $\log\left(\frac{[PB]}{\left[B(OH)_3\right]}\right)$ vs. $\log[P]$ at a specific pH, the slope and the intercept will give m and $\log K_C$, respectively.

CHAPTER 4

MATERIALS AND METHODS

4.1. Materials

In the polymer synthesis, N-Vinyl formamide (Aldrich 98%) monomer was freshly purified via vacuum distillation with hydroquinone. 2, 2-Azo-bis (2-methyl propionamidine) dihydrochloride (AMPD) (Aldrich) was used as the water soluble initiator. N,N-diallyl N,N-dimethyl ammonium chloride (DADMAC) (Aldrich, 65% aqueous solution) was used as comonomer. Glycidol (Accross) was freshly distilled under vacuum before use. Other chemicals which were used as purchased were methanol (Lab Scan HPLC grade), acetone (Lab Scan HPLC grade), isopropanol (Lab Scan HPLC grade), NaOH powder (Merck), hydrochloric acid (HCl, %37 aqueous solution, Merck).

Microfiltration membrane (Osmonics Sepa RH02, pore size: 0.8µ, pH range: 5-13) and ultrafiltration membrane (Millipore Regenerated Cellulose, MWCO: 10kDa, pH range: 2-13) were used for fractionation and purification of the polymer. In continuous ultrafiltration experiments; polyether sulfone membrane (Osmonics Sepa YMPTSP1905, flow area: 155cm^2, MWCO: 5kDa, pH range: 2-11), poly sulfone membrane (Osmonics Sepa YMERSP1905, flow area: 155cm^2, MWCO: 20kDa), poly sulfone membrane (Osmonics Sepa HG19, flow area: 155cm^2, MWCO: 20kDa) were used. Boric Acid (Merck), potassium chloride (J.T. Baker) and sodium sulfate powder (J.T. Baker) were other chemicals for solution preparation. Solutions for pH control were prepared from NaOH (Merck) and HNO_3 (Merck). In batch-mode experiments, polyether sulfone membrane (Osmonics Sepa YMPTSP1905, flow area: 155cm^2, MWCO: 5kDa, pH range: 2-11) was used. Ultrapure water with a specific conductance of 18.3μΩcm^{-1} was obtained by a water purification system (Human RO&UP Water Purification Systems) and geothermal water sample was obtained from discharge of Balçova Geothermal Source in İzmir. For the calibration of pH-meter, commercial buffer solutions (J.T. Baker) were used.

Geothermal water was filtered with 0.45µm cellulose acetate membrane filters (C045A047A Membrane Filtration Systems) before use. Aqueous samples were filtered with 0.45µm syringe filters (Minisart RC 25 Sartorius Stedim) before analysis. For the preparation of HPLC mobile phase citric acid (Merck) and ammonia (J.T. Baker) were used.

4.2. Equipment

Polymerization was carried out inside a three-necked glass flask with a back-coolant assembly. Stirring and temperature control was maintained by a heater-stirrer set-up (Heidolph MR HEI Standard). Polymerization set-up is demonstrated in Figure 4.1. Polymer purification and fractionation was carried out in batch ultrafiltration cell (Amicon-Millipore Model 8050). Ubbe-Lohde type viscosimeter was used for viscosity average molecular weight determination. The dynamic and static light scattering (D&SLS) measurements were performed by ALV/CGS-3 Compact Goniometer System. ^{1}H-NMR spectra of polymers were obtained by a Bruker 250 MHz NMR spectrometer and ^{13}C-NMR spectrum was obtained by a Bruker 80 MHz NMR spectrometer using D_2O as solvent. FT-IR spectra were recorded by Perkin Elmer FT-IR Spectrum One B spectrometer.

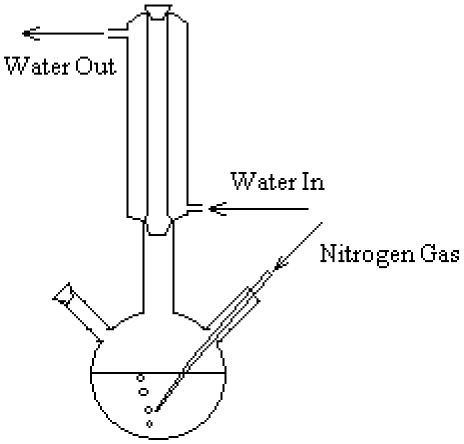


Figure 4.1. Polymerization set-up with a back-coolant assembly.

Continuous ultrafiltration set-up is shown in Figure 4.2. The set-up mainly consists of water bath (1), feed tank (2), pH-meter (3), feed pump (4) which is equipped with a by-pass valve (5), flow-meter (6), Osmonics Sepa CF Membrane Cell (7), UF membrane (8), pressure gauge (9), Cell holder (10), pressurized air (11), back-pressure valve (12), permeate line (13) and retentate line (14).

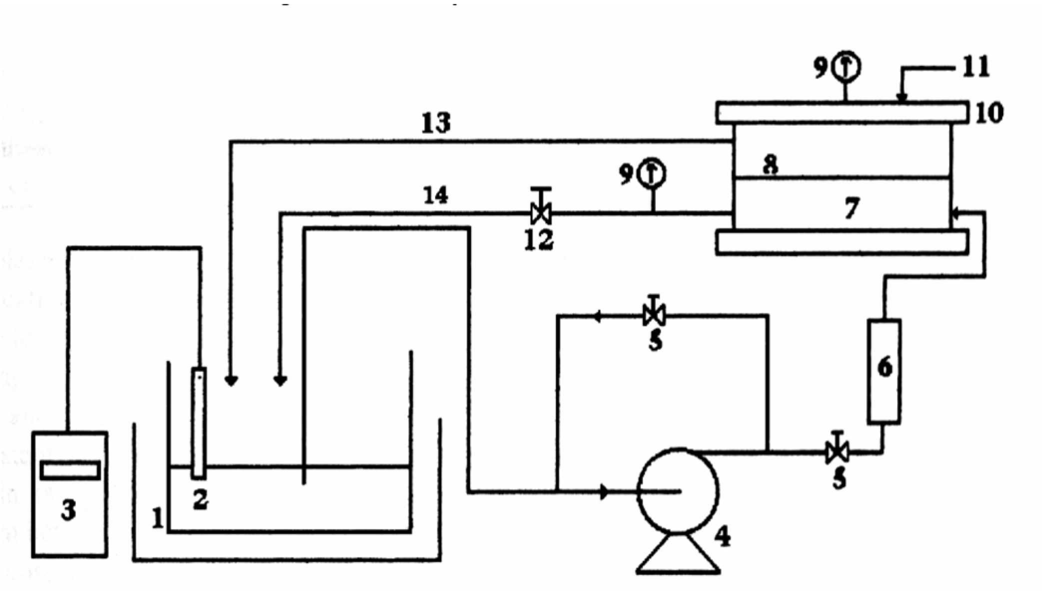


Figure 4.2. Continuous ultrafiltration set-up [15].

Batch mode ultrafiltration equipment composed of an ultrafiltration cell (Amicon-Millipore Model 8050) with a capacity of 300mL. Commercial Nitrogen tank was connected to the batch cell for supplying high pressure. A magnetic stirrer is included in the system for well mixing and preventing polymer accumulation on membrane. This set-up is illustrated in Figure 4.3.

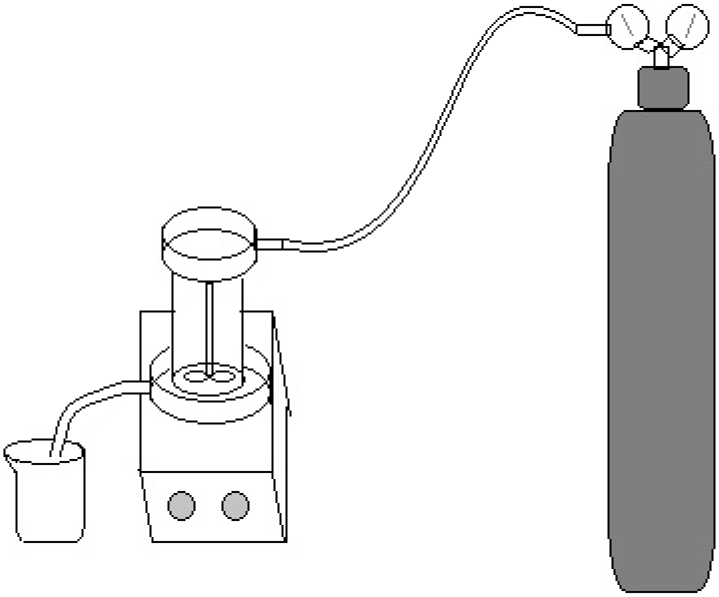


Figure 4.3. Batch Ultrafiltration Set-up

Solution pH and temperature were monitored by a pH-meter (WTW 315 i). Boron concentrations were measured by Direct Reading Echelle Inductively Coupled Plasma Optical Emission Spectrometer (DRE ICP-OES Leeman Labs Inc.). Carbon analysis was conducted by a Total Organic Carbon Analyzer (Shimadzu TOC-V CPH). Chloride analysis was performed in HPLC set-up which consists of Conductivity Detector (Waters 432), HPLC Pump (Waters 1525) and Anion Exchange Column (IC Pak Anion HR 4.6x75 WAT026765). A UV-Spectrophotometer (Shimadzu UV-1201) was used for sulfate analysis. Lithium, sodium and potassium in geothermal water were analyzed with a flame photometer (Jenway PFP7). An atomic absorption spectrometer (Shimadzu AA-6300) was used for determination of calcium, magnesium and silicon concentrations in geothermal water.

4.3. Polymer Synthesis and Purification

4.3.1. Synthesis of GPVA

4.3.1.1. Polymerization of N-vinyl formamide

30.2g (425 mmoles) of distilled N-vinyl formamide was dissolved in 67g water in a three-necked glass flask which was then combined with a back coolant assembly as shown in Figure 4.1. Nitrogen gas was passed through this solution to get rid of oxygen gas and 0.38g (1.40 mmoles) initiator (2, 2-Azo-bis (2-methyl propionamidine) dihydrochloride) was dissolved in this solution which was being stirred with magnetic stirrer. Reaction temperature was set to 65°C. Relevant reaction is shown in Figure 4.4. Polymerization ended in 1.5h. Polyvinyl formamide was precipitated with acetone and dried in vacuum oven at 60°C in one hour.

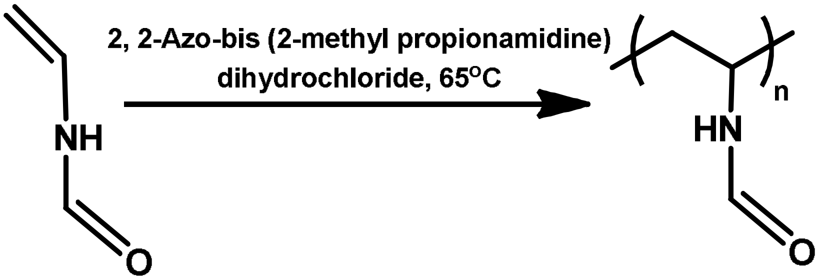


Figure 4.4. Polymerization of N-vinyl formamide.

4.3.1.2. Basic hydrolysis of polyvinyl formamide

230g sodium hydroxide aqueous solution (55% by weight) was prepared and slowly poured into the aqueous polyvinyl formamide solution while it is being stirred. Polyvinyl amine was obtained as a white precipitate according to the reaction shown in Figure 4.5. The aqueous base solution is poured away and the polymer was dried with a drying paper.

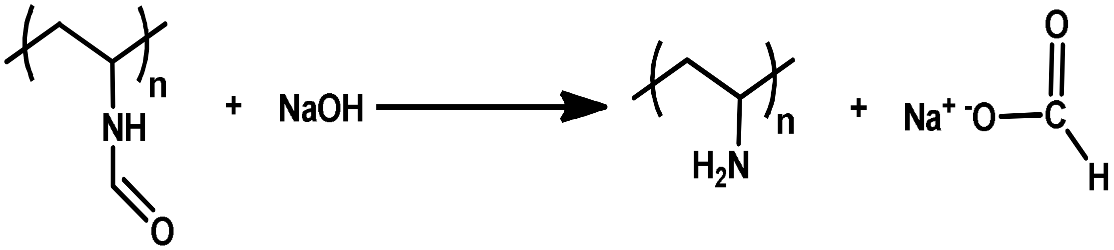


Figure 4.5. Basic hydrolysis of polyvinyl formamide to form polyvinyl amine.

4.3.1.3. Glycidole addition

Polyvinyl amine was dissolved in 150mL water. 100mL glycidole was taken to dropping funnel and it was added drop by drop very slowly (approximately 1 drop/ 3seconds) while viscous polymer solution was being mechanically stirred. During this glycidole addition, exothermic reaction caused an increase in temperature of the medium. It was immersed in ice bath at that instant and glycidole addition was continued. The reaction of GPVA formation is as shown in Figure 4.6.

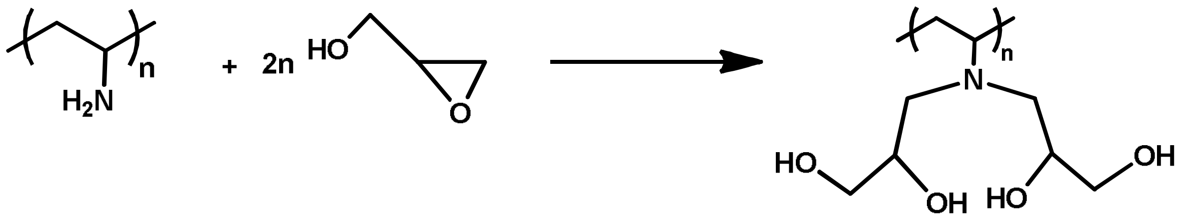


Figure 4.6. Formation of GPVA via functionalization of polyvinyl amine with glycidole.

4.3.2. Synthesis of GPVA-*co*-DADMAC copolymers

GPVA-*co*-DADMAC were synthesized in three different DADMAC number percent (2%, 5% and 10%). Synthesis of GPVA-*co*-2%DADMAC is prescribed in details while the synthesis of GPVA-*co*-5%DADMAC and GPVA-*co*-10%DADMAC were carried out according to the same prescription except for using corresponding amount of DADMAC solution in the polymerization step.

4.3.2.1. Copolymerization of N-vinyl formamide and DADMAC

44mL distilled water, 28.4g (400 mmoles) of N-vinyl formamide and 2.0g of commercial DADMAC solution (Aldrich, 65% aqueous solution) were mixed in a three-necked glass flask. 4.08 mmoles of 2, 2-azo-bis-(2-methyl propionamidine) dihydrochloride (AMPD) (Aldrich) was dissolved in the monomer solution while nitrogen gas was being bubbled through the solution. After the set-up was equipped with a back-coolant assembly, the heater temperature was adjusted to 65^{o}C and the copolymerization ended in 2 hours. The related reaction is presented in Figure 4.7.

For purification of the resulting copolymer poly (N-vinyl formamide-*co*-DADMAC), acetone was used for precipitation and water was used as solvent. Precipitation-dissolution cycles were repeated three times. Then, the copolymer was dried at 45°C under vacuum.

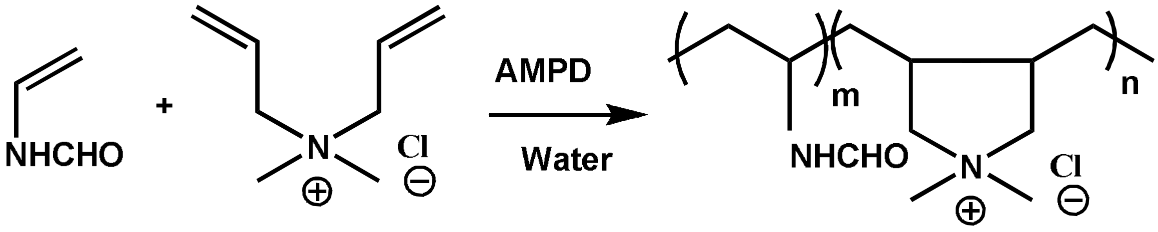


Figure 4.7. Copolymerization of N-vinyl formamide and DADMAC.

4.3.2.2. Formation of poly (vinyl amine-*co*-DADMAC) via acidic hydrolysis

23.4g dry poly (N-vinyl formamide-*co*-DADMAC) was dissolved in 35 mL water. 70g of hydrochloric acid solution (Merck, %37 aqueous solution) was slowly added to the polymer solution while stirring. Hydrolysis reaction was maintained overnight at 75°C in a glass flask combined with a back-coolant assembly. Poly (vinyl amine-*co*-DADMAC) was obtained according to the reaction shown in Figure 4.8. The acidic aqueous solution was decanted and the wet polymer was dissolved in 15mL water. Since the amine groups should be in non-protonated form for efficient glycidole addition, the solution was taken to ice-bath and treated dropwise with 25g of 70% NaOH solution. The precipitated polymer was taken and dried with a drying paper.

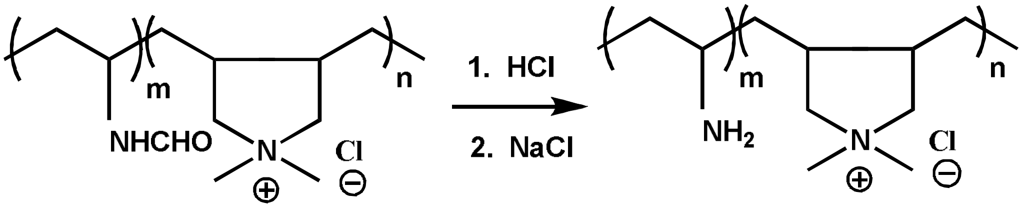


Figure 4.8. Hydrolysis of poly (N-vinyl formamide-*co*-DADMAC).

4.3.2.3. Formation of GPVA-*co*-DADMAC

15.2g poly (vinyl amine-*co*-DADMAC) was dissolved in 120 mL water. 100 mL distilled glycidole was transferred into a dropping funnel and then added slowly (~1drop/3seconds) to the polymer solution while being stirred. The solution was immersed in ice bath in order to prevent temperature increase due to exothermic reaction. Formation reaction of GPVA-*co*-DADMAC is depicted in Figure 4.9.

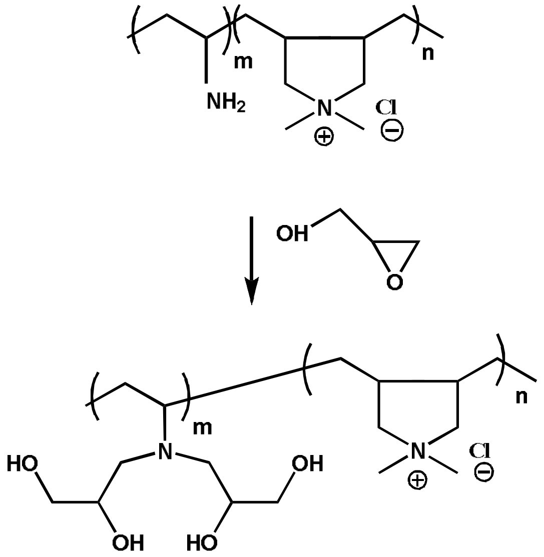


Figure 4.9. Modification of poly (vinyl amine-*co*-DADMAC) with glycidol for preparing the boron chelating polymer.

It was determined that GPVA-*co*-DADMAC was a water soluble polymer, as predicted. For purification via repeated dissolution and precipitation, isopropanol was found to be a suitable non-solvent for the polymer after many trial-errors. However, membrane separation was employed for further purification as described in the following part.

4.3.3. Purification and fractionation of polymers

Aqueous polymer solution of 15g.L^{-1} was prepared. Small gel particles were filtered from the solution using microfiltration membrane (Osmonics Sepa RH02, pore size: 0.8µ). Then, low molecular weight compounds were removed from the solution by ultrafiltration (Millipore Regenerated Cellulose, MWCO: 10kDa, pH range: 2-13), which was driven by 300kPa pressure drop until one tenth of the initial solution volume remained inside the UF cell.

4.4. Ultrafiltration Experiments

4.4.1. Continuous Mode

Desired amount of polymer was dissolved in approximately 1L ultra pure water. Boric acid was then added to the polymer solution. After that, the pH of the solution was adjusted by adding droplets of previously prepared solutions of pH control agents which are 0.1M sodium hydroxide and 0.1M nitric acid solutions. The solution was kept stirred for at least 1.5 hours. Then pH was again brought to the set-value by pH control agents if needed. The solution was ultrafiltered continuously in total recycle mode in other words sending the retentate and permeate streams back to the feed solution.The aim is to keep the feed concentration constant during the 4 hours of experiment and to ensure obtaining the steady state results. Solution pH was kept appreciably close to the set-value using the same pH control solutions during the ultrafiltration. Polyether sulfone membrane (Osmonics Sepa YMPTSP1905) with 5 kDa molecular weight cut-off was used in the experiments and recommended operational pH range by the manufacturer is between 2 and 11. Ultrafiltration pressure difference and feed flow rate were 200 kPa and 0.063 m^3/h, respectively. Solution temperature was kept constant at 25±2°C during both complexation and UF. Samples were taken from both the feed solution and the permeate stream for boron and carbon analysis. In order to calculate the permeate flux value, permeate volume was divided to effective membrane area ($0.0155m^2$) and to the time elapsed to collect that volume of permeate.

4.4.1.1. Boron removal from binary solution via PEUF

Depending on the desired polymer concentration, a predetermined amount of polymer was dissolved in ultrapure water (~ 1L). Boric acid (Merck) was dissolved in this solution resulting in $10mg.L^{-1}$ boron. Potassium chloride or sodium sulfate was also dissolved in the same solution so that desired anion concentration was obtained (sulfate: $100mg.L^{-1}$, chloride: $10mg.L^{-1}$ or $100mg.L^{-1}$). Then, solution pH was adjusted by adding droplets of previously prepared sodium hydroxide (0.1M) and nitric acid (0.1M) solutions as pH controlling agents. The resulting feed solution was stirred and kept at the set-value of pH using the same acid and base solutions when needed. At least 1.5 hours of period was devoted for this complexation. Polyether sulfone membrane (Osmonics Sepa YMPTSP1905, MWCO: 5kDa) was placed inside the UF compartment and the system was compressed at 5bar (gauge) using nitrogen gas in order to prevent any undesired leakage from the closed UF cell. Continuous PEUF runs were carried out in total recycle mode in which retentate and permeate streams were sent into the feed solution for providing a constant feed concentration during the four hours of UF run. Thus, the steady state results could easily be determined. Throughout each UF run, solution pH was monitored by a pH-meter (WTW 315i). UF pressure drop was adjusted as 200kPa by back-pressure valve and feed flow rate was maintained at 0.063 m^3/h. Temperature of the feed solution could be measured from the same pH-probe and it was kept at 25±2^{o}C during both complexation and UF. For the analysis of boron, carbon, chloride and sulfate, samples were collected from both the feed and permeate solutions at the end of each hour.

4.4.1.2. Pretreatment of geothermal water before PEUF Experiments

40L of geothermal discharge water was collected from İzmir Balçova region in two plastic containers and stored at 4^{o}C. Prior to use, required amount was filtered with cellulose acetate membrane filters (C045A047A Membrane Filtration Systems, pore size: 0.45μm) under vacuum below 10^{o}C. This procedure was carried out before the analysis and the PEUF experiments in order to discard non-dissolved particles and thus to prevent any possible damage both to the membrane and to the measurement instruments. Table 4.1 shows the physicochemical characteristics of this filtered water taken from two separate containers.

Table 4.1. Physicochemical characteristics of filtered water sample from Balçova Geothermal in İzmir (at 25 ^{o}C) (Sample was collected in 27.03.2010)

Parameter	Unit	Container 1	Container 2
pH	-	7.9	7.8
Conductivity	uS	1870	1822
Total Carbon	mg.L^{-1}	134	136
Inorganic Carbon	mg.L^{-1}	131	134
B	mg.L^{-1}	12.9	12.6
Si	mg.L^{-1}	61	60
Na^+	mg.L^{-1}	412	407
K^+	mg.L^{-1}	33	36
Li^+	mg.L^{-1}	1.4	1.2
Ca^{2+}	mg.L^{-1}	1.9	2.2
Mg^{2+}	mg.L^{-1}	0.3	0.4
SO_4^{2-}	mg.L^{-1}	123	116
Cl^-	mg.L^{-1}	252	245

4.4.1.3. Boron removal from geothermal water via PEUF

Desired amount of polymer was dissolved in geothermal water (~ 1L). Some of the experiments were performed at the original pH of the resulting solution, for some, the solution pH was adjusted by using sodium hydroxide (0.1M) or nitric acid (0.1M) solutions. For complexation, the solution was stirred at the set pH and at 25^{o}C for at least 1.5 hours. Continuous UF was conducted as described in part 4.4.1.

4.4.2. Batch Mode

Some of the experiments were conducted in batch-mode. Amicon Millipore (Model 8050) membrane cell was used in these experiments. The solution preparation and pH adjustment steps before UF and the membrane used were the same as in the continuous mode. However, the feed volume is approximately 300mL and except for the initial adjustment, pH control could not be performed during ultrafiltration since the system is always pressurized. Pressure drop was kept at 200kPa. Samples of 20mL were collected from permeate stream for boron analysis and duration was noted for each sample collection in order to determine permeate flux. Samples from feed side were also taken both at the beginning and at the end of the ultrafiltration for measurements of boron concentration.

4.5. Measurements

4.5.1. Estimation of polymer molecular weights

Using Mark-Houwink constants $K=5.43\times10^{-4}$ and $\alpha=0.715$ [49], molecular weight of polyvinyl formamide was calculated from the intrinsic viscosity $[\eta]$ according to the following equation:

$$[\eta] = K.M_V^{\alpha} \qquad \text{(Eqn. 4.1)}$$

where M_V is viscosity average molecular weight of the polymer. In order to find the intrinsic viscosity, specific viscosity η_{sp} of its aqueous solutions are found at different concentrations with Ubbe-Lohde viscosimeter, divided by the polymer concentration to give reduced viscosities η_{red} and then extrapolated to zero concentration. Since the number of repeating units do not change during functionalization, the molecular weight of poly (vinyl amino-N, N'-bis-propane diol) (GPVA) was calculated by multiplying the molecular weight of polyvinyl formamide with 2.69, which is the ratio of molecular weights of GPVA to polyvinyl formamide with the same number of repeating units.

4.5.2. Concentration measurements

Boron concentrations of the feed and the permeate samples were analyzed by Direct Reading Echelle Inductively Coupled Plasma Optical Emission Spectrometer (DRE ICP-OES Leeman Labs Inc.). Signal wavelength, RF power and pump flow rate were 249.773nm, 1.1kW and 1.1mL/min, respectively. Standard solutions for feed and permeate samples were prepared separately since they have different matrix. The feed calibration solutions were prepared in water with different boron concentrations and with the same amount of polymer as in the feed samples in order to compensate for the effect of polymer on measurement [41]. On the other hand, the permeate calibration solutions were solely boric acid solutions with different concentration values. Intensity of the signals for both the standards and the samples were recorded and a linear calibration curve was plotted in order to obtain the relation between the concentration and intensity. For obtaining linear calibration curves, analysis concentration range was taken up to 15ppm. Samples which are supposed to be more than 15ppm were diluted before analysis and the results were multiplied by the ratio of dilution.

Polymer amounts of the feed and the permeate samples were measured by a Total Organic Carbon Analyzer (Shimadzu TOC-V CPH) in order to verify that permeate is free of polymer. TOC readings for both feed and permeate samples were compared for each ultrafiltration run.

Concentrations of chloride in binary solutions were measured by Conductivity Detector (Waters 432) in HPLC set-up equipped with IC Pak Anion HR Column (WAT026765). Citric acid-ammonia buffer was prepared at pH 9.0 to use as mobile phase. Chloride concentrations in geothermal water were determined by titration with aqueous $AgNO_3$ solution with potassium dichromate as indicator. Sulfate concentrations were determined by a UV-Spectrophotometer (Shimadzu UV-1201) using cuvette test (Hach Lange LCK153) at 440nm.

4.5.3. Dynamic and static light scattering (D&SLS) measurements

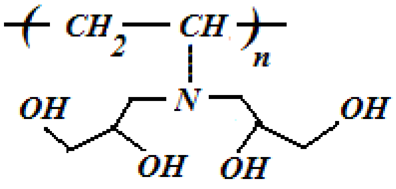
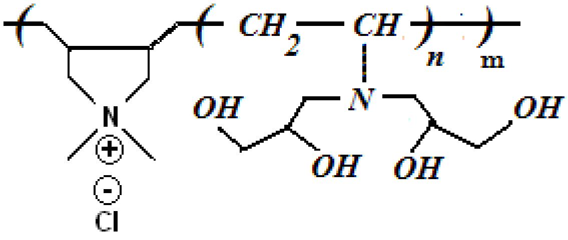
For dynamic and static light scattering measurements (D&SLS), polymer solutions with the desired concentrations were prepared in distilled water and the pH was adjusted by droplets of 0.1M NaOH and/or 0.1M HNO_3 solutions of negligible volumes [16]. Some of the samples were prepared with boric acid together with polymer and solutions with different concentrations were obtained by the dilution of the main solution in order to keep the loading constant. All the solutions were filtered with 0.45µm syringe membrane before the D&SLS analysis. The light source was argon ion laser with 35mW power and 633nm wavelength. Intensity of the scattered light was measured at 13 different angles in the range $30^o \leq \theta \leq 150^o$ and at 25^oC. Average of three different intensity data was taken for each angle. Normalization was done using toluene as reference material. Radius of gyration values were calculated by Guinier plot.

CHAPTER 5

RESULTS AND DISCUSSIONS

The purpose of this study is to prove an efficient polymer for selective separation and high boron rejection from its dilute aqueous solutions via PEUF. Two novel polymers which have dense hydroxyl functional groups (four per repeating unit) were synthesized. One of them is poly (vinyl amino-N, N’-bis-propane diol) (GPVA) and the other is its copolymer poly (vinyl amino-N, N’-bis-propane diol-*co*-DADMAC) (GPVA-*co*-DADMAC). The copolymer was synthesized with three different DADMAC number percent (2%, 5% and 10%). The molecular structures of the polymers are presented in Table 5.1.

Table 5.1. Molecular structures of the polymers

GPVA	**GPVA-*co*-DADMAC**
	

Experimental parameters are pH, loading (boron to polymer mass ratio), boron concentration, competing anion concentration and number percent of DADMAC units in the copolymer. Both synthetic and geothermal water samples which contain boron were used as feed solution. Besides the continuous mode ultrafiltration; batch-mode separation was also performed when some of the feed solutions were treated with high amount of polymer. High boron retention is the main aim while determining the optimum operational parameters. However, there are other important concerns such as reversibility and selectivity of the complexation. Reversibility is investigated by the effect of pH on retention while selectivity is examined by the boron retention in the presence of competing anions. In addition, some practical considerations such as reproducibility of the polymer synthesis and effect of non-adjustable parameters (i.e. boron concentration) are discussed.

5.1. Characterization of the Synthesized Polymers

5.1.1. ^{1}H-NMR, ^{13}C-NMR and FTIR Analysis

In order to see whether the polymer synthesis was achieved with the expected chemical transformations at each step, ^{1}H-NMR, ^{13}C-NMR and FTIR spectroscopy were used. In Figure 5.1, ^{1}H-NMR spectra of polyvinyl formamide, polyvinyl amine and poly (vinyl amine-N, N'-bis propane diol) (GPVA) are plotted.

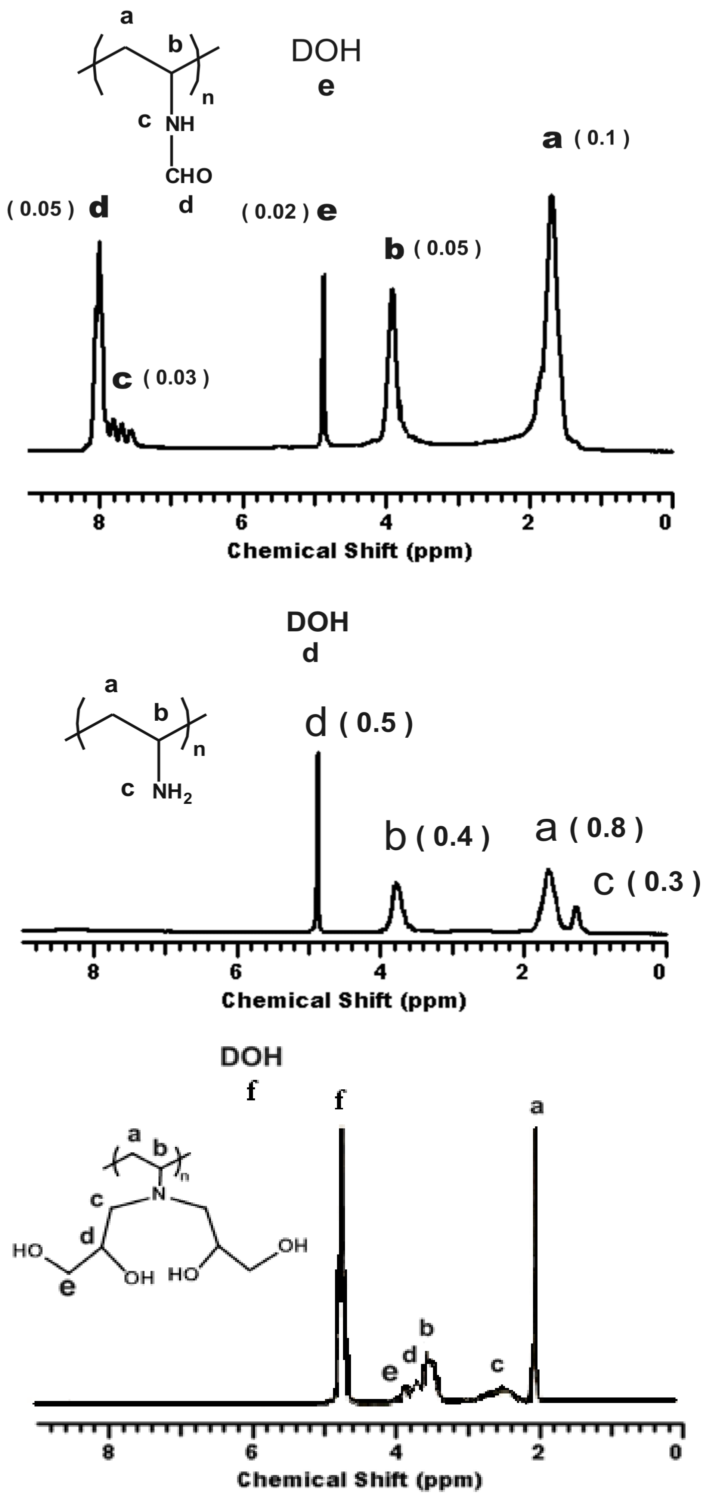


Figure 5.1. ^{1}H-NMR spectra of polyvinyl formamide, polyvinylamine and poly (vinyl amino-N, N'-bis-propane diol).

In ^{1}H-NMR spectrum of the polyvinyl formamide (Figure 5.1), four different proton signals were observed as expected. The proton signals of -CH_2, -CH, –NH and -CHO groups are observed respectively at 1.85 ppm (a), 3.9 ppm (b), 7.8 ppm (c) and 8.1 ppm (d). As seen in the figure integral ratio of –NH proton (0.03) shows lower value than expected (0.05) due to the proton exchange from NH labile proton to D_2O so in the spectrum DOH proton appears at 4.9 ppm and integral ratio of this peak (0.02) completes exact integral value of NH proton as expected. Comparison of the ^{1}H-NMR spectra of polyvinyl formamide and polyvinyl amine shows that the protons of –NH and -CHO groups disappear and a new peak appears at 1.2 ppm (c) corresponding –NH_2 protons in polyvinyl amine spectrum. This is a clear evidence for the complete hydrolysis of polyvinyl formamide. In the ^{1}H-NMR spectrum of GPVA (Figure 5.1), the proton signals of –CH_2-, -CH-N, -CH_2-N, -CH-O and –CH_2-O are observed at 2.05 ppm (a), 3.5 ppm (b), 2.5 ppm (c), 3.7 ppm (d) and 3.9 ppm (e), respectively. The proton signal at 1.2ppm corresponding -NH_2 in polyvinyl amine spectra does not exist in the spectrum of GPVA. This indicates that the final reaction step reaches almost to completion.

FTIR spectra of polyvinyl formamide and polyvinyl amine are depicted in Figure 5.2. At 1530 cm^{-1} typical amide plane bending vibration and at 1220 cm^{-1} NH-CHO stretching vibration disappears after hydrolysis of polyvinyl formamide and also at 3300 cm^{-1} the peak becomes broader due to formation of NH_2.

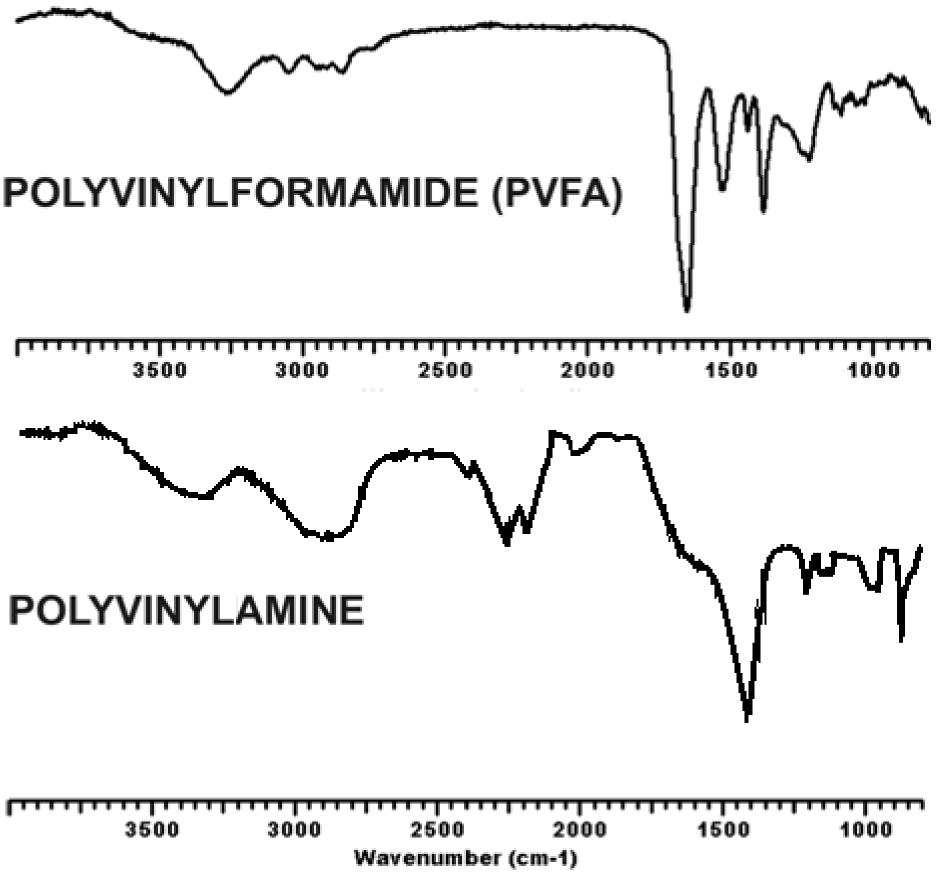


Figure 5.2. FT-IR spectra of polyvinyl formamide and polyvinylamine.

^{13}C-NMR spectrum of poly (vinyl amino- N, N'-bis-propane diol) was obtained with 16000 scans. The relevant spectrum is shown in Figure 5.3. Five different carbon atoms are observed in the synthesized polymer as expected and the chemical shifts are at 30.24 ppm (-CH_2-) (a), 62.65 ppm (-CH_2-N) (c), 64.33 ppm (-CH_2-O) (e), 70.45 ppm (-CH-N) (b) and 72.22 ppm (-CH-O) (d). ^{13}C-NMR spectrum of GPVA is another indication of almost complete functionalization of polyvinyl amine with glycidole, otherwise resulting in more than 5 different peak values in the spectrum.

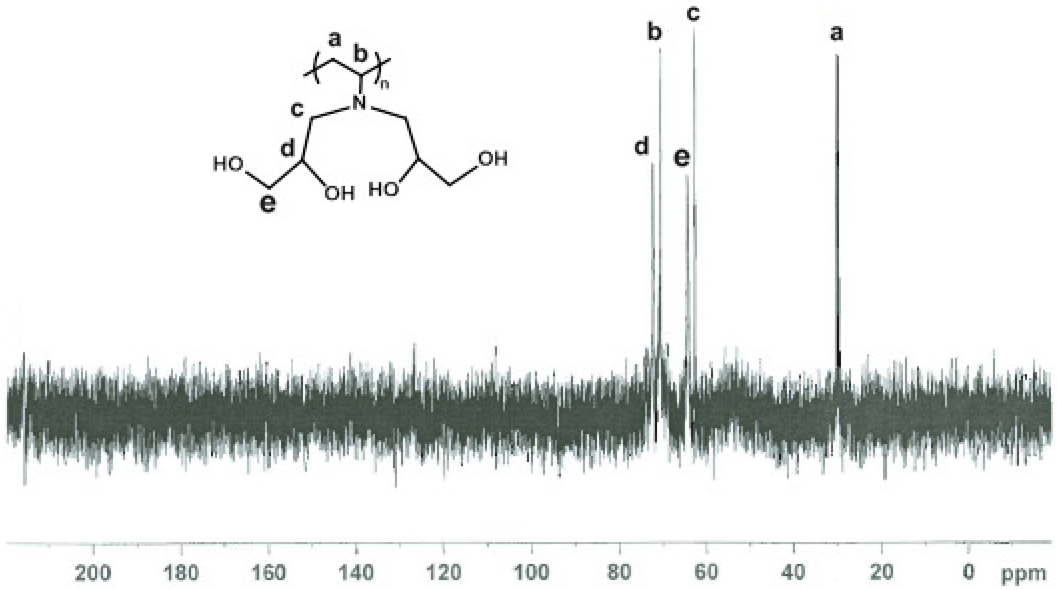


Figure 5.3. ^{13}C-NMR spectrum of poly (vinyl amino- N, N'-bis-propane diol) (GPVA).

The synthesized copolymers were characterized by ^{13}C-NMR spectroscopy to see the validity of the expected transformations during synthesis of GPVA-*co*-DADMAC. The spectra in Figure 5.4. were obtained for copolymers with 10% DADMAC in order to obtain clear signals for DADMAC carbons. The peak representing the carbon which is double-bonded to oxygen, can easily be differentiated at 163.5ppm. Disappearance of this peak in the spectrum of the hydrolysis product reveals successful hydrolysis and formation of poly (vinyl amine-*co*-DADMAC). Appearance of three new peak signals (at 62.8ppm, 64.7ppm and 73.6ppm) in the spectrum of GPVA-*co*-DADMAC, most probably shows that glycidole addition yielded the expected functional copolymer.

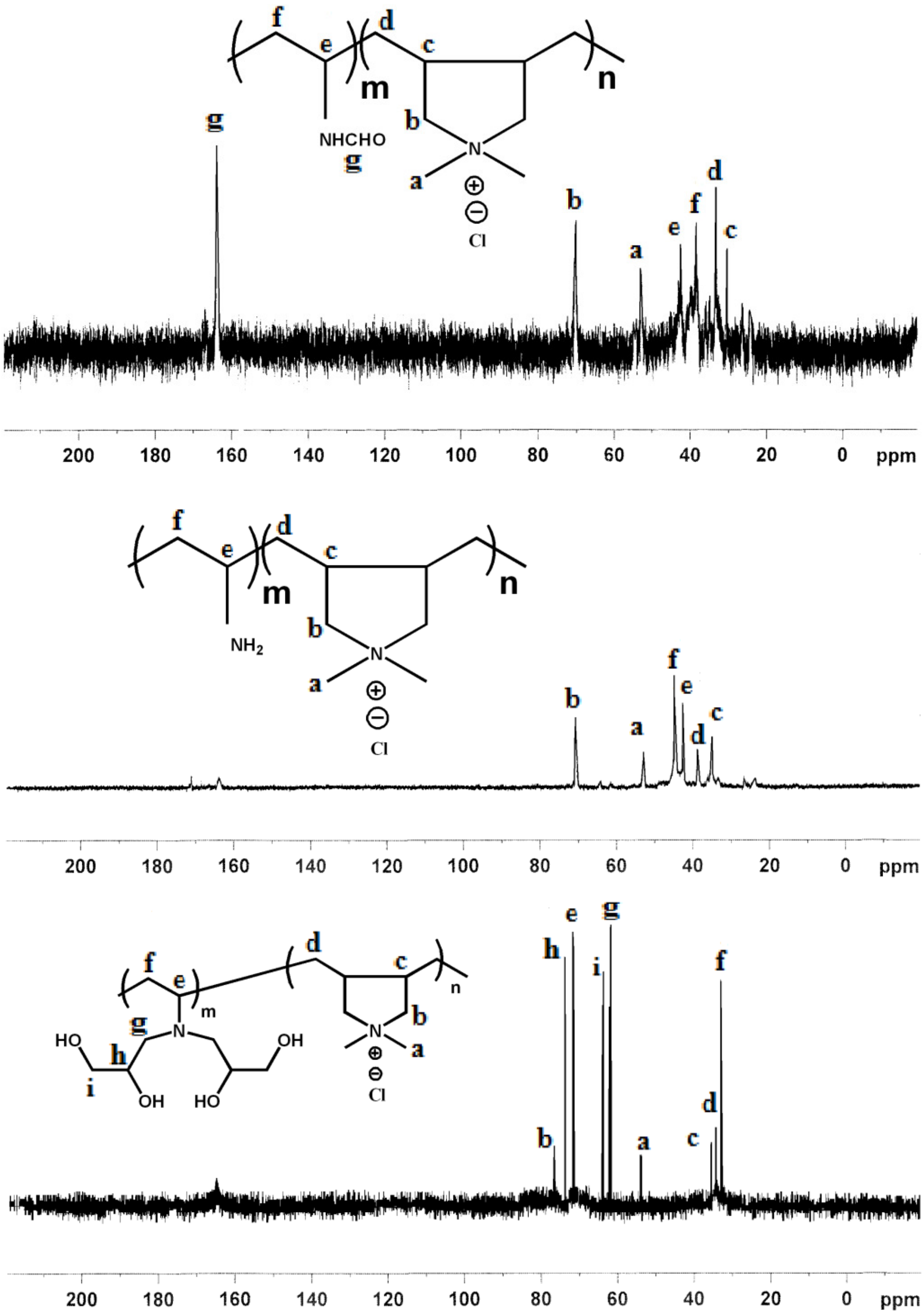


Figure 5.4. ^{13}C-NMR spectra of poly (N-vinyl formamide-*co*-10%DADMAC), poly (vinyl amine-*co*-10%DADMAC) and poly (vinyl amino-N, N'-bis-propane diol-*co*-10%DADMAC).

5.1.2. Estimation of Molecular Weights of the Synthesized Polymers

Polymer molecular weights were estimated from the measurement of the viscosity average molecular weight of synthesized polyvinyl formamide. Time of flight data for the aqueous solutions of polyvinyl formamide-1 (starting polymer of GPVA-1) are presented in Table 5.2. Each data is an average of three measurements and the corresponding %RSD values are also shown.

Table 5.2. Time of flight data with respect to concentration of Polyvinyl formamide-1 in aqueous solution at 25°C.

Concentration, C (g/dL)	**Time of flight values, t (s)**			**Average time of flight, t (s)**	**%RSD of t**	**Reduced viscosity η_{red} or $(t-t_o)/(t_oC)$**	**%RSD of η_{red}**
	1st run	**2nd run**	**3rd run**				
0	105	104	105	105	0.5 (n=3)	-	-
0.215	131	131	133	132	0.9 (n=3)	1.20	4.1
0.645	198	201	200	200	0.8 (n=3)	1.40	1.7
0.774	239	238	238	238	0.2 (n=3)	1.64	0.9

From the intercept, intrinsic viscosity is found as 1.15 dL/g. Using the Mark-Houwink constants, molecular weight of polyvinyl formamide-1 is estimated as:

$$[\eta] = K.M_V^{\alpha}$$

$$1.15 dL/g = 5.43\times10^{-4} M_V^{0.715}$$

$$M_V \cong 44800 g/mole$$

The same measurements were repeated also for the other two polymers synthesized with the same recipe and their M_V values were found as 69kDa and 64kDa. Multiplying the molecular weights of polyvinyl formamide by 2.69 as explained in measurements part, molecular weights of GPVA were estimated as approximately 120kDa (GPVA-1), 187kDa (GPVA-2) and 172kDa (GPVA-3).

In polymerization step, polyvinyl formamide synthesized three times with the same procedure gave three different molecular weights. Percent relative standard deviation of molecular weight of polyvinyl formamide is 22% with the implemented synthesis route. This is most probably due to the nature of chain-reaction polymerization. In chain-reaction polymerization, although a rough estimate of the molecular weight can be predicted by the initiator-to-monomer ratio it is known that random events may affect the molecular weight appreciably [50].

Viscosity measurements of aqueous PVFA-*co*-DADMAC solutions were conducted similarly. Intrinsic viscosity [η] and corresponding viscosity average molecular weight M_V of the copolymers are presented in Table 5.3. Based on the fact that GPVA-*co*-DADMAC polymers contain the same number of repeating units as the starting copolymers in an average chain, their molecular weights could simply be found as 361 kDa (GPVA-*co*-2%DADMAC), 296 kDa (GPVA-*co*-5%DADMAC) and 313 kDa (GPVA-*co*-10%DADMAC), respectively. Although the same procedure was employed for preparing the copolymers, the molecular weights attained slightly differ from each other (117-139 kDa). This might be not only due to changing the comonomer composition but also uncontrollable slight changes in the reaction conditions, so called random events [50].

Table 5.3. Estimated molecular weights of poly (N-vinyl formamide-*co*-DADMAC) in aqueous solution at 25^{o}C.

Polymer	[η] (dL/g)	M_V (kDa)
PVFA-*co*-2%DADMAC	2.58	139
PVFA-*co*-5%DADMAC	2.29	117
PVFA-*co*-10%DADMAC	2.51	134

5.1.3. pH Characteristics of GPVA

Solutions of GPVA-1 with various concentrations were prepared in pure water and pH values were measured by a pH-meter at equilibrium in order to obtain the pH as a function of polymer concentration. The related data is shown in Table 5.4. The pH of the solution was observed to increase with increase in polymer concentration. This observation may be attributed to the basic nature of GPVA due to amino groups. The result is consistent with literature since amino groups are known to act as proton sinks [13].

Table 5.4. pH values of GPVA-1 solutions in water.

GPVA Concentration (g/L)	0.05	0.10	0.20	0.50	1.0	2.0	5.0	10.0
pH	7.37	7.51	7.80	9.30	9.64	9.77	10.03	10.31

The same experiment was also carried out with 10ppm boron in the solution medium and pH values are collected for various polymer concentrations. The corresponding data is given in Table 5.5. At constant boron concentration, solution pH rises with increasing polymer concentration (or decreasing loading).

This result is consistent with the one obtained in the absence of boron. Moreover, a comparison between Table 5.4 and Table 5.5 shows that significant reductions in pH values were observed upon boric acid addition for each studied concentration. This is an expected result probably due to the weak acidity of boric acid.

Table 5.5. pH values of aqueous solutions of GPVA-1 and boron for constant boron concentration of 10ppm.

GPVA Concentration (g/L)	0.05	0.10	0.20	0.50	1.0	2.0	5.0	10.0
pH	7.13	7.31	7.60	7.82	8.34	8.86	9.58	10.01

5.1.3.1. Estimation of the Acid Dissociation Constant of GPVA-*co*-10%DADMAC

By volumetric titration with NaOH solution, Henderson-Hasselbach plot was obtained for 1% (w/w) aqueous solution of GPVA-co10%DADMAC and it is presented in Figure 5.5.

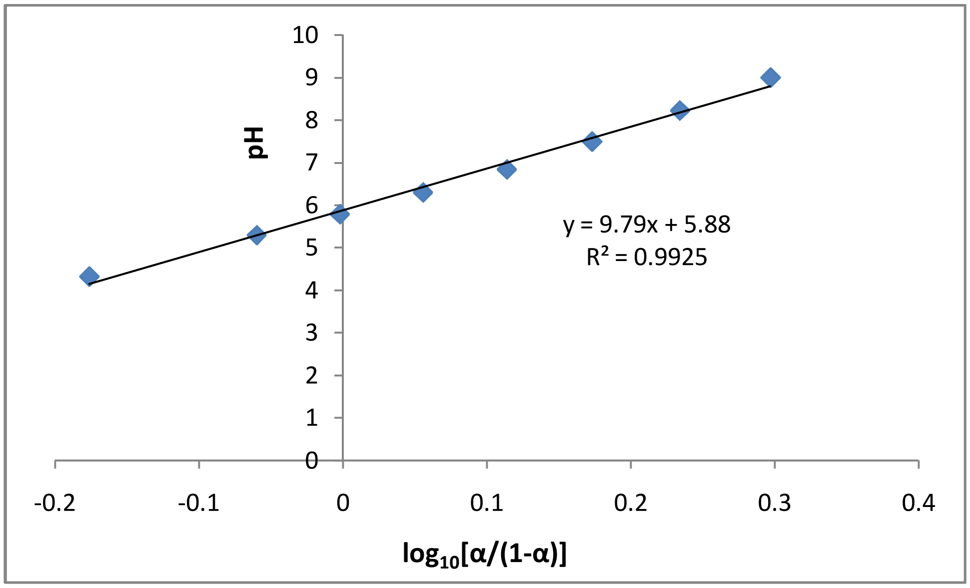


Figure 5.5. Henderson-Hasselbach plot for 1% (w/w) aqueous solution of GPVA-co10%DADMAC.

$$pH = pK_a + n\, log\left(\frac{\alpha}{1-\alpha}\right) \qquad \text{(Eqn. 5.1.)}$$

In Eqn. 5.1, α is the fraction of the polymer repeating units in non-protonated form. From the intercept and the slope of Figure 5.5, pK_a and n are found respectively as 5.88 and 9.79 for GPVA-co10%DADMAC.

5.1.4. D&SLS measurements of Polyvinyl amine

Gyration radius, R_g is defined as the root mean square distance of all the atoms in a molecule from its center of gravity. Effect of pH and concentration on radius of gyration (R_g) was investigated for aqueous polyvinyl amine solutions and the results are demonstrated in Figure 5.6. As seen in Figure 5.6, R_g becomes larger at lower pH values for all the polymer concentrations studied. Results are in good agreement with the study reported by Canizares [51] for polyethyleneimine –a polymer which contains sites that can be protonated- in the pH range between 5 and 9. This observation seems reasonable since increasing acidity enhances the extent of protonation of amine groups and results in a higher ionic repulsion of repeating units. In addition, R_g of polyvinyl amine was observed to increase with dilution as expected (Figure 5.6). This is considered to be resulted from increasing ionization of the polymer while the concentration diminishes.

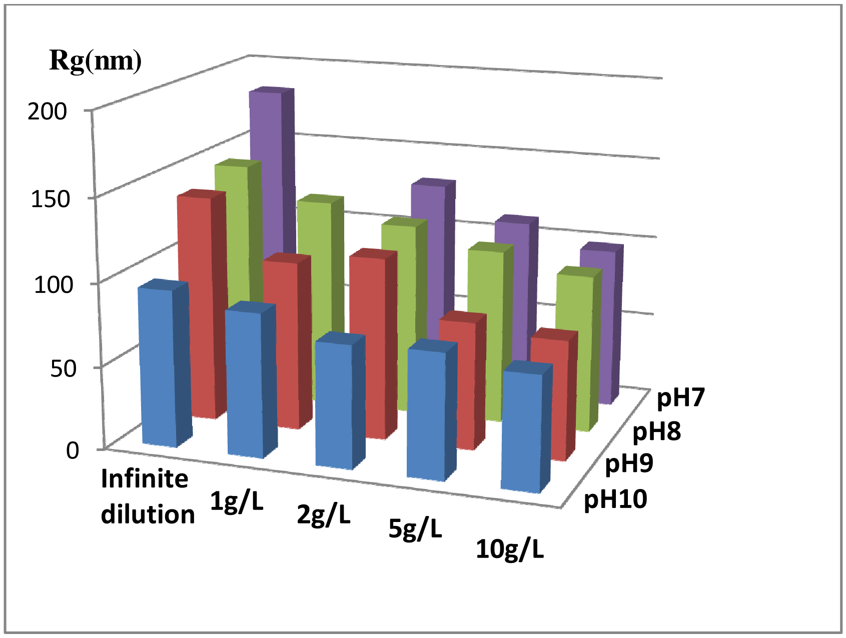


Figure 5.6. Effect of polymer concentration and pH on gyration radius of polyvinyl amine in the absence of boron.

Similar experiments were also carried out for boron containing polyvinyl amine solutions with a loading of 0.001. The relevant results are depicted in Figure 5.7. As seen in Figure 5.7, R_g of polyvinyl amine increases when pH decreases. This observation can be explained again by increasing protonation of amine groups. Moreover, obtaining higher values of R_g at lower concentrations (Figure 5.7), the response of the polymer size to concentration change in the presence of boron is also similar to the one observed in the absence of boron (Figure 5.6). Comparing Figure 5.6 and Figure 5.7, it is observed that boric acid has no appreciable effect on the size of polyvinyl amine. As expected, this may be an indication of negligible interaction between boric acid and polyvinyl amine.

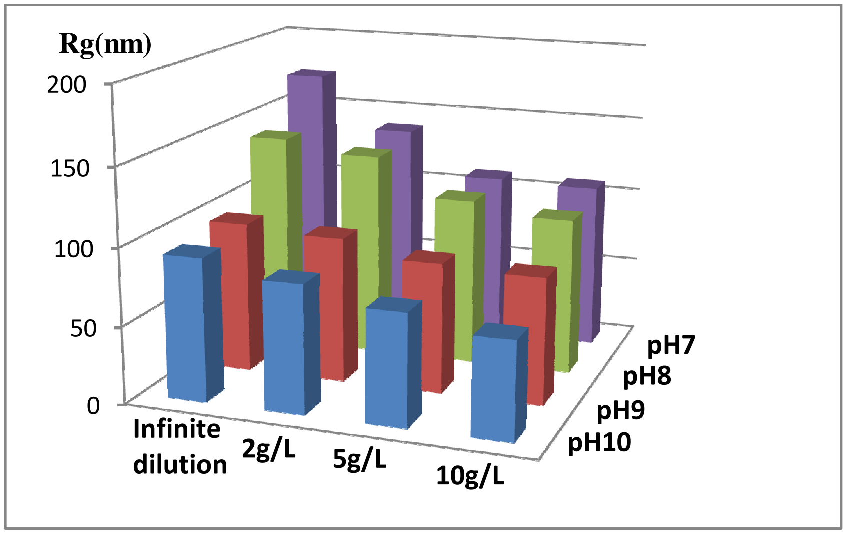


Figure 5.7. Effect of polymer concentration and pH on gyration radius of polyvinyl amine in the presence of boron at loading of 0.001 (concentrations correspond to polymer).

5.1.5. D&SLS measurements of GPVA

Solutions of GPVA-3 were prepared at different pH values and polymer concentrations and radius of gyration (R_g) values were measured by D&SLS. The related data is represented in Figure 5.8.

In Figure 5.8, when the R_g values at different pH values are compared for infinite dilution, higher radius of gyration was observed at higher pH. Although decrease in R_g by decrease in pH seems to be unexpected, this can be explained in terms of intermolecular hydrogen bonding of multi-hydroxy groups. It is well known that hydronium or ammonium cations well protonate the hydroxyl groups and disrupt the hydrogen bonding. Overall result would then be decreasing coalescence tendency of the molecules and reduction in R_g.

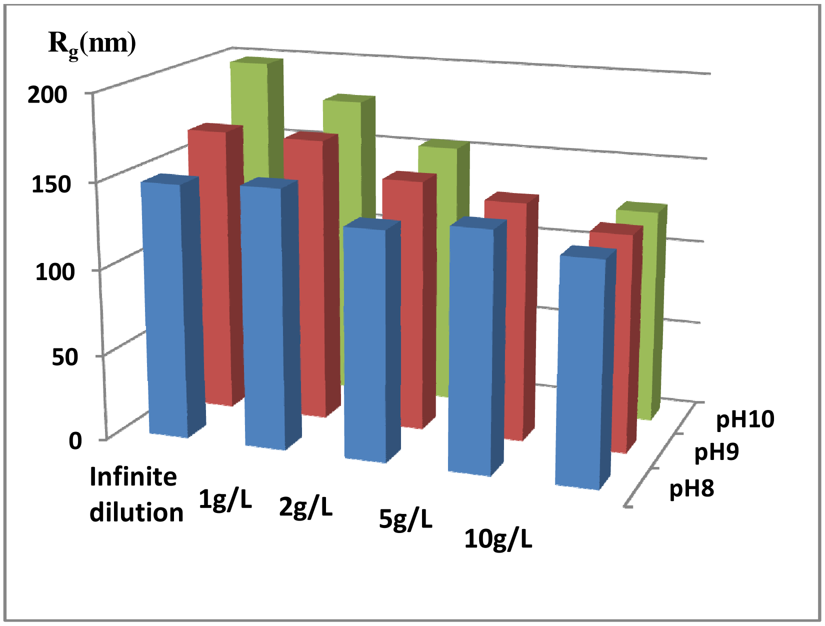


Figure 5.8. Effect of polymer concentration and pH on gyration radius of GPVA in the absence of boron.

Effect of concentration on polymer conformation is also seen in the Figure 5.8. R_g is observed to increase as the concentration decreases at constant pH. Decrease in concentration most probably causes an increase in the extent of ionization of the amino groups and increasing protonation of the tertiary amine groups would induce polyelectrolyte effect in which the macromolecule tends to expand and thus causes an increase in R_g.

Considering the variation of R_g by pH and polymer concentration, one can conclude that size and shape of the polymer in aqueous solution would be changed under the influence of two opposite effects: polyelectrolyte effect of the amino group and hydrogen bonding via four hydroxyl groups of imino-bis propane diol (IBPD) function. Logically, protonation of the amine nitrogen induce polyelectrolyte effect, which imposes expansion of the polymer chains, obviously this would give rise to increase R_g. Hydrogen bonding effect of the hydroxyl groups, on the other hand, might be operative at high pHs and causes to somewhat associating effect on the polymer chains. As a result, apparent R_g would become larger. The negligible pH dependency of R_g values at high polymer concentrations may be due to low ionization of the amino groups. These results are consistent with those reported in a previous study on a different polymer with similar functional groups [16].

5.1.6. D&SLS measurements of GPVA-*co*-DADMAC copolymers

Gyration radii of the copolymers were measured at different pH values and the extrapolated results at infinite dilution are shown in Figure 5.9. It is seen in Figure 5.9 that radius of gyration is in the order, GPVA-*co*-5%DADMAC < GPVA-*co*-10%DADMAC < GPVA-*co*-2%DADMAC which is in accordance with the order of the molecular weights. Although for GPVA-*co*-5%DADMAC, there is a small increase in R_g followed by a decrease with increasing pH, R_g values of the other two polymers slightly diminish with a rise in pH. This decline may result from decrease in protonated amine fraction when pH increases and thus leading to less intra-molecular repulsion. On the other hand, a possible coalescence tendency which might be caused by intermolecular attraction between hydroxyl groups does not seem to be effective probably due to appreciable repulsion between permanently charged quaternary ammonium sites.

To investigate the effect of concentration on the conformation, radius of gyration values were measured at different polymer concentrations (2-20g/L) at constant pH for the three copolymers. The related results are demonstrated in Figure 5.10. It is clearly seen in Figure 5.10 that R_g strictly increases upon dilution. The result is consistent with R_g data obtained by a different polymer previously studied in the literature [16]. This is most probably due to increased percentage of ionized amino groups in low polymer concentrations.

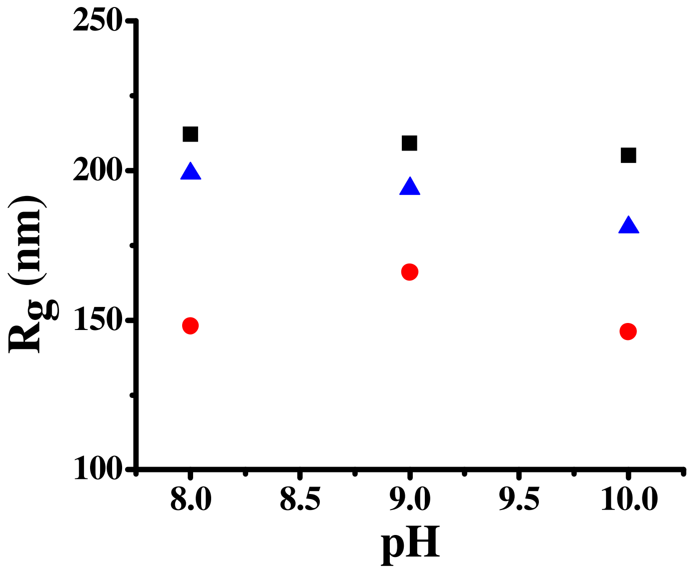


Figure 5.9. Effect of pH on radius of gyration at infinite dilution in the absence of boron at 25°C (■ GPVA-*co*-2%DADMAC, ● GPVA-*co*-5%DADMAC, ▲ GPVA-*co*-10%DADMAC).

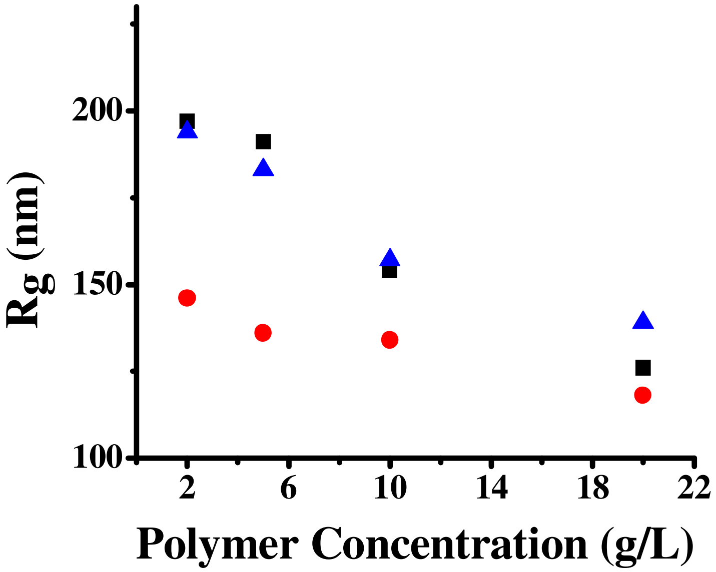


Figure 5.10. Effect of concentration on radius of gyration in the absence of boron at 25°C (pH: 8.0, ■ GPVA-*co*-2%DADMAC, ● GPVA-*co*-5%DADMAC, ▲ GPVA-*co*-10%DADMAC).

5.2. Boron Complexation of the Polymer

In this work, the target is the design of new, more efficient and regenerable boron chelating polymers. Polymer crosslinking by boron may be a problem for boron chelation performance. In the literature, polymer crosslinking induced by boron was suggested and supported with some evidence [12, 19, 52]. Polyvinyl alcohol, for instance, has low solubility and undergoes rapid gelation when contacted with boric acid solution, due to complexation of boron by hydroxyl groups located at different polymeric chains [19, 52]. Owing to instantaneous crosslinking, some of hydroxyl groups of polyvinyl alcohol remain unoccupied in the gel matrix. This results in reduction of boron chelating capacity. It was considered that the crosslinking can be avoided by specially designed polymers possessing boron chelating sites such as imino-bis propane diol (IBPD) groups. Bearing this in mind, IBPD functional polymer was synthesized by reaction of high molecular weight polyvinyl amine with glycidole. Four hydroxyl groups of IBPD function are enough to occupy coordination with boron. Since opening of oxirane ring by action of amine group yields *trans*-diol, complexation with boric acid must give neutral boron ester moiety rather than four-coordinated borate complex with minus charge as illustrated in Figure 5.11. and as reported before [32, 53]. Therefore, three hydroxyl groups of four involve in boron complexation while the fourth one remains unoccupied. The experiments showed that reaction of IBPD functional polymer with boric acid in aqueous solution does not result in any observed precipitation even after waiting for 1 week. This observation can be considered as a clear-cut proof of the above assumption. In other words, a linear polymer may still remain soluble after complexation with boron. The ultimate result of this phenomenon would be a nearly full complexation of IBPD groups when enough boron is present in the medium [53].

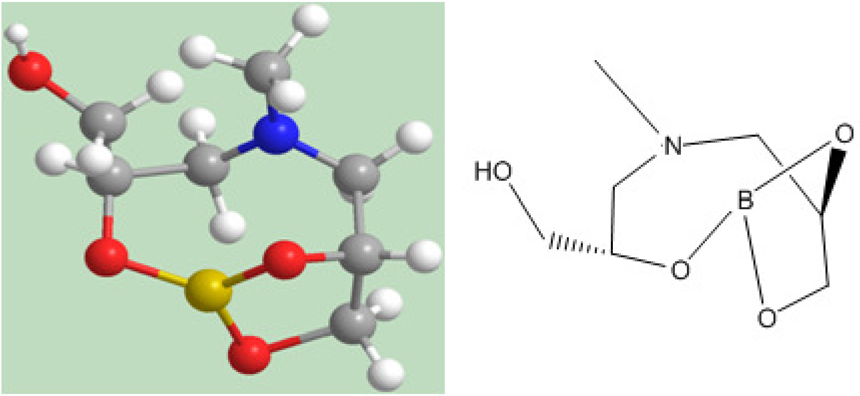


Figure 5.11. Ball-stick (ORTEP) model for the conformation of boron-IBPD complex structure (Atoms are represented as follows: C(grey), N(blue) , H(white), O(red), B(yellow)).

5.2.1. D&SLS Measurements of GPVA in the presence of boron

To investigate the effect of boron on polymer conformation, D&SLS measurements were performed with boron containing polymer solutions. In these experiments, radii of gyration were determined at various pH and polymer concentrations in the presence of boron. The relevant results are plotted in Figure 5.12.

Figure 5.12 shows that radius of gyration is proportional to polymer concentration at pH 9.0 and 10.0, whereas at pH 8.0 the proportionality becomes reverse. This controversy can be explained by residual hydroxyl groups retained after complexation of boron with three of the hydroxyl groups. Thus, the residual hydroxyl groups would probably form relatively weak intermolecular boron bridging among the macromolecular chains. Most probably this is due to vicinity of the polymer chains at relatively high concentrations. Thus, at low polymer concentration they may be too far from each other for the boron bridging. This trend was not observed in a previous study [16] possibly due to absence of residual hydroxyl groups in the polymers employed in those studies.

However, when the solution pH was 8.0, increasing concentration reduced the radius in the presence of boron. The reason might be due to the fact that, acid-base interaction of protonated amine with borate anion is depressed at low pHs and the IBPD-boron complexation would decrease. This may also suppress the boron bridging tendency via residual hydroxyl groups and overall result would be decrease in Rg.

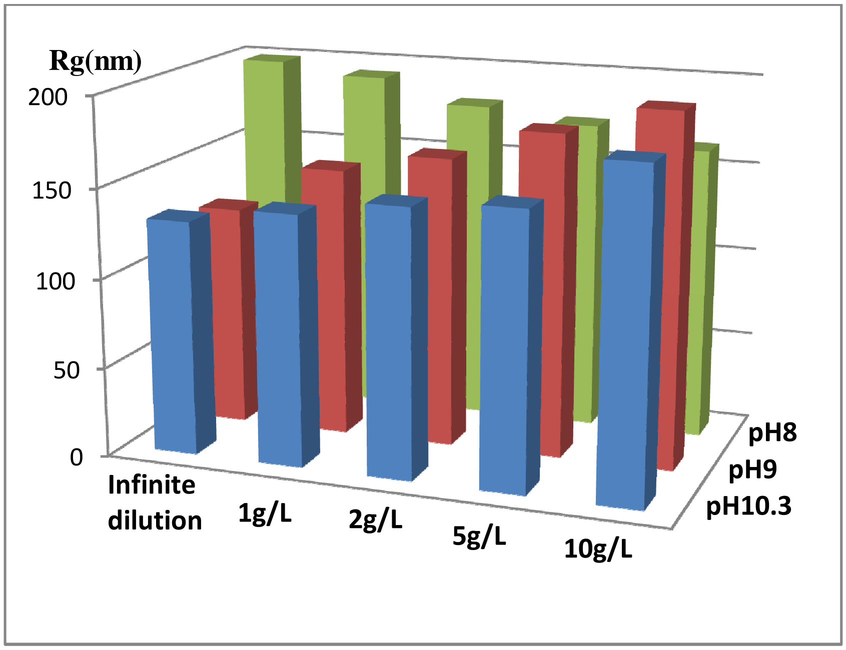


Figure 5.12. Effect of pH and concentration on gyration radius of GPVA in the presence of boron at loading 0.001 (Concentrations correspond to polymer).

5.2.2. D&SLS Measurements of GPVA-co-DADMAC copolymers in the presence of boron

Effect of polymer concentration on R_g of copolymer was also investigated in the presence of boron at constant loading (0.001). The related results are plotted in Figure 5.13. It is apparent that R_g again increases monotonically while reducing the polymer concentration. This might indicate that an inter-molecular boron bridging may be suppressed which may result from permanent charge on DADMAC units. Comparison of Figure 5.12 and Figure 5.13 implies that presence of boron induce significant effect on the radius of gyration of the polymers. R_g is under influence of two opposite effects: first, repulsion between the quaternary amino groups of DADMAC segments and the second one is bridging effect of inter-molecular boron complexation via residual hydroxyl groups. These two effects are in competition with each other, due to this fact R_g of the copolymer with 2% DADMAC segments rises from 197 nm to 208 nm. Similarly, in the case of copolymer with 5% DADMAC, R_g increases from 146 nm to 185 nm, while R_g of the copolymer containing 10% DADMAC remaining almost unchanged due to increasing polyelectrolyte effect.

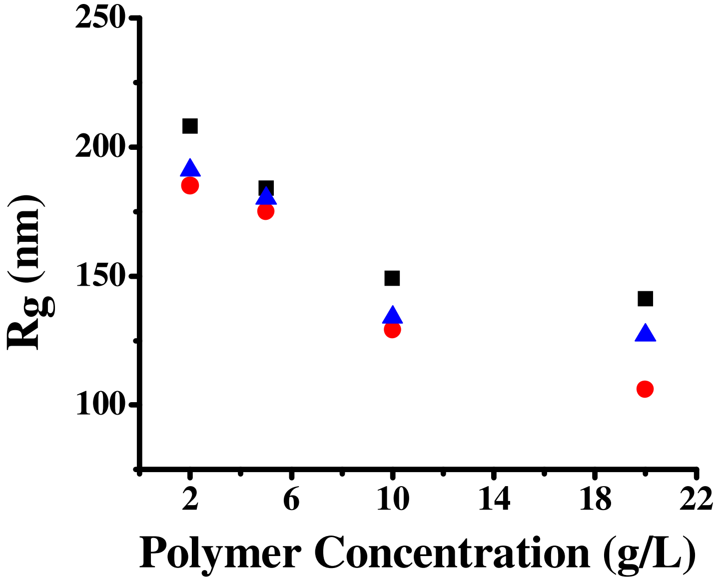


Figure 5.13. Effect of concentration on radius of gyration in the presence of boron at 25°C (Loading: 0.001, pH: 10.1±0.1, ■ GPVA-*co*-2%DADMAC, ● GPVA-*co*-5%DADMAC, ▲ GPVA-*co*-10%DADMAC).

5.3. Effect of GPVA Concentration on Solution Viscosity

Viscosity of a flowing solution is industrially important since it is related to the pressure drop and operational cost. Therefore, the effect of polymer concentration on viscosity was studied in this part.

Viscosities of aqueous solutions with different polymer concentrations were determined at 25°C by Ubbe-Lohde Viscosimeter in order to get an idea about the possible problems that may occur such as high pressure difference both across the membrane and through the pipes which carry the polymer solution. These experimental data depicted in Table 5.6, show that increase in the viscosity of water even for high GPVA concentration is not significantly high: it becomes only 2.33 fold after dissolving 10g/L polymer.

Table 5.6. Viscosity values of aqueous solutions with different GPVA concentrations

GPVA concentration (g/L)	Viscosity Relative to Water at 25°C
0	1.00
1	1.52
1.33	1.60
2	1.81
5	1.94
10	2.33

5.4. UF Experiments in the Absence of Polymers

First of all, boron retention only due to membrane itself should be determined in order to reveal the contribution of membrane to retention values. Therefore, ultrafiltration experiments were carried out without using any polymer at different pH values between 7.0 and 10.0 with 0.5 increments. These results are tabulated in Table 5.7. Results have shown that membrane has a significant rejection of

52% for 10ppm boron at pH 10 whereas smaller rejections for lower pH values. Moreover, at high boron concentration in feed (30ppm), smaller retention values were obtained.

Table 5.7. Boron retention values by the membrane (YMPTSP1905, MWCO: 5 kDa) itself in the absence of polymer for different pH and feed boron concentration values.

pH	**%Retention for 5ppm feed boron concentration**	**%Retention for 10ppm feed boron concentration**	**%Retention for 30ppm feed boron concentration**
7.0	-	0	-
7.5	-	1	-
8.0	5	8	5
8.5	-	11	-
9.0	24	21	9
9.5	-	38	-
10.0	56	52	26

The retention in the absence of polymers is considered to be most probably due to ionic rejection of the membrane since boron is mostly in borate form at pH 10 whereas it is mostly in boric acid form at pH values less than or equal to 8. This ionic retention behavior of the membrane was also justified using potassium and magnesium cations and chromate anion with 10ppm feed solutions at pH 10. Results are depicted in Table 5.8.

Table 5.8. Retentions of selected ions by the membrane YMPTSP1905 (PES MWCO 5kDa) without using any polymer at pH 10.

Dissolved Compound	$K_2Cr_2O_4$	KCl	$MgSO_4$
Ion	$Cr_2O_4^{2-}$	K^+	Mg^{2+}
% Retention	90	38	43

The important deduction is that the reason behind these retention values in the absence of any polymer can neither be pore size (MWCO: 5kDa) which is much larger than boric acid molecule nor adsorption and accumulation of boron on the membrane surface, it must be nothing but the ionic rejection of the membrane. Otherwise, concentration of the feed solution would drop significantly after 4 hours of operation -some of the experiments were repeated even for a complete day- also considering the permeate flow rate (~160mL/h) and the feed volume (~1500mL). Moreover, retention of K^+ -a very stable cation- supports this idea.

After justifying the ionic rejection of the membrane PES MWCO 5kDa, same ultrafiltration experiments were also carried out in the absence of polymers with two different type membranes (Osmonics YMERSP1905 and HG19). Percent boron retention values are presented in Table 5.9.

Table 5.9. Percent boron retention values in the absence of polymers for two different type membranes (10ppm feed boron concentration)

Membrane	**pH 8.0**	**pH 8.5**	**pH 9.0**	**pH 9.5**	**pH 10.0**
YMERSP1905	2	8	24	24	30
HG19	1	-	16	-	17

As seen in Table 5.9, the membrane YMERSP1905 shows similar retention behavior with the membrane YMPTSP1905 below pH 9.0. On the other hand, much less retention values were obtained with HG19 type membrane. Although it is desired to use a membrane with low boron retention values in order to be able to observe the contribution of the boron binding functional polymer clearly, HG19 type membrane is not an appropriate membrane to continue with since it is not manufactured any more. However, pH range of target geothermal water streams is between 5.8 and 9.4 (as presented in Tables 2.1 and 6.8) and contribution of the membrane YMPTSP1905 to boron retention values is small enough in this pH range. Thus, YMPTSP1905 type membrane is selected as the ultrafiltration membrane.

5.5. PEUF Experiments for Boron Removal in the Absence of Counter-ions

Ultrafiltration performance is characterized by flux and retention. Flux values were calculated dividing permeate flow rate by membrane area. Percent retention values were calculated for each ultrafiltration run using the expression (Eqn. 5.2) depicted below:

$$\%R = 100\left(1 - \frac{C_B^P}{C_B^F}\right) \qquad \text{(Eqn. 5.2.)}$$

where C_B^P and C_B^F are mass concentrations of boron in permeate and feed streams, respectively. Loading as defined by boron-to-polymer mass ratio inside the feed solution is an operational parameter which can be formulated as:

$$L = \frac{C_B^F}{C_P^F} \qquad \text{(Eqn. 5.3.)}$$

where C_P^F denotes mass concentration of polymer dissolved in feed.

5.5.1. Polymer Permeation Through the Membrane

It is important to assure that the polymer permeation through the membrane is negligible since permeate stream should be free of polymer. In order to make sure that polymer concentration on the permeate stream was negligible for all runs, TOC measurements of feed and permeate streams were performed for each ultrafiltration experiment. These measurements showed that permeate polymer concentration was always less than 0.83% of the feed polymer concentration. This negligible polymer permeation was achieved by synthesizing GPVA with sufficiently high molecular weight (≥ 120kDa) as well as using a membrane with MWCO (5 kDa) much less than polymer molecular weight. However, polydispersity index reported for polyvinyl formamide in the literature was appreciably high (between 2.2 and 7.9) and this may imply existence of polymer molecules smaller than membrane pore size. Considering the negligible permeation of GPVA, this problem seems to have been eliminated by diafiltration of aqueous GPVA solution prior to usage as proposed by Canizares [51].

5.5.2. General Evaluation of PEUF Experiments

During each ultrafitration run, samples from feed and permeate were collected and the permeate flow rate was measured at different times in order to observe whether steady state is reached and to assure the precision of the boron analysis. Steady-state was determined by time-dependent flux measurements and ultrafiltration was ended appreciably later than steady-state. In Table 5.10, time dependent retention and flux results of a representative run are depicted. In each experimental run as well as in this representative one, it was observed that duration of 30 minutes seems to be adequate for reaching steady-state. This result is similar to the ones obtained with the same UF set-up in previous studies [15, 16].

In Table 5.10, temperature, pH, feed and permeate boron concentrations are also given with their percent relative standard deviations for the representative run. Considering the tabulated %RSD values, these results show that the steady state is reached and thus time devoted to boron complexation before PEUF seems more than sufficient. %RSD values are somewhat in comparable closeness with a previous study [16]. Every PEUF experiments are tabulated in the same way in Appendix A.

Table 5.10. Experimental results for a representative PEUF run (pH is 10, loading is 0.001 and UF pressure is 200kPa)

Time (min)	T(^{o}C)	pH	Feed Conc.(ppm)	Permeate Conc. (ppm)	% Retention	Permeate Flux (L/m^2.h)
0	25.4	9.95	10.9	-	-	-
30	25.2	9.99	11.0	1.1	90	10.9
60	25.6	9.94	10.4	1.0	90	10.6
90	25.3	9.99	11.1	1.0	91	10.4
120	25.5	9.98	10.7	1.0	91	10.7
150	25.3	9.97	10.8	1.2	89	10.7
180	24.9	9.99	11.0	1.0	91	10.5
210	25.4	9.96	11.1	1.0	91	10.4
240	25.5	9.97	11.4	1.2	89	10.3
%RSD	0.8	0.2	2.6	8.6	1.0	1.9

Reproducibility of PEUF and boron measurements is considered as essential in order to prove reliability of the system, methodology and measurements [12]. Some of the PEUF experiments were repeated several times so as to investigate the precision of boron retention values. The related results are given with their experimental conditions in Table 5.11.

As indicated in the table, %RSD values seem acceptable when compared with the literature [12, 16] and the implemented procedures of PEUF and measurements appear to be statistically adequate.

Table 5.11. Statistical analysis of boron retention results using GPVA-1 (L: 0.01; T: 25^{o}C)

pH	**%Boron Retention**	**%RSD**
10.0	53 59 57	5.5 (n=3)
9.0	52 59 59 53	6.8 (n=4)
8.0	32 33	2.2 (n=2)

5.5.3. Effect of Polymer Concentration on Permeate Flux

Steady-state permeate flux was determined at different GPVA concentrations using the same membrane. The related permeate flux results are plotted in Figure 5.14. In the corresponding figure, permeate flux values follow a nearly constant value with change in polymer concentration up to 10g/L. In general, permeate flux tends to decrease with increasing macromolecule concentration due to concentration polarization resulting from mass transfer resistence on the membrane surface [11]. However, there are also many UF studies in which polymer concentration has no appreciable effect on permeate flux [12, 15, 16, 41]. As discussed in a previous study, this observation may be explained by prevention of concentration polarization due to adequate shear force induced by continuous feed flow tangent to the membrane surface [15]. Reynolds number on the feed side of the membrane was calculated as 413.

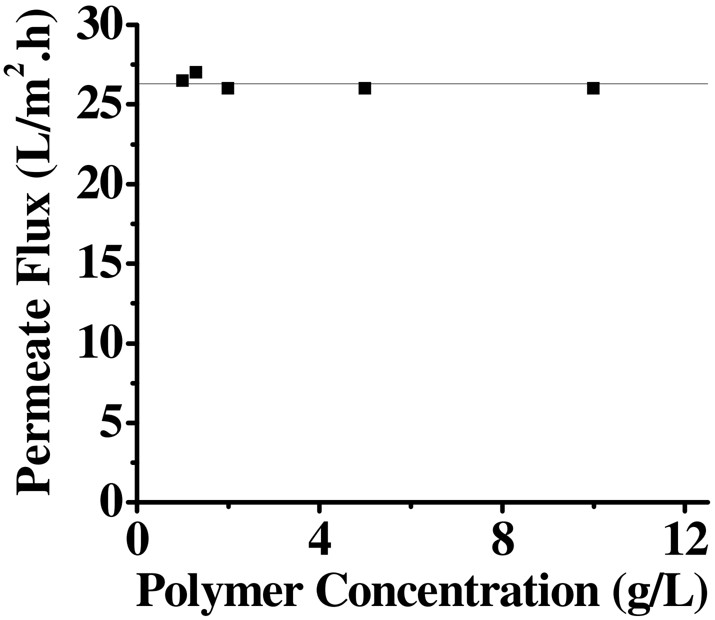


Figure 5.14. Effect of GPVA concentration on permeate flux for 200kPa pressure difference and 10ppm feed boron concentration at 25°C.

Concentration polarization or gel formation is frequently encountered in membrane processes and results in a decrease in permeate flux [24]. It may cause operational drawbacks such as reduction in UF performance and requirement of frequent membrane cleaning process. Employment of GPVA in PEUF applications seems to be free of these drawbacks of concentration polarization for the studied ranges of polymer concentration, UF pressure and feed flow rate.

Also for the copolymer, steady-state permeate fluxes were calculated for the same membrane at various polymer concentrations. Variation of permeate flux with polymer concentration is depicted in Figure 5.15. It is clearly seen that permeate flux is nearly independent of the polymer concentration between 0 and 10g/L. Similar results were reported in many UF studies [12, 15, 16, 41]. This concentration independency in flux may be explained by existence of sufficient shear force due to sufficiently high cross-velocity (Reynolds number: 413) and thus overcoming a possible concentration polarization [15]. It may also be inferred that suitable conformation and highly charged chains of copolymer probably prevent accumulation of the macromolecules on the membrane surface even at high polymer concentrations. In some of UF studies, a decline in permeate flux with a rise in polymer concentration was observed and explained by concentration polarization induced by mass transfer resistance on the membrane surface [11]. Concentration polarization or gel formation may limit the application of UF by reducing the performance and necessitating frequent membrane cleaning process. The copolymer presented in this study appears to eliminate these drawbacks if the polymer concentration, UF pressure and feed flow rate are adjusted properly. It should still be noted that the observation is valid for the studied ranges of parameters and a further increase in the polymer concentration (exceeding 10g/L) may cause a decrease in permeate flux.

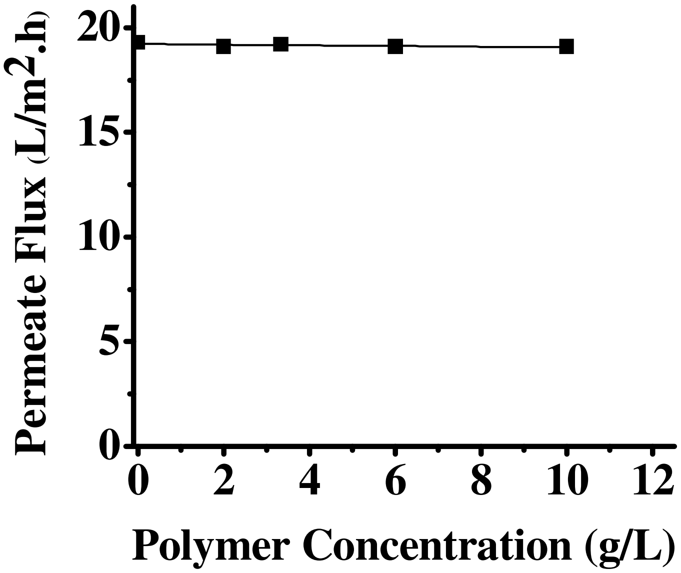


Figure 5.15. Effect of GPVA-*co*-5%DADMAC concentration on permeate flux at 25°C.

5.5.4. Effect of pH on Boron Retention via PEUF

In order to investigate the effect of pH on boron retention with GPVA, retention of boron was determined at different pH values of feed solution at two different loading values. Experiments were performed in continuous UF mode for 10ppm boron in feed and for loading values of 0.01 and 0.001. The corresponding results are demonstrated in Figure 5.16. As presented in Figure 5.16, boron retention increased sharply from pH 7.0 to 9.0 at both loadings. On the other hand, in the pH range of 9.0 to 10.0, it is constant at loading of 0.01 while it slightly diminished at loading of 0.001. It is clearly seen that the optimum pH range is the same (9.0 to 10.0) for both loading values (0.001 and 0.01). Since operating pH should be less than 11.0 as recommended by the membrane manufacturer, experiments could not be performed at pH values higher than 10.0.

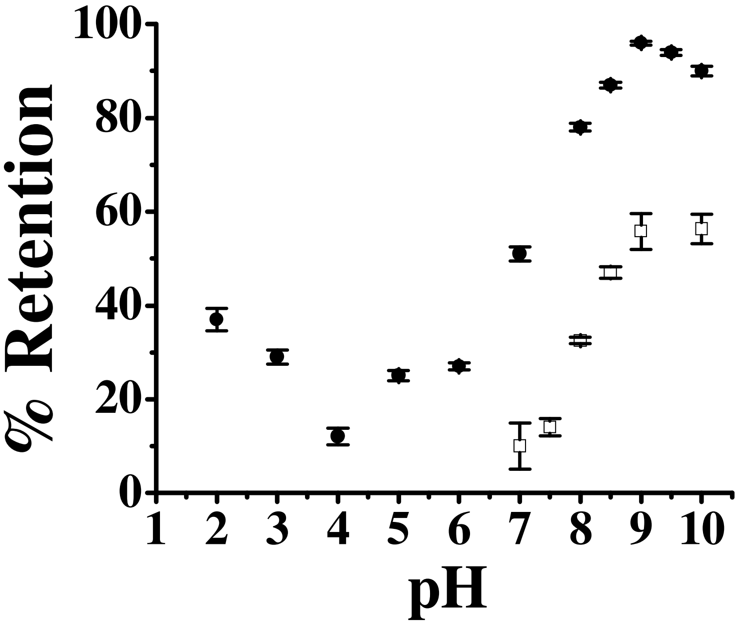


Figure 5.16. Effect of pH on boron retention for 10ppm boron in feed at 25^{o}C (● Loading = 0.001, □ Loading = 0.01).

Similar pH dependency of boron complexation was reported in previous studies in which increase in pH caused increase in boron retention [12, 16]. In this work, the reason might be as follows: borate anion ratio increases with increase in pH and this enhances the approach of borate anion to macromolecular chain via acid-base interaction of protonated amine cation with borate anion. Furthermore, it is clearly seen from Figure 5.16 that change in boron retention is very sensitive to change in pH.

It is also seen in Figure 5.16 that boron retention gets its minimum value at pH 4. Increase in boron retention with decrease in pH below 4 might result from a change in polymer structure due to reaction with nitric acid existing in significant amount in the feed medium at this acidic pH range (pH 2-3).

For large scale application of boron removal via PEUF, polymer regeneration should be considered definitely. With regard to this, after the removal of boron from water at pH 9, polymer can be regenerated by a successive UF performed at neutral pH owing to high pH dependency of boron complexation. In this study, optimizing the conditions for high boron-polymer complexation is mainly targeted.

Solution pH was adjusted by adding negligible volumes of (1-10 drops for each experiment) 0.1M NaOH and HNO_3 solutions and effect of these compounds on boron retention should be investigated. For this reason, boron separation via PEUF was performed also without any pH adjustment: experiments were carried out at three different loading values at their original pH values. Since the original pHs of the solutions are naturally fixed by the polymer and boron concentrations, they do not necessarily correspond to the ones in the studied solutions with adjusted pH (7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0). Therefore, for comparison, interpolated boron retentions were used. In Table 5.12, original feed pH values and retention values are tabulated and compared with the corresponding interpolated values in case of pH control.

Table 5.12. Boron retention with GPVA-1 at different loading values without pH adjustment and interpolated retention values with pH adjustment.

Loading	**Feed pH**	**% Retention without pH adjustment**	**% Retention with pH adjustment** (Interpolated results for the corresponding pH values)
0.01	8.1	29	36
0.002	9.3	88	91
0.001	10.0	94	90

Being somewhat comparable with experimental errors, negligible deviation was observed between the retention values. This indicates that there is not any significant deviation in boron retentions resulting from pH control agents (NaOH and HNO_3 for this study). Buffer solutions could have been chosen for pH control but they might have an effect on the results.

In order to investigate the effect of comonomer ratio on boron retention, copolymers with three different number percents of DADMAC repeating units were used separately for boron removal. Boron retentions were experimentally found for the three copolymers at pH 9 and at two different loadings (0.001 and 0.005). It was possible to prepare solutions with very high polymer concentrations (very low loadings), which demonstrates that, even small percentage of DADMAC segments imparts sufficient solubility even at high polymer concentrations. The relevant results are tabulated in Table 5.13. Results in Table 5.13 show that boron retentions do not significantly depend on DADMAC content within the loading range studied. Although higher availability of functional groups (better conformation) for boron binding may be expected for the polymers with higher DADMAC contents due to increasing charged segments, this enhancement in conformation may be suppressed by the decrease in boron chelating imino-bis-propane diol sites. Another reason may be the fact that conformations of three copolymers do not differ significantly from each other after the introduction of boron, as inferred by R_g results in the presence of boron (Figure 5.13). Since the boron retentions are very close for all investigated conditions, all the copolymers can be employed in boron removal in PEUF. Thus, all the other PEUF experiments were carried out with GPVA-*co*-5%DADMAC.

Table 5.13. Comparison of boron retention values among three copolymers (pH: 9; T: 25^{o}C; 10 ppm boron in feed).

Loading	**% Boron Retention with GPVA-*co*-2%DADMAC**	**% Boron Retention with GPVA-*co*-5%DADMAC**	**% Boron Retention with GPVA-*co*-10%DADMAC**
0.001	90	92	90
0.005	63	64	63

To investigate the dependence of boron retention on pH, several continuous PEUF experiments were carried out with GPVA-*co*-5%DADMAC at different pH values from 7.0 to 10.0 for constant loading (0.001) and constant feed boron concentration (10ppm). The related experimental results are plotted in Figure 5.17. It is observed that boron retention increases sharply (from 55% up to 92%)

with increasing pH from 7.0 to 9.0 while it decreased slightly (to 89%) with pH from 9.0 to 10. It is consistent with the results obtained with the homopolymer GPVA. This observation may result from relatively high borate-to-boric acid ratio at higher pH values leading to higher ionic interaction between borate and the positively charged amine groups which probably enhance approach of boron to macromolecular chain.

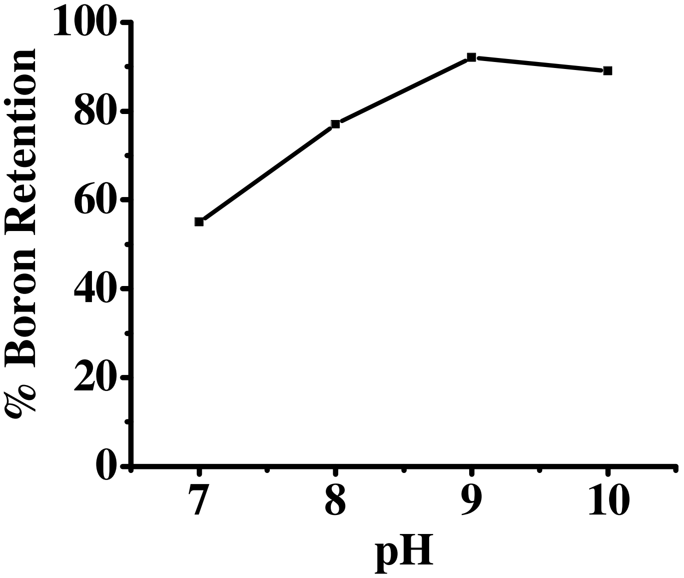


Figure 5.17. Effect of pH on boron retention for GPVA-*co*-5%DADMAC in synthetic water at 25°C and loading of 0.001.

As seen in the Figure, retention takes its highest vales 92% and 89% at pH 9.0 and 10.0, respectively while it gets its lowest value 55% at neutral pH. The corresponding results show that the response of boron retention to pH change is almost the same as the homopolymer. This is simply because the functional group responsible for boron binding is the same for both homopolymer and copolymer.

High pH dependency of boron retention can be exploited for efficient regeneration of the polymer: High boron removal can be achieved at high pH after which the polymer can be regenerated by acidifying the boron loaded polymer. Recovery of the boric acid can be achieved by a successive ultrafiltration and the polymer becomes ready for the next cycle.

5.5.5. Effect of Loading on Boron Retention

Loading (boron-to-polymer ratio) is a parameter which can be adjusted by the amount of polymer dissolved in the feed solution. Determining the optimum loading for maximum retention is aimed. Retention is supposed to increase with decrease in loading (increase in polymer concentration) but there can be a limit such as polymer solubility, decrease in flux or extremely high retention values with no need for further increase. Therefore, effect of loading on boron retention should be studied for finding the optimum loading value.

To obtain an idea about the optimum loading value for the separation of boron, experiments were performed at different loading values from 0.001 up to 0.01 for 10ppm boron in feed at constant pH values. The corresponding results are as shown in Figure 5.18. As expected, boron retention values strictly increased when loading decreased for both pH values 8.0 and 9.0. Similar results were encountered in the literature in which retention increases with decreasing loading [12, 15, 16]. This probably results from the increase in available functional groups which bind boron.

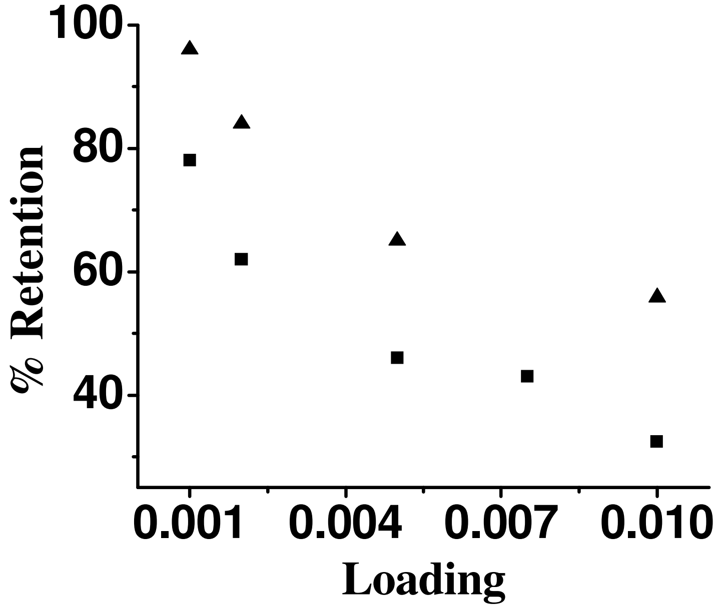


Figure 5.18. Effect of loading on boron retention using GPVA for 10ppm boron in feed at 25°C (■ pH=8.0, ▲ pH=9.0).

Highest boron retention was obtained as 96% at loading 0.001 (corresponding to polymer-to-boron molar ratio of 56:1) and pH 9.0. When compared with other boron chelating polymers, GPVA outperforms polyvinyl alcohol [12] and PNS [16] with which maximum boron retentions were reported as 28% and 57%, respectively.

In order to find the optimum loading for boron removal using GPVA-*co*-DADMAC via continuous PEUF, retention studies were carried out at different loading values (from 0.001 to 0.01) at pH 9.0. The relevant data is plotted in Figure 5.19. As expected, boron retention increases by decreasing loading. This is in accordance with results obtained by GPVA and results obtained in a previous study with another polymer [12], and might be due to increase in the available complexing sites. Highest retention was obtained as 92% at pH 9 and loading

0.001. When the result is compared with retention values (28% and 57%) obtained in previous studies [12, 16], it is seen that the imino-bis-propane diol functional copolymer shows a much higher boron binding.

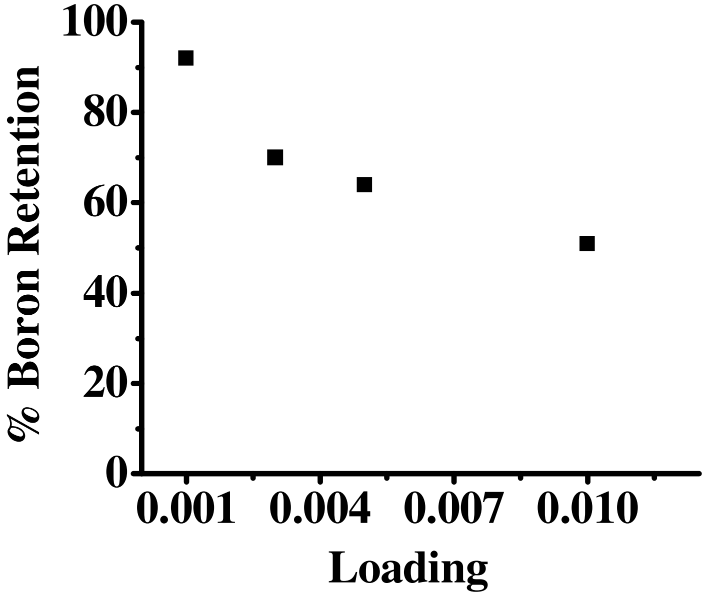


Figure 5.19. Effect of loading on boron retention for GPVA-*co*-5%DADMAC in synthetic water (T: 25°C, pH=9.0, 10 ppm boron in feed).

5.5.6. Effect of Polymer Concentration on Boron Retention at Constant Loading

Effect of polymer concentration on boron retention was investigated at constant loading. Corresponding boron retention values obtained via continuous PEUF, are tabulated for different feed concentrations in Table 5.14. Surprisingly, retention values rise with increase in concentrations of both boron and polymer for constant loading. This seems contradictory to results obtained by other functional polymers investigated in the literature [14, 15]. This interesting observation may result from an enhancement in boron chelating capacity due to increasing tendency of boron bridging by residual hydroxyl groups at higher concentrations. This result seems parallel to the D&SLS results of GPVA solutions in the presence of boron.

Table 5.14. Effect of feed boron concentration on retention and on permeate boron concentration at constant loading.

Loading	pH	Feed boron conc. (ppm)	% Retention	Permeate boron conc. (ppm)
0.002	8.0	5	52	2.5
		10	60	4.0
		30	78	6.9
	9.0	5	67	1.7
		10	81	2.0
		30	92	2.5
0.01	9.0	5	41	2.7
		10	48	5.4
		30	57	13.2

Enhancement in boron retention with increasing concentration promises efficient boron removal in real applications. During a batch-mode separation, simultaneous enrichment of boron and polymer in feed solution would probably favor increasing boron retention. Thus, PEUF experiments in batch-mode were also performed so as to observe boron retention when the feed gets more concentrated. Initial and final results of retention and concentration values are tabulated in Table 5.15. It is clearly seen in Table 5.15 that final retention values are higher than the initial ones. This increase in retention during each run is consistent with the continuous PEUF results at different boron concentrations (Table 5.14) and it can be attributed both to a decrease in loading and to a simultaneous increase in boron and polymer concentrations. Furthermore, highest boron retention was obtained as 99% at pH 9 in batch-mode PEUF (Table 5.15). Corresponding permeate boron concentration (0.4 ppm) is well below the regulated limits (< 1 ppm).

Table 5.15. Results of batch-mode PEUF experiments of boron solutions with GPVA at pH 9.0.

Initial Loading	Initial Feed Boron Conc. (ppm)	Initial Permeate Boron Conc. (ppm)	Initial %Boron Retention	Final Loading	Final Feed Boron Conc. (ppm)	Final Permeate Boron Conc. (ppm)	Final %Boron Retention
0.002	5.3	1.7	69	0.0017	10.4	1.2	88
0.001	10.4	0.9	91	0.00056	27.0	0.4	99
0.0005	10.3	0.7	93	0.00026	24.7	0.4	98

Effect of boron concentration on retention was also studied for GPVA-*co*-5%DADMAC at constant loading and for this, continuous PEUF experiments were performed in two different boron concentrations (10ppm and 30ppm) each for two different loading values (0.005 and 0.003). The relevant results are listed in Table 5.16. It is apparent that higher retentions were obtained at higher boron concentrations for both loading values. This result shows that boron retention is a function of boron concentration as well as loading. In the previous studies, it was demonstrated that in some cases retention of the target species does not depend on concentration but loading [15] and in some other cases it also depends on concentration as well as loading [14], depending strongly on type of polymer and target ion. Normally boron complexation with polymer takes place mostly by forming neutral boron ester chelate as depicted in Figure 5.11. In this scheme, three of four hydroxyl groups of imino bis-propane diol function involves in chelation with boron. The residual –OH group seems to retain unreacted. However, at high boron concentrations this group may tend to interact with boron. Increasing boron retention at high boron concentrations might be due to this fact. Obviously, one isolated hydroxyl group is not sufficient to hold boron and additional hydroxyl groups from neighboring groups may be necessary. This may happen either by incorporation of *intra*- or *inter*-molecular hydroxyl groups, although the intermolecular interaction becomes less favored due to repulsion of the quaternary ammonium groups of DADMAC segments.

Table 5.16. Boron retention values from synthetic water with GPVA-*co*-5%DADMAC at pH 9.0 and 25^{o}C.

Loading	**Feed Boron Conc. (ppm)**	**% Boron Retention**
0.005	**10**	64
	30	75
0.003	**10**	70
	30	83

Higher boron retention for more concentrated solution promises efficient boron removal. Simultaneous enrichment of boron and polymer during batch-mode PEUF may be compensated by this interesting rise in retention. For this reason, PEUF experiments were carried out in batch-mode to investigate the change in boron retention during separation. In Figure 5.20(a) and 5.20(b), time-dependent feed and permeate boron concentrations are shown for two different loading values (0.005 and 0.01) both at pH 9.0.

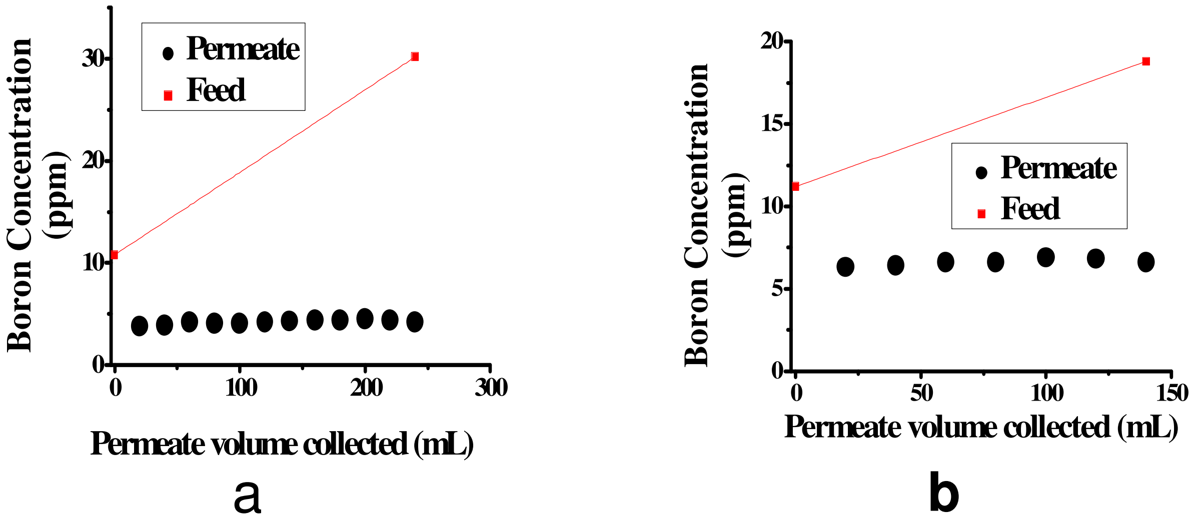


Figure 5.20. Time dependent boron concentration data with batch-mode PEUF using GPVA-*co*-5%DADMAC at pH 9.0 and 25°C (initial feed volumes are 300mL **(a)** and 200mL **(b)** initial loadings are 0.005 **(a)** and 0.01 **(b)**.

Interestingly; for both loading values, permeate boron concentration stayed almost constant during the dead-end ultrafiltration while boron enriched in feed (Figure 5.20). This probably results from increase in boron concentration as well as decrease in loading due to negligible polymer permeation. Slow shift in complexation equilibrium and/or polymer accumulation on the membrane surface may also be considered among the possible reasons for constant permeate boron concentration. Comparison of boron retentions obtained via batch and continuous PEUF runs may be helpful in evaluating these possibilities. As shown in Table 5.17, the boron retention at pH 9.0 was found as 65% (feed boron conc. 10.8ppm, loading 0.005) initially with batch-mode PEUF whereas it was 64% (feed boron conc. 10ppm, loading 0.005) in the corresponding continuous PEUF experiment. Final boron retention, on the other hand, was determined as 86% (feed boron conc. 30.2ppm, loading 0.003) for batch-mode PEUF whereas the retention was 83% (feed boron conc. 30ppm, loading 0.003) for corresponding continuous-mode PEUF (Table 5.17). Since boron retentions for continuous-mode PEUF represent steady-state values as demonstrated in Table 5.10, very close retention values in the batch (86%) and in continuous (83%) runs can be ascribed to fast equilibration of the polymer with boric acid during the course of batch-mode PEUF, which eliminates slow shift possibility.

Table 5.17. Comparison of boron retention values obtained in batch-mode and continuous-mode PEUF runs using GPVA-*co*-5%DADMAC (pH: 9; T: 25^{o}C). (*i*) represents the initial values and (*f*) represents final values for batch-mode PEUF.

Boron Concentration (ppm)	**Loading**	**%Boron retention**	
		Batch-mode	**Continuous-Mode**
~10 (*i*)	**0.005**	65	64
~30 (*f*)	**0.003**	86	83

It is important to reduce the feed volume as much as possible in PEUF studies [17]. Obtaining desired permeate concentration usually restricts the lowest value of the filtration factor which is defined as the volume ratio of the filtrate to volume in the cell [18]. The presented copolymer seems to overcome this limitation by providing constant boron concentration in permeate throughout the batch-mode filtration (Figure 5.20). This may indicate that boron binding is not inhibited by crowding of the macromolecules. Hence, the copolymer appears as a promising chelating agent for boron due to this efficient binding property.

5.5.7. Effect of Polymer Molecular Weight on Boron Retention

Polymer molecular weight is an important variable considered to determine pore size of the UF membrane and thus may affect the permeate flux. High molecular weight polymers enable usage of UF membranes with high MWCO [16], thus making high flux values possible at moderate trans-membrane pressure drops. Having obtained the functional polymer GPVA with three different molecular weights, the effect of molecular weight on boron retention could be studied. In Table 5.18, boron retention values were compared for the three polymers at various experimental conditions.

It was observed (Table 5.18) that slightly lower retentions were obtained for the high molecular weight GPVA (GPVA-2) than GPVA-1. However, the deviations are comparable with the experimental error ranges which are demonstrated in Table 5.18. This weak dependence of retention on molecular weight is an expected result also reported previously for various polymers in other PEUF studies [12, 16]. Small decrease in boron retention may be caused by slight reduction in the availability of functional sites on the polymer chain with increase in molecular weight.

Table 5.18. Comparison of PEUF results for GPVA polymers with three different molecular weights.

Loading	**pH**	**%Retention (GPVA-1) (Polym. Mwt: 120kDa)**	**%Retention (GPVA-3) (Polym. Mwt: 172 kDa)**	**%Retention (GPVA-2) (Polym. Mwt: 187 kDa)**
0.01	9.0	55 ± 3.8	48 ± 1.7	44 ± 1.6
0.005	8.0	46 ± 2.6	-	41 ± 1.0
0.001	9.0	96 ± 0.4	90 ± 1.2	91
0.001	8.0	78 ± 0.8	-	77 ± 1.3
0.002	9.0	84 ± 1.2	81 ± 1.8	-
0.002	8.0	62 ± 2.4	60 ± 2.4	-

5.5.8. Modelling of PEUF experiments using GPVA-*co*-5%DADMAC

As Eqn. 3.16 implies, values of $\log\left(\frac{[PB]}{\left[B(OH)_3\right]}\right)$ were plotted with respect to $\log[P]$ using experimental data obtained at pH 9 and this plot was fitted to a linear line. Since the slope of the best fit was a non-integer (0.82) it was rounded to the nearest integer value, 1 and a line with a slope of unity was fitted to the plot. The relevant plot is depicted in Figure 5.21 in which the slope and the intercept are m=1 and $\log K_C$ = 2.27, respectively. Belcher (1970) reported different reaction orders between 1.0 and 2.9 with respect to concentrations of chelating agents such as sorbitol, mannitol, fructose, glycerol and ethylene glycol [48]. The order found in the present study reveals that complexation is nearly first order with respect to concentration of the functional sites of the polymer. This may indicate a one-to-one complexation between boron and functional repeating unit and might be explained by sufficient boron coordination provided by each imino-bis-propane diol functionals. Moreover, the value $\log K_C$ = 2.27 is in accordance with the ones found by Belcher (1970): $\log K_n$ values extracted from that study varied in the range between 0.54 and 5.5 for boric acid complexation with various chelating agents [48]. The value $\log K_C = 2.27$ corresponds to an equilibrium constant of, $K_C = 186$ L.mol^{-1} and this amount confirms high boron binding efficiency of the imino-bis-propananediol chelating units when compared with the equilibrium constant, $K_C = 111$ L.mol^{-1} obtained using 1,2,3-triol-PEI in the study of Smith [13].

Having obtained the equilibrium parameters for polymer-boron binding at pH 9, predictions for boron retention could easily be generated at various loading and boron concentrations in feed. In Figure 5.22, the predicted retentions for two different boron concentrations in feed (10 and 30 ppm) are depicted as a function of loading together with the experimentally obtained results. As seen in Figure 5.22, the boron retentions estimated from the equilibrium model are in fairly well agreement with the experimental results. The predicted boron retentions are slightly higher than the experimentally obtained ones for high concentration (30 ppm boron) while they are slightly less than experimental ones for low concentration (10 ppm boron). The reason may be due to slightly less suitable polymer conformation at higher concentration and similar results were derived from D&SLS measurements where R_g was found to decrease with increasing concentration.

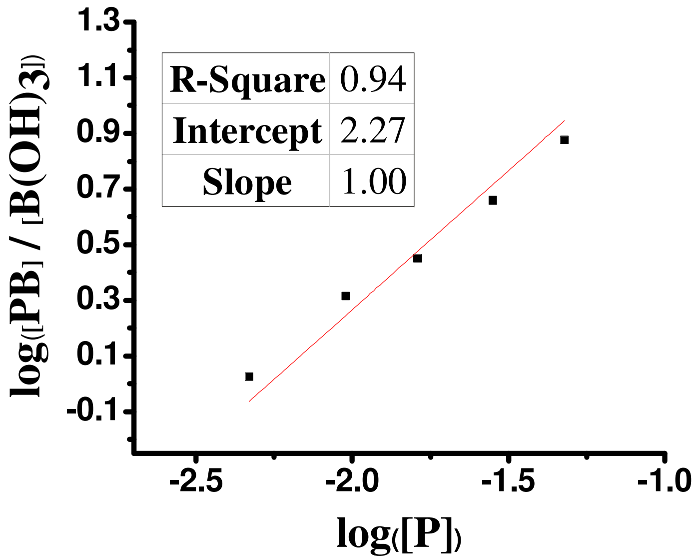


Figure 5.21. Correlation of experimental boron retention results for GPVA-*co*-5%DADMAC at pH 9.0 with model equation.

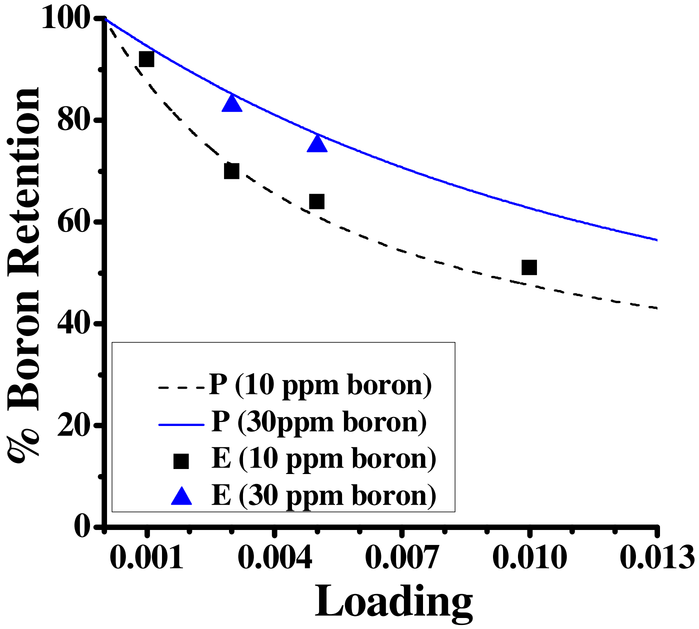


Figure 5.22. Comparison of the theoretical and experimental boron retentions for GPVA-*co*-5%DADMAC in 10 and 30 ppm boron concentrations at pH 9 (**P**: Predicted; **E**: Experimental).

5.6. Boron removal from binary solutions via PEUF

In order to observe the effect of chloride anions on the boron retention, PEUF experiments were carried out using GPVA in solutions containing 10mg.L^{-1} and 100mg.L^{-1} chloride. In Table 5.19, the relevant results are compared with the ones obtained in a previous study in the absence of any anion other than borate. As seen in Table 5.19, introduction of 10mg.L^{-1} chloride did not have any observable effect on boron retention whereas a slight decrease in the retention of boron was observed when 100mg.L^{-1} chloride is present in the solution. This slight deviation is somewhat comparable with the experimental errors which are presented as %RSD (Table 5.19). It was known that boron binding with totally ion-pairing mechanism, can be fully suppressed by dissolving adequate amount of salt while ester formation is not affected by the existence of counter ions [13]. Negligible effect of chloride anion on boron removal most probably shows that boron complexation is dominated by the contribution of chelation mechanism. However, due to existence of protonated amine sites within the macromolecule, a relatively weak ionic attraction may also contribute more or less to complexation. This may explain the slight decrease in boron retention in the presence of chloride in which the effect of protonated amine sites on borate attraction is probably repressed. In addition, the chloride retentions were insignificant as shown in Table 5.19. These results reveal that chloride anions do not compete appreciably with boron in complexation with the polymer. This weak competition is most probably due to non-ionic binding upon formation of coordination bond between the polymer and boric acid.

Table 5.19. Effect of Cl^- anion on boron retention with GPVA (Boron in feed: 10mg.L^{-1}, temperature: 25°C).

Cl^- Conc. (mg.L^{-1})	Loading	pH	% Boron Retention	% Boron Retention in the absence of Cl^-	% Cl^- Retention
10	0.01	9.0	45 ± 2.1	44 ± 1.6	2
100	0.01	9.0	37 ± 2.0	44 ± 1.6	4
100	0.005	8.0	37 ± 1.7	41 ± 1.0	6
100	0.005	9.0	62 ± 0.6	65 ± 1.8	-
100	0.001	9.0	89 ± 0.5	91	2

A similar comparison was made for sulfate which is a divalent anion and the corresponding boron retention results were compared in Table 5.20. It is clearly seen that boron retentions slightly decreased after the introduction of sulfate anions. In addition, the effects of sulfate (Table 5.20) and chloride (Table 5.19) on boron retention do not differ appreciably from each other. The results do not agree with the metal-polyelectrolyte retention studies in which divalent ions suppressed the removal significantly more than monovalent ions [14]. The reason may be as follows: since GPVA possesses both ionic and chelating sites, with the full saturation of protonated amine groups, boron retention results most probably correspond to chelation capacity of imino-bis-propane diol functions and thus a further decrease in boron retention could not be observed in the presence of a divalent ion. Therefore, it can be inferred from Table 5.20 that 61% and 87% boron retention values most probably correspond to chelation capacities at pH 9 for loading values of 0.005 and 0.001, respectively.

Table 5.20. Effect of SO_4^{2-} anion on boron retention with GPVA (Boron concentration in feed: 10mg.L^{-1}, SO_4^{2-} concentration in feed: 100mg.L^{-1}, pH: 9.0, temperature: 25°C).

Loading	**% Boron Retention**	**% Boron Retention in the absence of SO_4^{2-}**
0.005	61 ± 0.5	65 ± 1.8
0.001	87 ± 1.0	91

Salt suppression studies were also conducted for GPVA-*co*-5%DADMAC copolymer. Data in Table 5.21 is related to boron retention results via PEUF using the copolymer in the presence of chloride and sulfate anions. It is clearly seen that presence of counter anion -even 10 times higher than boron concentration- caused a slight reduction in boron retention. This weak effect of counter anions probably means that boron complexation is dominated by chelation mechanism rather than ionic attraction in spite of the existence of charged DADMAC segments inside the macromolecule. As stated before, complexation mechanism is similar for GPVA and GPVA-*co*-5%DADMAC due to the same boron binding units. This explains the fairly well agreement of the decrements in boron retention in Table 5.19 and Table 5.20 with the ones in Table 5.21. Moreover, the decrease in boron retention is independent from the valency of the anion. Similar to homopolymer, boron chelation capacities of copolymer at loading values 0.005 and 0.001 probably correspond to 61% and 88%, respectively.

Table 5.21. Effect of Cl^- and SO_4^{2-} anions on boron retention values with GPVA-*co*-5%DADMAC (Boron in feed: 10mg.L^{-1}, pH: 9.0, temperature: 25°C).

Cl^- Conc. (mg.L^{-1})	SO_4^{2-} Conc. (mg.L^{-1})	Loading	% Boron Retention	% Boron Retention in the absence of other ions
100	**-**	0.005	61 ± 0.8	65 ± 1.8
-	**100**	0.005	61 ± 0.8	65 ± 1.8
-	**100**	0.001	88 ± 0.8	92 ± 1.0
100	**-**	0.001	88 ± 0.8	92 ± 1.0

5.7. Boron removal from Balcova Geothermal Water

Although filtered with microfilter of 0.45μm pore size, in case there is particulate adsorption and accumulation -especially silicate particles- on the UF membrane, the geothermal water is ultrafiltered without recycle of the permeate stream back into the solution and feed and permeate streams were analyzed and the results are represented in Table 5.22. Si concentration is the same for both streams and this value as well as flux do not change with time, which shows there is no significant adsorption and accumulation of Si compounds on the UF membrane.

Table 5.22. Ultrafiltration of 1500mL pre-microfiltered (0.45µm) Balçova geothermal water

Time (min)		**0**	**295**	**655**
Permeate Volume Collected (mL)		0	506	1106
Feed Temp. (^{o}C)		24.8	24.7	25.7
Flux (L/m^2.h)		6.6	6.8	6.5
B (ppm)	**Feed**	-	12.3	12.7
	Permeate	-	12.6	12.9
Si (ppm)	**Feed**	-	59.8	61.4
	Permeate	-	59.1	60.7
Cl^- (ppm)	**Feed**	-	231	234
	Permeate	-	233	229
SO_4^{2-} (ppm)	**Feed**	-	117	121
	Permeate	-	119	118

Table 5.23 shows the results of boron removal studies using geothermal water sample and the functional polymer GPVA at different pH and loading values. The results are compared with the ones found in the absence of other ions. Boron retention values in case of using geothermal water are slightly less than those obtained using boric acid-water solution in the studied range of pH and loading. However, the results are pretty close to each other (for loadings of 0.001 and 0.0005) compared with experimental error range depicted (Table 5.23). Although the geothermal water possesses a rich ionic content (Table 4.1), boron retention is not significantly affected by this environment. This is in compliance with the results obtained in binary solutions (Tables 5.19 and 5.20). The same reasoning seemingly holds probably since there is no other species than boron in geothermal water which form complex with –OH functional on the polymer chain. Ionic species in geothermal water are probably responsible for only the blockage of the charged amine sites on the macromolecule which may partially prevent boron

complexation. Thus, boron retentions in geothermal water most probably correspond to boron-chelation capacities of GPVA in the specified conditions. When compared with data in Table 5.20, 87% boron retention found at pH 9 and loading 0.001 can be a straightforward support for this deduction.

It is seen in Table 5.23 that when the loading was decreased from 0.01 to 0.001, boron retention increased 26% to 87% and this may be explained by increase in the available functional units. However, a small reduction in boron retention (from 87% to 82%) was encountered with a decrease in loading from 0.001 to 0.0005. It is also worth noting that the lowest loading value which could be achieved was 0.0005 due to solubility limitation for GPVA.

Table 5.23. Comparison of boron retention values for geothermal water with the results in the absence of any other ions using GPVA with continuous-mode PEUF at 25^{o}C.

Loading	pH	% Boron Retention in Geothermal Water	% Boron Retention in the absence of other ions	% Cl$^-$ Retention in Geothermal Water
0.0005	**9.0**	82 ± 0.5	-	-
0.001	**Uncontrolled pH (9.6-9.7)**	87 ± 0.8	91 ± 1.2	15 ± 6.4
	9.0	87 ± 0.5	91	7 ± 0.7
	8.0	74	77 ± 1.3	5 ± 4
0.01	**9.0**	26 ± 1.7	44 ± 1.6	-

When Table 5.24 is examined, there is no significant difference among the retention values obtained using three copolymers regardless of the number percent of DADMAC repeating units in the macromolecular chain. However, although a decrease in the boron retention was observed for homopolymer beyond the loading value of 0.001, retention strictly increased for the copolymer up to 98% until the loading value of 0.0002. Moreover, unlike GPVA, loading of 0.0002 could be achieved with GPVA-*co*-5%DADMAC owing to its better solubility. This is an important difference between the homopolymer and the copolymers. Intramolecular ionic repulsion among the DADMAC repeating units might have prevented the contraction of the polymer, the effect of which is most probably responsible for the decrease in the performance of GPVA at high concentrations.

Table 5.24. Comparison of boron retention values between homopolymer and three copolymers for boron separation from geothermal water (* indicates the results obtained at the beginning of batch mode ultrafiltration experiments).

Loading	**pH**	**% Boron Retention with GPVA**	**% Boron Retention with GPVA-co-2%DADMAC**	**% Boron Retention with GPVA-co-5%DADMAC**	**% Boron Retention with GPVA-co-10%DADMAC**
0.001	9.0	87 ± 0.5	83 ± 0.5	82 ± 0.6	84 ± 0.5
0.001	8.0	74	68 ± 1.3	67 ± 2.1	68 ± 0.5
0.0005	9.0	82 ± 0.5	92*	91 ± 0.5	94*
0.0002	9.0	-	-	98*	-

Table 5.25, on the other hand, includes the results of PEUF experiments for Balçova geothermal water with the three different copolymers. As can be seen in both tables, permeate boron concentration is nearly the same for both initial and

final permeate samples for each run. In addition, it stays constant during each run, not presented in these tables but can be seen from the corresponding detailed tables given in Appendix A.

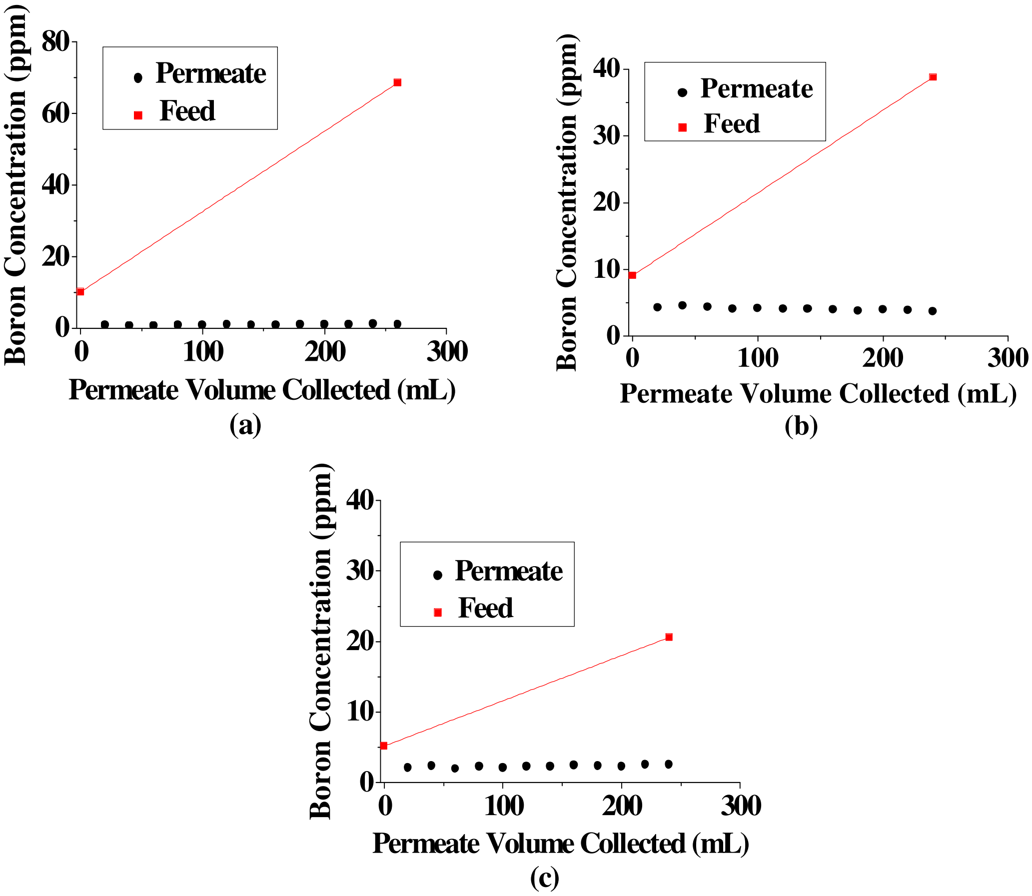
Table 5.25. Results of batch-mode PEUF experiments of Balçova geothermal water at pH 9.0.

Polymer	**GPVA-co2% DADMAC**	**GPVA-co5% DADMAC**			**GPVA-co10% DADMAC**
Initial Loading	0.0005	0.0005	0.0005	0.0002	0.0005
Initial Feed Boron Conc. (ppm)	12.5	12.6	12.5	12.7	12.5
Initial Permeate Boron Conc. (ppm)	1.0	0.8	0.8	0.3	0.8
Initial % Boron Retention	92	94	94	98	94
Final Loading	0.00042	0.00042	0.0005	0.0002	0.00054
Final Feed Boron Conc. (ppm)	32.0	53.0	14.8	15.3	29.0
Final Permeate Boron Conc. (ppm)	0.9	0.7	1.0	0.4	0.7
Final % Boron Retention	97	99	93	97	98

As can be understood from the deductions made above, retention depends not only upon the loading but also the concentration of both boron and the polymer. This is in agreement with the results represented in Table 5.14 in section 5.5.6 under which the reason was discussed.

5.8. Polymer Recovery Experiments

Recovery of polymer was investigated by PEUF experiments which were carried out in batch set-up. In the first part of the experiment, boron removal was performed with PEUF using GPVA in 300mL aqueous solution at pH 9.0 and loading 0.001. Ultrafiltration was conducted until the retentate volume was equal to 40mL. In the second part, the polymer solution which was retained in the cell was completed to 300mL by addition of ultrapure water, the pH of the solution was adjusted to 7.0 and 4.0 for two different runs. In the third part, polymer recovery was repeated. Relevant experiments are demonstrated in Figure 5.23 and Figure 5.24 for recovery pH 7.0 and 4.0, respectively.

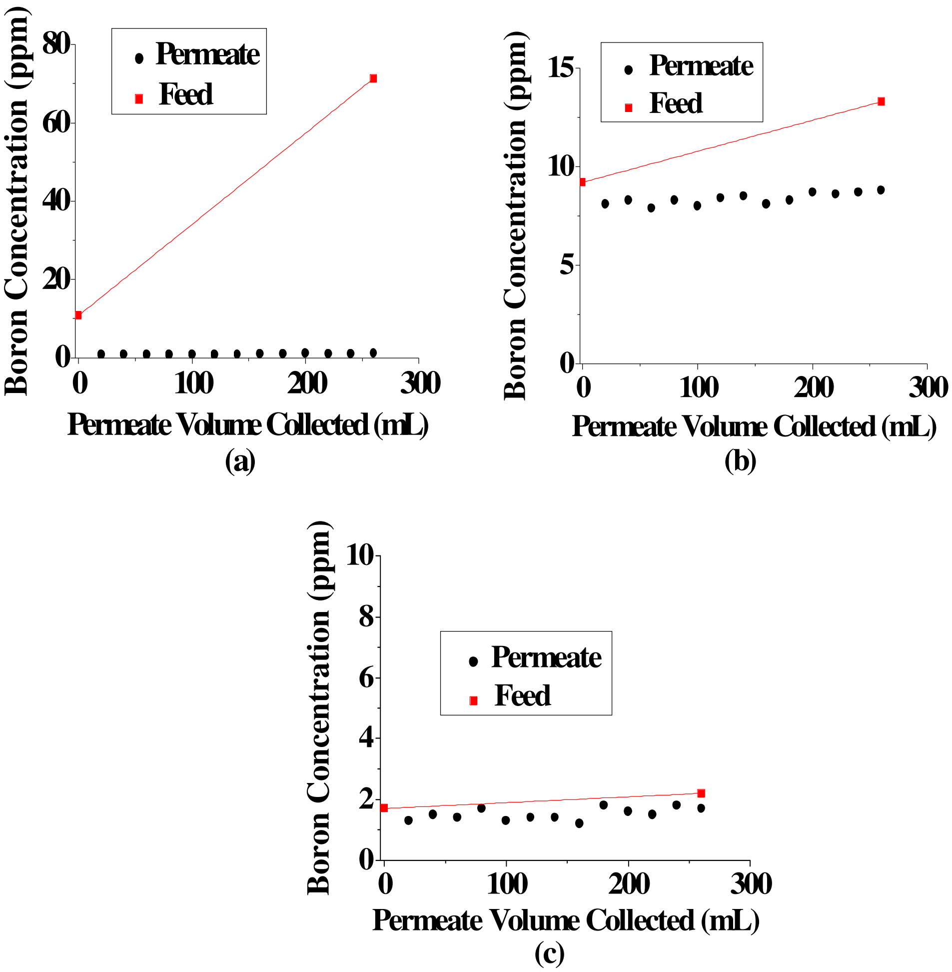


(a)

(b)

(c)

Figure 5.23. Boron removal at pH=9 L=0.001 (a) followed by polymer recovery at pH=7 (b) and (c).



(a)

(b)

(c)

Figure 5.24. Boron removal at pH=9 L=0.001 (a) followed by polymer recovery at pH=4 (b) and (c).

As seen in Figures 5.23 and 5.24, permeate boron concentrations were almost constant for all runs while boron enriched in feed. This is in agreement with the results shown in Figure 5.20. Moreover, much better polymer recovery could be obtained at pH 4 with 97% boron filtered out of the solution when compared with 73% boron filtered out at pH 7. This is an expected result based on the pH-dependency of boron-polymer complexation discussed in part 5.5.4 in details.

CHAPTER 6

CONCLUSIONS

Following conclusions can be drawn from this study:

- A novel water soluble boron chelating polymer, GPVA and a novel functional copolymer, GPVA-*co*-DADMAC were synthesized starting from N-vinyl formamide monomer.
- The polymers with IBPD groups were demonstrated to be efficient boron binding materials. High molecular weight polymers did not show any dissolution problem which may be attributed to permanently charged moieties on the macromolecular chain. Moreover, boron binding occurs without crosslinking or precipitation. The results revealed that the polymers are very efficient for reducing boron concentration to 1-2 ppm even in the presence of other ions with retention values higher than 90%.
- Boron retention was found to be very sensitive to pH change and this promises regeneration ability of the polymer. Regarding with its structure

constituting with non-hydrolizable linkages, repeated use of polymer in PEUF process seems to be possible.

- The highest boron retentions up to 96% were attained using GPVA for 10ppm boron in feed at pH 9.0 and loading of 0.001 in continuous operation while in batch-mode PEUF, the highest retention was obtained as 99% (initial boron concentration: 10ppm, pH: 9 and initial loading: 0.001).
- Employment of the copolymers in continuous PEUF operation showed that boron binding is almost independent from comonomer ratio. High pH dependency of the boron complexation implies regenerability and recycling ability of the copolymers which is important for application viewpoint. Maximum boron retention using copolymers was obtained as 92% (for 10 ppm boron, pH: 9, loading: 0.001) via continuous PEUF, which means the boron concentration in aqueous solutions could be lowered to acceptable concentrations.
- Effect of feed boron concentration on boron retention at constant loading was also investigated and increase in retention was observed when boron concentration increased at constant loading.
- It was found in batch-mode experiments that permeate boron concentration remained almost constant during whole filtration implying an enhancement in boron binding efficiency with increasing concentrations of boron and

polymer. A boron complexation model was proposed and correlated with the experimental boron retentions.

- Reproducibility of the polymer synthesis was investigated by synthesizing the same polymer three times with the same procedure. Almost the same retention values were obtained and small deviations in the boron retention values are most probably due to difference in polymer molecular weights which was caused by the implemented polymerization technique.
- PEUF experiments for the removal of boron were also carried out in the presence of chloride anions. Negligible decrease in boron retention was observed and this may be attributed to blockage of the protonated amine groups and/or the increase in the ionic strength and thus its effect on the conformation of the ionic polymer GPVA. However; the differences are negligibly small, which shows that GPVA is a polychelatogen for boric acid.
- Boron removal from a Geothermal water –from Balçova, İzmir- was achieved from 12.8ppm down to 1.7ppm by PEUF technique with GPVA for a loading of 0.001 both at pH 9.0 and at the solution pH. The retention values of boron were found to be slightly less for geothermal water than for the boric acid solution prepared without any other ionic species at the corresponding pH and loading conditions. However, this is a negligible decrease and it is another indication of the coordination bond between GPVA and boric acid.
- There is not any significant difference between the boron retention values obtained by homopolymer and copolymers up to a loading value of 0.001. However; in the PEUF of Balçova Geothermal water samples, increase in retention could be achieved for less than the loading value of 0.001 with

copolymers while decrease in retention was observed below the same loading with homopolymer. Hence, copolymer seems to have a more promising property for industrial applications.

- Owing to high boron affinity at high pH values and easy decomplexation ability at low pH (pH 4), the novel homopolymer and copolymers can be considered as promising candidates for real applications in boron removal via PEUF.

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APPENDIX A

DATA TABLES OF PEUF EXPERIMENTS

Table A.1. Experiments in the absence of polymer

Membrane: YMPTSP1905 **pH:10.0** **Anion:Boron**									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	4.2	4.3	4.4	4.3	4.3	4.3	4.3	4.4
pH (Feed)	10.01	9.95	10.02	10.01	9.96	10.0	9.93	9.95	9.91
T (^{o}C)	17.2	23.4	23.7	24.9	24.5	24.1	24.7	24.8	25.6
C_f (ppm)	10.8	10.9	10.7	10.8	11.0	11.1	10.9	10.8	10.9
C_p (ppm)	-	5.6	5.7	5.5	5.7	5.7	5.8	6.0	5.9
%R	-	49	48	49	48	49	47	44	46
	$F_{p,avg}$=4.3		**$C_{f,avg}$=10.9**		**$C_{p,avg}$=5.7**			**%R_{avg}=48**	

Membrane: YMPTSP1905 **pH:10.0 Anion:Boron**									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	8.7	9.1	8.9	8.8	8.9	9.1	9.2	9.2
pH (Feed)	9.90	10.06	10.01	9.96	9.97	9.97	9.99	9.99	9.94
T (^{o}C)	26.0	24.4	24.8	25.1	24.8	24.9	24.9	25.0	25.1
C_f (ppm)	9.6	9.6	9.5	9.6	9.7	9.9	9.7	9.8	9.7
C_p (ppm)	-	4.8	4.7	4.9	4.9	5.0	4.9	5.1	5.1
%R	-	51	50	49	49	50	49	48	47
	$F_{p,avg}$= 9.0		**$C_{f,avg}$=9.7**		**$C_{p,avg}$=4.9**			**%R_{avg}=49**	

Table A.1 (continued)

Membrane: YMPTSP1905 **pH:10.0 Anion:Boron ΔP: 800kPa**							
t (min)	**0**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	34.9	35.3	35.3	35.5	35.7	35.1	35.3
pH (Feed)	10.01	9.95	9.97	9.97	9.97	10.00	9.99	9.97
T (^{o}C)	18.7	20.5	21.3	21.4	21.7	21.8	21.9	22.0
C_f (ppm)	10.4	10.2	10.6	10.4	10.3	10.4	10.6	10.6
C_p (ppm)	-	4.7	4.6	4.5	4.8	4.3	4.7	4.6
%R	-	54	56	57	54	58	56	56
	$F_{p,avg}$= 35.3		**$C_{f,avg}$= 10.4**		**$C_{p,avg}$=4.6**		**%R_{avg}= 56**	

Membrane: Polysulfone pH:10.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	36.3	35.9	36.3	35.7
pH (Feed)	9.97	9.90	9.96	9.96	9.95
T (^{o}C)	23.5	24.6	24.9	24.8	24.9
C_f (ppm)	12.2	12.0	12.1	12.1	11.1
C_p (ppm)	-	8.6	8.6	8.1	8.2
%R	-	28	29	33	26
	$F_{p,avg}$= 36.0	**$C_{f,avg}$= 11.9**	**$C_{p,avg}$= 8.4**		**%R_{avg}= 30**

Membrane: HG19 pH:10.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	70.9	69.7	70.4	69.3
pH (Feed)	9.92	9.84	10.20	10.15	10.09
T (^{o}C)	22.8	25.0	24.5	25.0	25.2
C_f (ppm)	11.0	11.2	10.3	10.6	10.7
C_p (ppm)	-	9.0	8.8	8.9	9.0
%R	-	19	15	16	16
	$F_{p,avg}$= 70.1	**$C_{f,avg}$= 10.8**	**$C_{p,avg}$= 8.9**		**%R_{avg}= 17**

Table A.1 (continued)

Membrane: YMPTSP1905 **pH:7.0** **Anion:Boron**								
t (min)	**0**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	73	71	70	71	70	71	71
pH (Feed)	7.09	6.88	6.96	6.94	7.01	6.99	6.95	6.94
T (^{o}C)	25.3	26.6	26.7	26.0	26.1	25.8	26.7	26.8
C_f (ppm)	11.6	11.8	11.9	12.1	11.9	11.6	11.8	11.5
C_p (ppm)	-	12.0	11.9	11.6	11.9	11.7	11.9	12.0
%R	-	0	0	4	0	0	0	0
	$F_{p,avg}$= 71		**$C_{f,avg}$= 11.8**		**$C_{p,avg}$= 11.9**		**%R_{avg}= 0**	

Membrane: YMPTSP1905 **pH:7.5** **Anion:Boron**								
t (min)	**0**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	60	59	59	59	59	58	58
pH (Feed)	7.62	7.46	7.44	7.27	7.49	7.58	7.54	7.50
T (^{o}C)	27.1	26.9	27.2	26.6	26.2	26.5	26.3	26.3
C_f (ppm)	11.7	12.1	11.8	12.1	11.7	11.9	11.9	11.6
C_p (ppm)	-	11.6	11.6	11.9	12.0	12.0	11.6	11.6
%R	-	4	2	2	0	0	3	0
	$F_{p,avg}$= 59		**$C_{f,avg}$= 11.9**		**$C_{p,avg}$= 11.8**		**%R_{avg}= 1**	

Membrane: YMPTSP1905 **pH:8.5** **Anion:Boron**								
t (min)	**0**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	58	57	59	56	57	57	58
pH (Feed)	8.49	8.48	8.53	8.50	8.48	8.43	8.52	8.50
T (^{o}C)	25.6	25.8	25.6	26.0	25.4	25.7	25.6	25.5
C_f (ppm)	12.3	12.0	12.1	11.6	11.5	12.1	12.4	12.4
C_p (ppm)	-	11.0	10.4	10.8	10.6	10.8	10.5	10.8
%R	-	9	14	6	8	10	16	13
	$F_{p,avg}$= 58		**$C_{f,avg}$= 12.0**		**$C_{p,avg}$= 10.7**		**%R_{avg}= 11**	

Table A.1 (continued)

Membrane: YMPTSP1905 **pH:10.0 Anion:Boron**									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	13.3	12.9	12.6	12.3	11.8	11.4	11.2	12.7
pH (Feed)	10.07	9.99	10.06	10.03	10.0	9.97	9.94	9.90	10.00
T (^{o}C)	24.5	25.9	25.1	25.0	25.1	24.8	24.7	23.9	23.3
C_f (ppm)	9.8	9.5	9.4	9.6	9.6	9.5	9.8	9.7	9.5
C_p (ppm)	-	4.7	4.6	4.6	4.8	4.7	4.4	4.6	4.6
%R	-	51	51	52	50	51	55	53	52
	$F_{p,avg}$=12.3		**$C_{f,avg}$=9.6**		**$C_{p,avg}$=4.6**			**%R_{avg}=52**	

Membrane: YMPTSP1905 **pH:9.0 Anion:Boron**									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	9.0	9.0	8.6	8.4	8.1	8.1	7.9	8.1
pH (Feed)	8.98	8.96	8.99	8.96	9.00	8.96	8.95	8.98	9.00
T (^{o}C)	25.1	25.9	24.9	26.3	25.7	25.6	25.5	25.4	25.1
C_f (ppm)	9.3	9.0	9.3	9.3	9.1	9.3	9.3	9.1	9.0
C_p (ppm)	-	7.4	7.1	7.1	7.5	7.3	7.3	7.3	7.2
%R	-	18	24	24	18	22	22	20	20
	$F_{p,avg}$= 8.1		**$C_{f,avg}$=9.2**		**$C_{p,avg}$=7.3**			**%R_{avg}=21**	

Membrane: YMPTSP1905 **pH:8.0 Anion:Boron**									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	7.7	7.6	7.3	7.3	7.3	7.3	7.3	7.3
pH (Feed)	7.96	7.92	8.01	7.97	7.97	8.04	7.97	8.01	7.91
T (^{o}C)	25.2	26.9	26.0	25.0	25.2	25.2	25.2	25.2	25.1
C_f (ppm)	9.2	9.2	9.3	9.1	9.0	9.1	9.1	9.0	9.3
C_p (ppm)	-	8.6	8.3	8.5	8.5	8.5	8.4	8.2	8.3
%R	-	7	11	7	6	7	8	9	11
	$F_{p,avg}$= 7.4		**$C_{f,avg}$=9.1**		**$C_{p,avg}$=8.4**			**%R_{avg}=8**	

Table A.1 (continued)

Membrane: PolySulfone pH:9.0 Anion:Boron								
t (min)	**0**	**60**	**120**	**180**	**240**	**300**	**360**	**1200**
F_p (L/m^{2}h)	-	21	21	22	22	22	22	21
pH (Feed)	9.02	9.05	9.02	8.99	8.97	8.96	9.02	8.80
T (^{o}C)	25.3	25.5	25.5	25.8	25.6	25.5	25.0	26.3
C_f (ppm)	9.7	9.9	9.4	9.3	10.2	9.6	10.2	9.3
C_p (ppm)	-	7.9	7.6	7.5	7.8	7.6	7.6	8.1
%R	-	20	19	19	23	21	25	13
	$F_{p,avg}$= 22 L/m^{2}h		**$C_{f,avg}$= 9.7**		**$C_{p,avg}$= 7.7**		**%R_{avg}= 21**	

Membrane: PolySulfone pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	23	23	23	23
pH (Feed)	8.94	8.87	8.92	8.86	8.85
T (^{o}C)	26.1	26.1	26.2	27.9	27.0
C_f (ppm)	9.3	9.7	9.0	9.2	9.1
C_p (ppm)	-	8.4	8.4	8.2	8.4
%R	-	13	7	10	8
	$F_{p,avg}$= 23 L/m^{2}h	**$C_{f,avg}$= 9.3**	**$C_{p,avg}$= 8.4**	**%R_{avg}= 10**	

Membrane: PolySulfone pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	21	21	22	22
pH (Feed)	8.06	8.00	7.99	7.98	7.99
T (^{o}C)	25.3	25.7	26.3	26.9	27.1
C_f (ppm)	9.6	9.5	9.4	9.2	9.0
C_p (ppm)	-	9.1	8.6	9.3	9.3
%R	-	4	9	0	0
	$F_{p,avg}$= 22 L/m^{2}h	**$C_{f,avg}$= 9.3**	**$C_{p,avg}$= 9.1**		**%R_{avg}= 2**

Table A.1 (continued)

Membrane: YMPTSP1905 **pH:9.5** **Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	26	26	26	26
pH (Feed)	9.50	9.50	9.49	9.44	9.49
T (^{o}C)	25.7	25.0	24.7	25.7	25.2
C_f (ppm)	9.7	9.8	9.7	9.4	9.5
C_p (ppm)	-	5.8	6.0	6.2	6.0
%R	-	41	39	34	37
	$F_{p,avg}$= 26 L/m^{2}h	**$C_{f,avg}$= 9.6**	**$C_{p,avg}$= 6.0**		**%R_{avg}= 38**

Membrane: PolySulfone **pH:8.5** **Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	21	21	20	21
pH (Feed)	8.48	8.47	8.51	8.52	8.53
T (^{o}C)	26.2	25.9	25.5	25.2	25.2
C_f (ppm)	8.2	8.2	8.1	7.8	7.8
C_p (ppm)	-	7.4	7.4	7.3	7.6
%R	-	10	9	6	3
	$F_{p,avg}$= 21 L/m^{2}h	**$C_{f,avg}$= 8.0**	**$C_{p,avg}$= 7.4**		**%R_{avg}= 8**

Membrane: PolySulfone **pH:9.0** **Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20	21	21	20
pH (Feed)	9.01	8.99	8.94	8.99	8.98
T (^{o}C)	25.0	24.8	25.9	25.9	25.9
C_f (ppm)	8.3	7.9	7.9	8.2	8.0
C_p (ppm)	-	6.1	6.1	5.9	5.9
%R	-	23	23	28	26
	$F_{p,avg}$= 21 L/m^{2}h	**$C_{f,avg}$= 8.1**	**$C_{p,avg}$= 6.0**		**%R_{avg}= 26**

Table A.1 (continued)

Membrane: PolySulfone pH:9.5 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	21	22	21	21
pH (Feed)	9.54	9.52	9.44	9.55	9.51
T (^{o}C)	25.6	25.5	26.5	25.5	26.0
C_f (ppm)	8.1	7.6	8.1	7.7	8.2
C_p (ppm)	-	5.8	6.0	6.2	6.2
%R	-	24	26	19	24
	$F_{p,avg}$= 21 L/m^{2}h	**$C_{f,avg}$= 7.9**	**$C_{p,avg}$= 6.0**		**%R_{avg}= 24**

Membrane: HG19 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	45.8	45.2	44.1	44.1
pH (Feed)	8.05	8.00	7.93	7.86	7.92
T (^{o}C)	25.5	26.5	25.6	26.2	25.9
C_f (ppm)	10.3	10.1	10.2	10.4	10.3
C_p (ppm)	-	10.1	10.1	10.4	10.2
%R	-	0	1	0	1
	$F_{p,avg}$= 44.8 L/m^{2}h	**$C_{f,avg}$=10.3**	**$C_{p,avg}$= 10.2**		**%R_{avg}= 1**

Membrane: HG19 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	44.7	44.1	45.2	45.8
pH (Feed)	8.98	8.98	9.03	8.98	8.92
T (^{o}C)	24.7	25.6	25.5	26.0	27.0
C_f (ppm)	10.4	10.3	10.4	10.1	10.4
C_p (ppm)	-	8.9	8.9	8.4	8.6
%R	-	14	14	17	17
	$F_{p,avg}$= 45.0 L/m^{2}h	**$C_{f,avg}$= 10.3**	**$C_{p,avg}$= 8.7**		**%R_{avg}= 16**

Table A.1 (continued)

Membrane: PolySulfone pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	26	26	26	25
pH (Feed)	8.99	9.02	9.05	9.01	8.96
T (^{o}C)	26.1	26.9	26.3	25.8	27.0
C_f (ppm)	9.3	9.2	9.4	9.8	10.0
C_p (ppm)	-	6.8	7.3	7.1	7.5
%R	-	26	22	28	25
	$F_{p,avg}$= 26 L/m^{2}h	**$C_{f,avg}$= 9.5**	**$C_{p,avg}$= 7.2**		**%R_{avg}= 24**

Membrane: YMPTSP1905 **pH:8.0 Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.1	19.0	18.8	19.1
pH (Feed)	8.04	8.02	7.95	7.99	8.01
T (^{o}C)	24.8	24.5	25.4	25.8	25.9
C_f (ppm)	32.0	31.8	32.4	32.1	32.0
C_p (ppm)	-	30.1	30.0	30.2	31.1
%R	-	5	8	6	3
	$F_{p,avg}$= 19.0 L/m^{2}h	**$C_{f,avg}$= 32.1**	**$C_{p,avg}$= 30.4**		**%R_{avg}= 5**

Membrane: YMPTSP1905 **pH:9.0 Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.2	19.0	19.2	19.1
pH (Feed)	9.01	9.00	9.00	9.02	9.00
T (^{o}C)	25.8	25.6	25.8	25.7	25.5
C_f (ppm)	31.7	32.0	31.8	31.6	31.7
C_p (ppm)	-	29.1	29.2	28.7	28.9
%R	-	9	8	9	9
	$F_{p,avg}$= 19.1 L/m^{2}h	**$C_{f,avg}$= 31.8**	**$C_{p,avg}$= 29.0**		**%R_{avg}= 9.0**

Table A.1 (continued)

Membrane: YMPTSP1905 **pH:10.0** **Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	18.9	19.1	19.1	19.2
pH (Feed)	9.96	9.99	10.02	9.98	9.96
T (°C)	25.2	25.3	25.5	25.2	25.8
C_f (ppm)	31.8	32.1	31.5	31.8	31.7
C_p (ppm)	-	23.5	24.4	22.9	22.6
%R	-	27	23	28	29
	$F_{p,avg}$= 19.1 L/m^2h	**$C_{f,avg}$= 31.8**	**$C_{p,avg}$= 23.4**		**%R_{avg}= 26**

Membrane: YMPTSP1905 **pH:10.0** **Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	19.2	19.2	19.0	18.9
pH (Feed)	9.98	10.02	10.02	10.00	10.01
T (°C)	25.4	25.2	25.5	25.3	25.1
C_f (ppm)	6.3	6.3	5.7	6.0	6.1
C_p (ppm)	-	2.7	2.7	2.7	2.7
%R	-	57	54	56	56
	$F_{p,avg}$= 19.1 L/m^2h	**$C_{f,avg}$= 6.1**	**$C_{p,avg}$= 2.7**		**%R_{avg}= 56**

Membrane: YMPTSP1905 **pH:9.0** **Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	19.0	19.1	19.1	19.1
pH (Feed)	9.03	8.99	8.96	8.98	8.96
T (°C)	25.4	26.1	25.6	25.9	26.1
C_f (ppm)	5.8	6.0	6.1	5.8	5.9
C_p (ppm)	-	4.6	4.5	4.6	4.4
%R	-	24	25	21	25
	$F_{p,avg}$= 19.1 L/m^2h	**$C_{f,avg}$= 5.9**	**$C_{p,avg}$= 4.5**		**%R_{avg}= 24**

Table A.1 (continued)

Membrane: YMPTSP1905 **pH:8.0** **Anion:Boron**					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.2	19.0	19.1	19.2
pH (Feed)	8.03	8.02	8.02	8.04	8.03
T (^{o}C)	25.4	25.5	25.5	25.4	25.4
C_f (ppm)	5.6	5.6	5.7	5.4	5.5
C_p (ppm)	-	5.3	5.3	5.3	5.3
%R	-	6	7	2	5
	$F_{p,avg}$= 19.1 L/m^{2}h	**$C_{f,avg}$= 5.6**	**$C_{p,avg}$= 5.3**		**%R_{avg}= 5**

Table A.2. Experiments with GPVA and synthetic water

Polymer: GPVA1 L:0.001 pH:9.0 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	11.9	11.5	11.5	11.1	11.0	11.2	11.1	11.1
pH (Feed)	8.98	8.99	8.98	8.99	8.96	8.97	8.97	8.97	8.96
T (^{o}C)	25.1	25.2	25.3	25.1	25.3	24.9	25.2	25.0	25.2
TOC (feed)									5593
TOC (perm.)									211
C_f (ppm)	11.9	11.7	11.9	12.1	12.6	12.8	12.8	13.2	13.5
C_p (ppm)		0.5	0.5	0.5	0.6	0.5	0.5	0.5	0.5
%R		96	96	96	95	96	96	96	96
	$F_{p,avg}$=11.3		**$C_{f,avg}$=12.5**		**$C_{p,avg}$=0.5**			**%R_{avg}=96**	
Polymer: GPVA1 L:0.001 pH:8.0 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	11.6	11.4	11.7	11.4	11.4	11.7	11.1	11.2
pH (Feed)	8.00	7.98	7.98	7.99	7.98	8.00	8.01	8.01	8.03
T (^{o}C)	25.2	25.3	25.2	25.0	25.4	25.3	25.3	25.2	25.3
TOC (feed)									3585
TOC (perm.)									106
C_f (ppm)	8.7	8.6	8.7	8.6	8.8	8.7	8.7	8.6	8.7
C_p (ppm)		2.0	2.0	2.0	1.9	1.9	1.8	1.8	1.8
%R		77	77	77	78	78	79	79	79
	$F_{p,avg}$=11.4		**$C_{f,avg}$=8.7**		**$C_{p,avg}$=1.9**			**%R_{avg}=%78**	

Table A.2 (continued)

Polymer: GPVA1 L:0.001 pH:7.0 Anion:Boron								
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**240**
F_p (L/m^{2}h)	-	11.7	10.9	11.0	10.8	10.8	10.9	11.0
pH (Feed)	6.94	7.03	7.06	7.03	7.05	7.03	7.06	7.02
T (^{o}C)	25.2	25.0	25.6	25.0	25.1	25.4	25.6	26.0
TOC (feed)								4085
TOC (perm.)								102
C_f (ppm)	8.0	8.1	8.1	8.1	8.1	8.0	8.1	8.0
C_p (ppm)		4.0	4.0	4.2	4.1	4.1	3.9	4.0
%R		51	51	48	49	49	52	50
	$F_{p,avg}$=11.0		**$C_{f,avg}$=8.1**		**$C_{p,avg}$=4.0**		**%R_{avg}=51**	

Polymer: GPVA1 L:0.01 pH:8.5 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)		12.4	12.2	12.4	12.5	12.5	12.6	12.6	12.8
pH (Feed)	8.49	8.48	8.47	8.50	8.49	8.48	8.49	8.49	8.48
T (^{o}C)	25.2	24.9	25.0	25.1	25.1	25.1	25.2	25.2	25.2
TOC (feed)									473
TOC (perm)									22
C_f (ppm)	9.9	9.9	9.9	10.0	10.1	10.2	10.2	10.4	10.3
C_p (ppm)		7.1	7.0	7.2	6.7	7.0	6.7	6.6	6.8
%R		28	29	28	34	31	34	37	34
	$F_{p,avg}$=12.5		**$C_{f,avg}$=10.1**		**$C_{p,avg}$=6.9**			**%R_{avg}=32**	

Table A.2 (continued)

Polymer: GPVA1 L:0.01 pH:7.5 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)		13.0	12.8	12.7	12.9	12.4	12.5	12.5	12.5
pH (Feed)	7.48	7.51	7.51	7.52	7.55	7.54	7.52	7.53	7.50
T (^{o}C)	25.2	25.3	25.3	25.4	25.5	25.3	25.3	25.2	25.2
TOC (feed)									534
TOC (perm)									21
C_f (ppm)	10.0	9.9	10.1	9.9	9.8	10.1	9.9	10.1	10.2
C_p (ppm)		8.0	8.4	8.4	8.8	9.0	8.7	-	9.1
%R		19	17	15	10	11	12	-	11
	$F_{p,avg}$=12.7		**$C_{f,avg}$=10.0**		**$C_{p,avg}$=8.6**			**%R_{avg}=14**	

Polymer: GPVA1 L:0.001 pH:10.0 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	10.9	10.6	10.4	10.7	10.7	10.5	10.4	10.3
pH (Feed)	9.95	9.99	9.94	9.99	9.98	9.97	9.99	9.96	9.97
T (^{o}C)	25.4	25.2	25.6	25.3	25.5	25.3	24.9	25.4	25.5
C_f (ppm)	10.9	11.0	10.4	11.1	10.7	10.8	11.0	11.1	11.4
C_p (ppm)		1.1	1.0	1.0	1.0	1.2	1.0	1.0	1.2
%R		90	90	91	91	89	91	91	89
	$F_{p,avg}$=10.6		**$C_{f,avg}$=10.9**		**$C_{p,avg}$=1.1**			**%R_{avg}=90**	

Table A.2 (continued)

Polymer: GPVA1 L:0.01 pH:8.0 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)		12.5	12.4	12.4	12.2	12.5	12.6	12.7	11.9
pH (Feed)	8.02	8.03	8.00	8.02	8.04	8.00	8.02	8.04	8.05
T (^{o}C)	24.0	24.3	24.4	24.6	24.4	24.7	24.6	24.6	24.6
TOC (feed)									703.6
TOC (perm)									21.9
C_f (ppm)	11.9	10.7	10.9	11.0	11.9	-	11.1	11.1	10.6
C_p (ppm)		7.8	7.6	7.4	7.5	7.5	7.6	-	7.7
%R		27	30	33	37	-	32	-	27
	$F_{p,avg}$=12.4		**$C_{f,avg}$=11.2**		**$C_{p,avg}$=7.6**			**%R_{avg}=32**	

Polymer: GPVA1 L:0.01 pH:9.0 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)		12.2	12.1	12.1	11.8	11.8	11.8	11.8	11.8
pH (Feed)	9.0	8.96	8.99	8.98	9.00	8.97	9.00	8.99	9.00
pH (Perm.)			8.65		8.68				
T (^{o}C)	24.3	25.7	25.0	25.3	25.0	25.3	25.2	24.9	24.6
C_f (ppm)	-	10.2	10.4	10.4	10.7	10.3	-	10.6	10.2
C_p (ppm)	-	5.2	4.8	5.2	5.0	5.1	5.1	4.9	5.0
%R		49	54	50	53	50	-	54	51
	$F_{p,avg}$=11.9		**$C_{f,avg}$=10.4**		**$C_{p,avg}$=5.0**			**%R_{avg}=52**	

Table A.2 (continued)

Polymer: GPVA1 L:0.01 pH:10.0 Anion:Boron									
t (min)	**0**	**30**	**60**	**90**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)		10.8	10.8	10.8	10.8		10.8		10.8
pH (Feed)		10.00	10.00	9.98	9.95		9.95		9.98
pH (Perm.)									9.84
T (^{o}C)		24.7	24.8	24.8	24.9		25.3		25.7
C_f (ppm)	10.9	-	-	10.4	10.6		10.6		11.0
C_p (ppm)		4.6	5.1	5.0	5.1		5.0		5.2
%R	-	-	-	52	52		53		53
	$F_{p,avg}$=10.8		**$C_{f,avg}$=10.7**		**$C_{p,avg}$=5.0**			**%R_{avg}=53**	

Polymer: GPVA1 L:0.01 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)		4.0	4.0	4.1	4.1
pH (Feed)	9.00	9.00	9.00	9.00	9.00
T (^{o}C)	22	22	22	22	22
C_f (ppm)	9.34	10.24	10.39	10.46	10.42
C_p (ppm)		4.42	3.84	4.45	4.12
%R		57	63	57	60
	$F_{p,avg}$= 4.1	**$C_{f,avg}$= 10.17**	**$C_{p,avg}$= 4.21**		**%R_{avg}= 59**

Polymer: GPVA1 L:0.01 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)		7.1	7.1	6.2	6.2
pH (Feed)	9.0	9.0	9.0	9.0	9.0
T (^{o}C)	25	25	25	25	25
C_f (ppm)	12.2	12.3	11.9	11.2	12.1
C_p (ppm)		5.0	5.1	4.9	5.0
%R		59	57	56	59
	$F_{p,avg}$=6.7	**$C_{f,avg}$= 12.1**	**$C_{P,avg}$= 5.0**		**%R_{avg}= 59**

Table A.2 (continued)

Polymer: GPVA1 L:0.01 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)		7.0	7.7	7.7	7.4
pH (Feed)	9.00	9.00	9.00	9.00	9.00
T (^{o}C)	25	25	25	25	25
C_f (ppm)	10.5	10.7	10.7	10.7	10.5
C_p (ppm)		4.9	4.2	5.9	5.3
%R		54	61	45	50
	$F_{p,avg}$=7.5	**$C_{f,avg}$=10.6**	**$C_{p,avg}$=5.1**		**%R_{avg}= 53**

Polymer: GPVA1 L:0.01 pH:10.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)		6.5	6.5	6.4	6.3
pH (Feed)	10.0	10.0	10.0	10.0	10.0
T (^{o}C)	25	25	25	25	25
C_f (ppm)	12.0	12.3	12.8	12.0	11.5
C_p (ppm)		4.9	5.1	5.0	5.0
%R		60	60	59	57
	$F_{p,avg}$=6.4	**$C_{f,avg}$= 12.3**	**$C_{P,avg}$= 5.0**		**%R_{avg}= 59**

Polymer: GPVA1 L:0.01 pH:7.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)		6.8	7.0	7.0	6.8
pH (Feed)	9.0	9.0	9.0	9.0	9.0
T (^{o}C)	25	25	25	25	25
C_f (ppm)	9.6	10.0	10.1	9.5	9.2
C_p (ppm)		8.4	-	8.7	8.3
%R		16	-	8	10
	$F_{p,avg}$=6.9	**$C_{f,avg}$= 9.8**	**$C_{P,avg}$= 8.5**		**%R_{avg}= 13**

Table A.2 (continued)

Polymer: GPVA1 L:0.01 pH:10.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)		8.3	8.3	7.7	7.7
pH (Feed)	10.0	10.0	10.0	10.0	10.0
T (^{o}C)	25	25	25	25	25
C_f (ppm)	11.3	12.8	12.9	11.9	11.4
C_p (ppm)		5.2	5.3	5.1	5.2
%R		59	59	57	54
	$F_{p,avg}$=8.0	**$C_{f,avg}$=12.1**	**$C_{p,avg}$=5.2**		**%R_{avg}= 57**

Polymer: GPVA1 L:0.01 pH:7.0 Anion:Boron							
t (min)	**0**	**60**	**120**	**150**	**180**	**210**	**240**
F_p (L/m^{2}h)	-	12.4	12.5	12.5	12.0	11.9	12.1
pH (Feed)	7.0	7.0	7.0	7.0	7.0	7.0	7.0
T (^{o}C)	25	24	23	24	24	23	24
C_f (ppm)	8.6	8.4	8.5	-	8.5	8.7	8.5
C_p (ppm)	-	8.1	8.2	8.1	8.0	8.2	7.8
%R	-	4	4	-	6	6	8
	$F_{p,avg}$=12.2		**$C_{f,avg}$=8.5**		**$C_{p,avg}$= 8.1**		**%R_{avg}=6**

Polymer: GPVA1 L:0.001 pH:9.5 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	26	26	25	26
pH (Feed)	9.61	9.43	9.45	9.45	9.42
T (^{o}C)	23.2	27.1	25.9	25.6	25.1
C_f (ppm)	10.7	10.7	10.3	10.7	10.9
C_p (ppm)	-	0.7	0.7	0.7	0.6
%R	-	94	93	94	94
	$F_{p,avg}$= 26 L/m^{2}h	**$C_{f,avg}$= 10.7**	**$C_{p,avg}$= 0.7**		**%R_{avg}= 94**

Table A.2 (continued)

Polymer: GPVA1 L:0.001 pH:8.5 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	26	26	26	26
pH (Feed)	8.49	8.48	8.40	8.41	8.46
TOC Feed					4380
TOC Permeate					74.5
T (°C)	24.9	24.0	25.7	25.3	25.0
C_f (ppm)	10.0	9.6	10.0	10.0	9.9
C_p (ppm)	-	1.2	1.4	1.3	1.3
%R	-	0.87	0.86	0.87	0.87
	$F_{p,avg}$= 26 L/m^2h	**$C_{f,avg}$= 9.9**	**$C_{p,avg}$= 1.3**		**%R_{avg}= 87**

Polymer: GPVA1 L:0.002 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	26	26	27	26
pH (Feed)	8.01	7.92	7.99	8.04	8.03
T (°C)	25.3	26.6	26.7	24.5	25.1
C_f (ppm)	8.9	8.9	9.1	9.3	8.8
C_p (ppm)	-	3.6	3.3	3.3	3.3
%R	-	59	64	64	63
	$F_{p,avg}$= 26 L/m^2h	**$C_{f,avg}$= 9.0**	**$C_{p,avg}$= 3.4**		**%R_{avg}= 62**

Polymer: GPVA1 L:0.005 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	26	26	26	26
pH (Feed)	8.01	8.03	8.01	8.01	7.99
T (°C)	24.4	24.4	24.8	24.9	24.9
C_f (ppm)	9.6	9.7	10.0	9.4	9.5
C_p (ppm)	-	5.2	5.1	5.3	5.2
%R	-	46	50	44	45
	$F_{p,avg}$= 26 L/m^2h	**$C_{f,avg}$= 9.6**	**$C_{p,avg}$= 5.2**		**%R_{avg}= 46**

Table A.2 (continued)

Polymer: GPVA1 L:0.0075 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	29	26	27	26
pH (Feed)	8.09	8.04	8.02	8.02	8.00
T (^{o}C)	25.0	25.8	25.5	25.5	25.5
C_f (ppm)	9.6	9.6	10.2	9.8	10.2
C_p (ppm)	-	5.6	5.9	5.5	5.5
%R	-	42	42	43	46
	$F_{p,avg}$= 27 L/m^{2}h	**$C_{f,avg}$= 9.9**	**$C_{p,avg}$= 5.6**		**%R_{avg}= 43**

Polymer: GPVA1 L:0.01 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	26	26	27	27
pH (Feed)	8.05	8.00	7.99	7.98	7.97
T (^{o}C)	24.9	25.5	25.6	25.7	25.7
C_f (ppm)	10.1	10.5	10.1	10.0	10.0
C_p (ppm)	-	6.9	6.7	6.8	6.9
%R	-	34	34	32	31
	$F_{p,avg}$= 27 L/m^{2}h	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 6.8**		**%R_{avg}= 33**

Polymer: GPVA1 L:0.01 pH:8.5 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	26	26	26	26
pH (Feed)	8.51	8.45	8.52	8.51	8.51
T (^{o}C)	25.7	25.7	25.7	25.7	25.7
C_f (ppm)	10.5	10.8	10.5	11.2	10.6
C_p (ppm)	-	5.6	5.6	5.8	5.7
%R	-	48	46	48	46
	$F_{p,avg}$= 26 L/m^{2}h	**$C_{f,avg}$= 10.7**	**$C_{p,avg}$= 5.7**		**%R_{avg}= 47**

Table A.2 (continued)

Polymer: GPVA2 L:0.005 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20.1	19.9	20.2	20.1
pH (Feed)	8.01	7.89	8.02	8.04	8.01
T (^{o}C)	24.9	24.5	25.3	25.3	24.8
C_f (ppm)	9.3	9.9	9.5	9.5	9.7
C_p (ppm)	-	5.9	5.6	5.5	5.6
%R	-	40	41	42	42
	$F_{p,avg}$= 20.1 L/m^{2}h	**$C_{f,avg}$= 9.6**	**$C_{p,avg}$= 5.7**		**%R_{avg}= 41**

Polymer: GPVA2 L:0.001 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20.6	20.6	20.6	20.3
pH (Feed)	8.13	8.00	8.03	8.01	8.02
T (^{o}C)	25.4	26.5	25.9	25.8	26.3
Feed TOC					4050
Permeate TOC					76
C_f (ppm)	11.4	11.3	11.2	11.4	11.3
C_p (ppm)	-	2.4	2.7	2.6	2.8
%R	-	78	76	77	75
	$F_{p,avg}$= 21 L/m^{2}h	**$C_{f,avg}$= 11.3**	**$C_{p,avg}$= 2.6**		**%R_{avg}= 77**

Polymer: GPVA2 L:0.001 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20.6	20.6	20.3	20.6
pH (Feed)	9.00	9.00	8.93	8.96	8.97
T (^{o}C)	25.5	25.7	25.2	25.4	25.7
C_f (ppm)	10.8	11.0	11.0	11.0	11.0
C_p (ppm)	-	1.0	1.0	0.9	0.9
%R	-	91	91	91	91
	$F_{p,avg}$= 21 L/m^{2}h	**$C_{f,avg}$= 11.0**	**$C_{p,avg}$= 1.0**		**%R_{avg}= 91**

Table A.2 (continued)

Polymer: GPVA2 L:0.01 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	20.2	20.6	20.0	20.2
pH (Feed)	9.06	8.99	9.13	9.14	9.01
T (^oC)	24.9	26.2	26.3	26.1	25.5
C_f (ppm)	10.2	10.0	10.1	10.4	9.9
C_p (ppm)	-	5.7	6.0	5.7	5.7
%R	-	43	41	45	42
	$F_{p,avg}$= 20.3 L/m^2h	**$C_{f,avg}$= 10.1**	**$C_{p,avg}$= 5.8**		**%R_{avg}= 43**

Polymer: GPVA2 L:0.01 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	20.4	20.0	20.4	20.6
pH (Feed)	9.05	9.02	8.99	9.03	9.02
T (^oC)	25.7	25.6	25.3	25.3	25.1
C_f (ppm)	9.7	9.7	9.6	9.5	9.7
C_p (ppm)	-	5.3	5.3	5.4	5.3
%R	-	45	45	43	45
	$F_{p,avg}$= 20.4 L/m^2h	**$C_{f,avg}$= 9.6**	**$C_{p,avg}$= 5.3**		**%R_{avg}= 45**

Polymer: GPVA3 L:0.001 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	19.3	19.2	19.0	19.3
pH (Feed)	9.04	9.05	9.02	8.99	8.98
T (^oC)	25.1	25.5	25.6	25.6	25.3
C_f (ppm)	10.4	10.5	10.9	10.8	10.6
C_p (ppm)	-	0.9	1.2	1.0	1.2
%R	-	91	89	91	89
	$F_{p,avg}$= 19.2 L/m^2h	**$C_{f,avg}$= 10.6**	**$C_{p,avg}$= 1.1**		**%R_{avg}= 90**

Table A.2 (continued)

Polymer: GPVA3 L:0.01 pH:9.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.0	19.1	19.1	18.9
pH (Feed)	9.02	9.01	9.02	9.00	9.03
T (^{o}C)	25.7	25.5	25.7	25.8	25.6
C_f (ppm)	29.9	31.0	30.7	30.4	30.3
C_p (ppm)	-	13.4	13.3	13.6	12.5
%R	-	57	57	55	59
	$F_{p,avg}$= 19.0 L/m^{2}h	**$C_{f,avg}$= 30.5**	**$C_{p,avg}$= 13.2**		**%R_{avg}= 57**

Polymer: GPVA3 L:0.01 pH:9.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.3	19.1	19.4	19.3
pH (Feed)	9.00	9.02	9.01	8.99	9.02
T (^{o}C)	25.1	25.4	25.3	25.5	25.2
C_f (ppm)	10.2	10.5	10.4	10.6	10.5
C_p (ppm)	-	5.4	5.1	5.5	5.5
%R	-	48	51	48	47
	$F_{p,avg}$= 19.3 L/m^{2}h	**$C_{f,avg}$= 10.4**	**$C_{p,avg}$= 5.4**		**%R_{avg}= 48**

Polymer: GPVA3 L:0.01 pH:9.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.4	19.4	19.1	19.2
pH (Feed)	9.03	9.00	8.99	9.01	8.98
T (^{o}C)	24.9	24.8	25.2	25.3	25.5
C_f (ppm)	4.5	4.6	4.7	4.5	4.7
C_p (ppm)	-	2.5	2.9	2.7	2.7
%R	-	44	38	40	43
	$F_{p,avg}$= 19.3 L/m^{2}h	**$C_{f,avg}$= 4.6**	**$C_{p,avg}$= 2.7**		**%R_{avg}= 41**

Table A.2 (continued)

Polymer: GPVA3 L:0.002 pH:8.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.3	19.0	19.1	19.1
pH (Feed)	8.02	7.98	8.01	8.01	8.03
T (^{o}C)	25.3	25.7	25.4	25.8	25.7
C_f (ppm)	9.9	10.0	9.8	9.8	9.8
C_p (ppm)	-	3.7	4.0	4.2	4.1
%R	-	63	59	58	58
	$F_{p,avg}$= 19.1 L/m^{2}h	**$C_{f,avg}$= 9.9**	**$C_{p,avg}$= 4.0**		**%R_{avg}= 60**

Polymer: GPVA3 L:0.002 pH:8.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.3	19.2	19.2	19.0
pH (Feed)	8.03	8.06	8.02	8.06	8.04
T (^{o}C)	25.9	25.6	25.1	25.2	25.5
C_f (ppm)	5.1	5.2	5.2	5.1	5.2
C_p (ppm)	-	1.9	2.7	2.7	2.8
%R	-	63	48	47	46
	$F_{p,avg}$= 19.2 L/m^{2}h	**$C_{f,avg}$= 5.2**	**$C_{p,avg}$= 2.5**		**%R_{avg}= 52**

Polymer: GPVA3 L:0.002 pH:9.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.3	19.3	19.0	19.2
pH (Feed)	9.01	8.98	9.03	9.05	9.02
T (^{o}C)	25.6	25.7	25.3	25.1	25.5
C_f (ppm)	5.1	5.2	5.2	5.2	5.2
C_p (ppm)	-	1.6	1.6	1.6	1.8
%R	-	69	69	69	65
	$F_{p,avg}$= 19.2 L/m^{2}h	**$C_{f,avg}$= 5.2**	**$C_{p,avg}$= 1.7**		**%R_{avg}= 67**

Table A.2 (continued)

Polymer: GPVA3 L:0.002 pH:9.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.0	18.9	19.1	19.1
pH (Feed)	8.95	8.98	9.02	8.96	8.98
T (^{o}C)	23.6	24.8	24.2	24.6	24.8
C_f (ppm)	30.4	30.4	30.5	30.5	30.4
C_p (ppm)	-	2.4	2.5	2.4	2.5
%R	-	92	92	92	92
	$F_{p,avg}$= 19.0 L/m^{2}h	**$C_{f,avg}$= 30.4**	**$C_{p,avg}$= 2.5**		**%R_{avg}= 92**

Polymer: GPVA3 L:0.002 pH:8.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	18.9	18.8	19.0	18.9
pH (Feed)	8.02	8.03	8.05	8.01	8.03
T (^{o}C)	24.9	25.2	25.0	25.1	25.2
C_f (ppm)	31.1	30.9	30.9	30.9	31.1
C_p (ppm)	-	6.8	6.9	7.0	6.8
%R	-	78	78	77	78
	$F_{p,avg}$= 18.9 L/m^{2}h	**$C_{f,avg}$= 31**	**$C_{p,avg}$= 6.9**		**%R_{avg}= 78**

Polymer: GPVA3 L:0.0005 pH:9.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	17.7	17.8	17.6	17.8
pH (Feed)	9.01	9.00	8.98	9.00	8.99
T (^{o}C)	25.5	25.5	25.3	25.6	25.7
C_f (ppm)	10.3	10.4	10.2	10.3	10.3
C_p (ppm)	-	0.7	0.7	0.7	0.7
%R	-	93	93	93	93
	$F_{p,avg}$= 17.7 L/m^{2}h	**$C_{f,avg}$= 10.3**	**$C_{p,avg}$= 0.7**		**%R_{avg}= 93**

Table A.2 (continued)

Polymer: GPVA3 L:0.002 pH:9.0 Anion: Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.3	19.2	19.1	19.3
pH (Feed)	9.05	9.03	9.06	9.02	9.03
T (^{o}C)	25.7	25.3	25.9	25.1	24.9
C_f (ppm)	10.5	10.3	10.4	10.3	10.3
C_p (ppm)	-	2.2	1.9	1.8	2.1
%R	-	79	82	83	80
	$F_{p,avg}$= 19.2 L/m^{2}h	**$C_{f,avg}$= 10.4**	**$C_{p,avg}$= 2.0**		**%R_{avg}= 81**

Table A.3. Experiments with GPVA and Cl^- in synthetic water

Polymer: GPVA2 L:0.005 pH:8.0 Anion:Boron and 100ppm Cl^-					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20.1	20.3	19.8	20.0
pH (Feed)	8.03	8.05	8.03	8.02	8.06
T (^{o}C)	25.4	25.9	26.1	25.8	25.5
C_f (ppm)	9.9	9.9	9.8	9.7	9.8
C_p (ppm)	-	6.1	6.4	6.3	6.1
Feed Cl (ppm)	105	102	100	106	101
Perm Cl (ppm)	-	98	98	97	94
%R	-	38	35	35	38
	$F_{p,avg}$= 20.1 L/m^{2}h	**$C_{f,avg}$= 9.8**	**$C_{p,avg}$= 6.2**		**%R_{avg}= 37**
		Cl Feed=103	**Cl Perm=97**		

Polymer: GPVA2 L:0.001 pH:9.0 Anion:Boron and 100ppm Cl^-					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20.0	20.6	20.6	20.3
pH (Feed)	9.09	9.07	9.06	9.07	9.06
T (^{o}C)	26.2	26.0	26.1	26.1	25.9
C_f (ppm)	11.2	11.2	11.1	11.3	11.3
C_p (ppm)	-	1.2	1.1	1.1	1.2
Cl Feed Conc. (ppm)	101	104	99	100	99
Cl Perm. Conc. (ppm)	-	99	99	98	99
%R	-	89	90	90	90
	$F_{p,avg}$= 20 L/m^{2}h	**$C_{f,avg}$= 11.2**	**$C_{p,avg}$= 1.2**		**%R_{avg}= 89**

Table A.3 (continued)

Polymer: GPVA2 L:0.01 pH:9.0 Anion:Boron and 100ppm Cl^-					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.9	20.0	20.1	20.0
pH (Feed)	9.01	9.03	9.01	8.98	9.02
T (^{o}C)	25.4	25.1	25.8	25.6	25.2
C_f (ppm)	8.7	8.5	8.4	8.4	8.5
C_p (ppm)	-	5.1	5.2	5.3	5.2
Feed Cl Conc.(ppm)	107	119	106	113	116
Perm Cl Conc.(ppm)	-	115	102	98	109
% B Retention	-	40	38	37	39
% Cl Retention	-	3	4	13	6
	$F_{p,avg}$= 20.0 L/m^{2}h	**$C_{f,avg}$= 8.5**	**$C_{p,avg}$= 5.2**	**Cl %R = 5**	**B R_{avg}= 39%**

Table A.3 (continued)

Polymer: GPVA2 L:0.01 pH:9.0 Anion:Boron and 100ppm Cl^-					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	20.2	20.2	20.4	20.0
pH (Feed)	9.01	8.93	8.94	9.00	9.01
T (^oC)	24.5	25.3	25.6	25.6	25.6
C_f (ppm)	8.6	9.0	9.0	8.6	9.0
C_p (ppm)	-	5.6	5.7	5.7	5.6
Feed Cl Conc.(ppm)	102	107	104	104	103
Perm Cl Conc.(ppm)	-	98	103	107	99
% B Retention	-	37	37	33	37
% Cl Retention	-	8	1	0	4
	$F_{p,avg}$= 20.2 L/m^2h	**$C_{f,avg}$= 8.8**	**$C_{p,avg}$= 5.7**	**Cl %R = 2**	**% B R_{avg}= 35**
	Cl Feed=104	**Cl Perm=102**			

Table A.3 (continued)

Polymer: GPVA2 L:0.01 pH:9.0 Anion:Boron and 10ppm Cl^-					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^2h)	-	20.4	20.4	20.2	20.0
pH (Feed)	9.04	9.01	8.98	9.03	9.01
T (^oC)	25.2	24.7	24.9	25.1	25.3
C_f (ppm)	9.9	10.1	10.0	9.7	10.4
C_p (ppm)	-	5.5	5.5	5.6	5.4
Feed Cl Conc.(ppm)	10.3	10.0	10.3	10.2	10.4
Perm Cl Conc.(ppm)	-	9.7	10.3	9.9	10.0
% B Retention	-	45	45	43	48
% Cl Retention	-	3	0	3	4
	$F_{p,avg}$= 20.3 L/m^2h	**$C_{f,avg}$= 10.0**	**$C_{p,avg}$= 5.5**	**Cl %R = 2**	**B R_{avg}= 45**
	Cl Feed= 10.2	**Cl Perm.=10.0**			

Table A.4. Experiments with GPVA-co-DADMAC and synthetic water

Polymer: GPVA-co-2%DADMAC L:0.01 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	38.7	38.1	39.4	38.1
pH (Feed)	9.05	8.97	8.97	8.96	8.98
T (^{o}C)	23.8	26.2	25.1	25.7	25.7
Feed TOC					486
Permeate TOC					23
C_f (ppm)	10.9	10.5	10.7	11.1	11.0
C_p (ppm)	-	5.9	6.0	5.6	6.1
%R	-	44	44	49	45
	$F_{p,avg}$= 39 L/m^{2}h	**$C_{f,avg}$= 10.8**	**$C_{p,avg}$= 5.9**		**%R_{avg}= 45**

Polymer: GPVA-co-2%DADMAC L:0.01 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	37.5	38.1	38.7	37.5
pH (Feed)	8.04	8.02	8.01	8.01	8.01
T (^{o}C)	23.7	25.9	25.6	25.5	26.3
C_f (ppm)	9.9	10.0	9.8	9.8	10.2
C_p (ppm)	-	7.9	7.8	7.8	7.5
%R	-	21	21	20	26
	$F_{p,avg}$= 38 L/m^{2}h	**$C_{f,avg}$= 9.9**	**$C_{p,avg}$= 7.8**		**%R_{avg}= 21**

Polymer: GPVA-co-5%DADMAC L:0.003 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.2	19.3	19.2	19.0
pH (Feed)	8.98	9.02	9.00	8.99	9.02
T (^{o}C)	25.2	24.9	25.3	25.5	25.3
C_f (ppm)	10.7	10.4	10.5	10.4	10.3
C_p (ppm)	-	2.9	3.2	3.3	3.3
%R	-	72	70	68	68
	$F_{p,avg}$= 19.2 L/m^{2}h	**$C_{f,avg}$= 10.5**	**$C_{p,avg}$= 3.2**		**%R_{avg}= 70**

Table A.4 (continued)

Polymer: GPVA-co-5%DADMAC L:0.005 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.0	19.2	19.2	19.1
pH (Feed)	9.01	9.03	8.98	8.96	8.97
T (^{o}C)	25.8	25.4	25.9	25.7	25.8
C_f (ppm)	30.9	31.4	30.7	30.5	31.8
C_p (ppm)	-	7.6	7.5	8.0	7.8
%R	-	76	76	74	75
	$F_{p,avg}$= 19.1 L/m^{2}h	**$C_{f,avg}$= 31.1**	**$C_{p,avg}$= 7.7**		**%R_{avg}= 75**

Polymer: GPVA-co-5%DADMAC L:0.005 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.0	19.1	19.0	19.2
pH (Feed)	9.04	9.02	9.01	9.03	8.94
T (^{o}C)	24.4	25.1	25.9	25.6	25.3
C_f (ppm)	10.3	10.1	10.2	10.4	10.1
C_p (ppm)	-	3.5	3.7	3.9	3.7
%R	-	65	64	63	63
	$F_{p,avg}$= 19.1 L/m^{2}h	**$C_{f,avg}$= 10.2**	**$C_{p,avg}$= 3.7**		**%R_{avg}= 64**

Polymer: GPVA-co-5%DADMAC L:0.003 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.1	19.1	19.3	19.0
pH (Feed)	8.96	9.01	9.02	8.99	9.03
T (^{o}C)	25.4	25.6	25.9	25.9	25.5
C_f (ppm)	29.5	29.7	29.8	30.2	29.8
C_p (ppm)	-	5.2	5.0	5.4	5.3
%R	-	82	83	82	82
	$F_{p,avg}$= 19.1 L/m^{2}h	**$C_{f,avg}$= 29.8**	**$C_{p,avg}$= 5.2**		**%R_{avg}= 83**

Table A.5. Experiments with Balçova Geothermal Water

Polymer: GPVA-co-10%DADMAC L:0.001 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.0	18.9	19.2	19.0
pH (Feed)	9.09	9.08	9.01	9.07	9.06
T (^{o}C)	26.3	26.8	28.1	25.9	26.3
C_f (ppm)	12.8	12.8	12.7	12.8	12.8
C_p (ppm)	-	2.0	2.0	1.9	1.9
%R	-	84	85	85	85
	$F_{p,avg}$= 19.0 L/m^{2}h	**$C_{f,avg}$= 12.8**	**$C_{p,avg}$= 2.0**		**%R_{avg}= 84**

Polymer: GPVA-co-10%DADMAC L:0.001 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	18.9	19.2	18.8	18.9
pH (Feed)	8.08	8.10	8.06	8.06	8.07
T (^{o}C)	26.9	26.6	26.7	26.1	26.3
C_f (ppm)	13.0	12.8	13.0	12.8	12.9
C_p (ppm)	-	4.0	4.2	4.1	4.1
%R	-	68	67	68	68
	$F_{p,avg}$= 19.0 L/m^{2}h	**$C_{f,avg}$= 12.9**	**$C_{p,avg}$= 4.1**		**%R_{avg}= 68**

Polymer: GPVA-co-5%DADMAC L:0.001 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	18.7	18.9	18.9	19.0
pH (Feed)	9.01	8.98	8.98	8.99	8.99
T (^{o}C)	25.3	25.5	25.6	25.1	25.4
C_f (ppm)	12.8	12.8	12.8	12.8	12.8
C_p (ppm)	-	2.3	2.3	2.2	2.2
%R	-	82	82	83	83
	$F_{p,avg}$= 18.9 L/m^{2}h	**$C_{f,avg}$= 12.8**	**$C_{p,avg}$= 2.3**		**%R_{avg}= 82**

Table A.5 (continued)

Polymer: GPVA-co-5%DADMAC L:0.001 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	18.9	19.1	19.0	18.9
pH (Feed)	8.05	8.05	8.06	8.09	8.08
T (^{o}C)	25.7	26.3	26.5	24.9	25.3
C_f (ppm)	12.8	12.9	12.8	12.8	12.7
C_p (ppm)	-	4.5	4.2	3.9	4.1
%R	-	65	67	70	68
	$F_{p,avg}$= 19.0 L/m^{2}h	**$C_{f,avg}$= 12.8**	**$C_{p,avg}$= 4.2**		**%R_{avg}= 67**

Polymer: GPVA-co-2%DADMAC L:0.001 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.0	18.9	18.9	19.1
pH (Feed)	9.01	9.02	9.00	9.01	9.01
T (^{o}C)	25.3	25.6	25.3	25.1	25.5
C_f (ppm)	12.8	12.9	12.9	12.9	12.8
C_p (ppm)	-	2.3	2.2	2.3	2.3
%R	-	83	83	83	82
	$F_{p,avg}$= 19.0 L/m^{2}h	**$C_{f,avg}$= 12.9**	**$C_{p,avg}$= 2.3**		**%R_{avg}= 83**

Polymer: GPVA-co-2%DADMAC L:0.001 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	18.9	19.0	18.9	18.9
pH (Feed)	8.06	8.10	8.03	8.05	8.06
T (^{o}C)	25.2	25.4	25.7	25.5	25.9
C_f (ppm)	12.8	13.0	12.9	13.0	12.9
C_p (ppm)	-	3.9	4.1	4.3	4.1
%R	-	70	68	67	68
	$F_{p,avg}$= 18.9 L/m^{2}h	**$C_{f,avg}$= 12.9**	**$C_{p,avg}$= 4.1**		**%R_{avg}= 68**

Table A.5 (continued)

Polymer: GPVA2 L:0.01 pH:Not Manipulated Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.2	18.7	18.3	18.9
pH (Feed)	8.32	8.28	8.30	8.35	8.38
T (^{o}C)	25.2	26.1	26.3	25.9	26.4
C_f (ppm)	12.3	12.4	12.3	12.2	12.3
C_p (ppm)	-	11.0	11.1	11.1	11.0
%R	-	11	10	10	11
	$F_{p,avg}$= 18.8 L/m^{2}h	**$C_{f,avg}$= 12.3**	**$C_{p,avg}$= 11.1**		**%R_{avg}= 10**

Polymer: GPVA2 L:0.01 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	18.6	18.9	19.2	18.7
pH (Feed)	8.97	8.98	8.98	8.99	8.99
T (^{o}C)	26.2	27.1	26.3	25.8	25.3
C_f (ppm)	12.4	12.3	12.3	12.3	12.5
C_p (ppm)	-	9.1	9.2	9.1	8.9
%R	-	26	25	26	29
	$F_{p,avg}$= 18.9 L/m^{2}h	**$C_{f,avg}$= 12.4**	**$C_{p,avg}$= 9.1**		**%R_{avg}= 26**

Polymer: GPVA2 L:0.0005 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	17.6	17.9	17.2	17.7
pH (Feed)	8.98	8.96	8.96	8.97	8.95
T (^{o}C)	25.1	27.2	27.3	26.4	27.1
C_f (ppm)	12.0	12.0	12.1	12.2	12.1
C_p (ppm)	-	2.2	2.2	2.1	2.2
%R	-	81	82	82	82
	$F_{p,avg}$= 17.6 L/m^{2}h	**$C_{f,avg}$= 12.1**	**$C_{p,avg}$= 2.2**		**%R_{avg}= 82**

Table A.5 (continued)

Polymer: GPVA2 L:0.001 pH:Not Manipulated Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20.2	20.2	19.9	20.1
pH (Feed)	9.67	9.59	9.56	9.59	9.60
T (^{o}C)	23.7	26.0	26.7	25.5	25.2
C_f (ppm)	12.7	13.0	12.5	12.6	12.8
C_p (ppm)	-	1.7	1.4	1.5	1.6
Feed Cl Conc.(ppm)	-	-	-	246	230
Perm Cl Conc.(ppm)	-	-	-	199	207
% B Retention	-	87	89	88	88
% Cl Retention		-	-	19	10
	$F_{p,avg}$= 20.1 L/m^{2}h	**$C_{f,avg}$= 12.7**	**$C_{p,avg}$= 1.6**	**% Cl R=15**	**% B R_{avg}= 87**

Table A.5 (continued)

Polymer: GPVA2 L:0.001 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	19.8	19.8	20.2	20.0
pH (Feed)	9.02	8.98	8.97	9.02	9.01
pH (Permeate)	-	8.96	8.95	8.99	8.99
T (^{o}C)	25.4	25.5	25.7	25.6	25.3
C_f (ppm)	13.0	12.7	12.4	12.5	12.5
C_p (ppm)	-	1.7	1.7	1.7	1.7
Feed Cl Conc.(ppm)	-	-	-	255	239
Perm Cl Conc.(ppm)	-	-	-	237	221
% B Retention	-	87	86	86	86
% Cl Retention	-	-	-	7	8
	$F_{p,avg}$= 20.0 L/m^{2}h	**$C_{f,avg}$= 12.6**	**$C_{p,avg}$= 1.7**	**% Cl R=7**	**% B R_{avg}= 87**

Table A.5 (continued)

Polymer: GPVA2 L:0.001 pH:8.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	20.1	20.3	19.8	20.0
pH (Feed)	8.06	8.07	8.05	8.06	8.04
pH (Permeate)	8.01	8.03	8.01	8.00	8.00
T (°C)	26.1	25.9	25.8	25.7	25.3
C_f (ppm)	13.0	12.7	12.4	12.5	12.5
C_p (ppm)	-	3.3	3.2	3.2	3.3
Feed Cl Conc.(ppm)	-	-	-	242	228
Perm Cl Conc.(ppm)	-	-	-	220	226
% B Retention	-	74	74	74	74
% Cl Retention		-	-	9	1
	$F_{p,avg}$= 20.1 L/m^{2}h	**$C_{f,avg}$= 12.6**	**$C_{p,avg}$= 3.3**	**% Cl R= 5**	**% B R_{avg}= 74**

Polymer: GPVA-co-5%DADMAC L:0.0005 pH:9.0 Anion:Boron					
t (min)	**0**	**60**	**120**	**180**	**240**
F_p (L/m^{2}h)	-	17.5	17.3	17.2	17.7
pH (Feed)	8.96	8.98	8.98	9.02	9.01
T (°C)	26.4	26.1	25.9	25.3	25.7
C_f (ppm)	12.7	12.6	12.7	12.7	12.7
C_p (ppm)	-	1.1	1.1	1.2	1.0
%R	-	91	91	91	92
	$F_{p,avg}$= 17.4 L/m^{2}h	**$C_{f,avg}$= 12.7**	**$C_{p,avg}$= 1.1**		**%R_{avg}= 91**

Table A.6. Batch-Mode Experiments

Water : Synthetic
Polymer Name : GPVA
Loading : 0.002
pH : 9.0
Anion : 5ppm Borate
ΔP : 200 kPa
Membrane : PolyetherSulfone
MWCO : 5000 Da
Initial Feed Volume: 236mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140
Feed Volume (mL)	216	196	176	156	136	116	96
Flux (L/m^2.h)	9.8	9.8	9.7	9.7	9.7	9.5	8.8
Feed Conc. (ppm)	5.3	-	-	-	-	-	10.4
Perm Conc. (ppm)	1.7	1.7	1.6	1.5	1.4	1.3	1.2
% Boron Retention	69	-	-	-	-	-	88

Water : Synthetic
Polymer Name : GPVA
Loading : 0.0005
pH : 9.0
Anion : 10ppmBoron
ΔP : 200 kPa
Membrane : PolyetherSulfone
MWCO : 5000 Da
Initial Feed Volume: 230mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180
Feed Volume (mL)	210	190	170	150	130	110	90	70	50
Flux (L/m^2.h)	16.8	16.8	15.9	15.0	13.3	11.5	9.2	7.0	4.5
Feed Conc. (ppm)	10.3	-	-	-	-	-	-	-	24.7
Perm Conc. (ppm)	0.7	0.7	0.7	0.3	0.4	0.2	0.3	0.4	0.4
% Boron Retention	93	-	-	-	-	-	-	-	98

Table A.6 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA
Loading	:	0.001
pH	:	9.0
Anion	:	10ppmBoron
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5000 Da
Initial Feed Volume:		230mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180
Feed Volume (mL)	210	190	170	150	130	110	90	70	50
Flux ($L/m^2.h$)	17.0	16.8	16.8	16.8	16.7	16.4	15.2	12.6	7.8
Feed Conc. (ppm)	10.4	-	-	-	-	-	-	-	27
Perm Conc. (ppm)	0.9	0.8	0.8	0.7	0.7	0.6	0.5	0.6	0.4
% Boron Retention	91	-	-	-	-	-	-	-	99

Table A.6 (continued)

Water	**:**	BALÇOVA Geothermal
Polymer Name	**:**	GPVA-co5%DADMAC
Loading	**:**	0.0005
pH	**:**	9.0
Anion	**:**	Borate
ΔP	**:**	200 kPa
Membrane	**:**	PolyetherSulfone
MWCO	**:**	5000 Da
Initial Feed Volume:		250mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200
Feed Volume (mL)	230	210	190	170	150	130	110	90	70	50
Flux ($L/m^2.h$)	10.1	10.1	10.0	9.9	9.8	9.2	8.4	6.6	5.5	4.3
Feed Conc. (ppm)	12.6	-	-	-	-	-	-	-	-	53
Perm Conc. (ppm)	0.8	0.8	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.7
% Boron Retention	94	-	-	-	-	-	-	-	-	99

Table A.6 (continued)

Water	:	BALÇOVA Geothermal
Polymer Name	:	GPVA-co2%DADMAC
Loading	:	0.0005
pH	:	9.0
Anion	:	Borate
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5000 Da
Initial Feed Volume:		209mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140
Feed Volume (mL)	189	169	149	129	109	89	69
Flux ($L/m^2.h$)	10.1	9.9	9.5	9.2	8.4	7.4	5.6
Feed Conc. (ppm)	12.5	-	-	-	-	-	32
Perm Conc. (ppm)	1.0	0.9	0.9	0.9	0.9	0.9	0.9
% Boron Retention	92	-	-	-	-	-	97

Table A.6 (continued)

Water	**:**	BALÇOVA Geothermal
Polymer Name	**:**	GPVA-co10%DADMAC
Loading	**:**	0.0005
pH	**:**	9.0
Anion	**:**	Borate
ΔP	**:**	200 kPa
Membrane	**:**	PolyetherSulfone
MWCO	**:**	5000 Da
Initial Feed Volume:		222mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140
Feed Volume (mL)	202	182	162	142	122	102	82
Flux ($L/m^2.h$)	9.9	10.0	9.7	9.5	9.1	8.2	7.0
Feed Conc. (ppm)	12.5	-	-	-	-	-	29
Perm Conc. (ppm)	0.8	0.8	0.7	0.8	0.7	0.7	0.7
% Boron Retention	94	-	-	-	-	-	98

Table A.6 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA-co5%DADMAC
Loading	:	0.005
pH	:	9.0
Anion	:	Borate
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5000 Da
Initial Feed Volume:		300mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240
Feed Volume (mL)	280	260	240	220	200	180	160	140	120	100	80	60
Flux ($L/m^2.h$)	9.9	9.8	9.9	9.8	9.8	9.8	9.8	9.8	9.8	9.9	9.8	9.4
Feed Conc. (ppm)	10.8	-	-	-	-	-	-	-	-	-	-	30.2
Perm Conc. (ppm)	3.8	3.9	4.2	4.1	4.1	4.2	4.3	4.4	4.4	4.5	4.4	4.2
% Boron Retention	65	-	-	-	-	-	-	-	-	-	-	86

Table A.6 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA-co5%DADMAC
Loading	:	0.01
pH	:	9.0
Anion	:	Borate
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5000 Da
Initial Feed Volume:		200mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140
Feed Volume (mL)	180	160	140	120	100	80	60
Flux ($L/m^2.h$)	9.8	9.9	9.8	9.8	9.8	9.8	9.8
Feed Conc. (ppm)	11.2	-	-	-	-	-	18.8
Perm Conc. (ppm)	6.3	6.4	6.6	6.6	6.9	6.8	6.6
% Boron Retention	44	-	-	-	-	-	65

Table A.7. Regeneration Experiments

Water : Synthetic
Polymer Name : GPVA
Initial Loading : 0.001
pH : 9.0
Initial Boron Conc.: 10ppm
∆P : 200 kPa
Membrane : PolyetherSulfone
MWCO : 5000 Da
Initial Feed Volume: 300mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240	260
Feed Volume (mL)	280	260	240	220	200	180	160	140	120	100	80	60	40
Flux ($L/m^2.h$)	20.4	20.7	20.6	19.0	17.5	16.7	15.6	14.6	13.6	12.2	7.3	7.7	3.7
Feed Conc. (ppm)	10.5	-	-	-	-	-	-	-	-	-	-	-	71
Perm Conc. (ppm)	0.9	0.8	0.9	0.9	0.9	0.9	1.0	0.9	0.9	0.9	1.1	1.1	1.0
% Boron Retention	91	-	-	-	-	-	-	-	-	-	-	-	99

Table A.7 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA
Loading	:	0.001
pH	:	7.0
Initial Boron Conc.	:	10ppm
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5000 Da
Initial Feed Volume	:	280mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240	260
Feed Volume (mL)	260	240	220	200	180	160	140	120	100	80	60	40	20
Flux (L/m^2.h)	20.3	20.1	19.1	17.2	15.9	14.8	14.4	12.7	11.6	6.8	6.2	3.4	2.8
Feed Conc. (ppm)	9.4	-	-	-	-	-	-	-	-	-	-	-	74.7
Perm Conc. (ppm)	4.4	4.5	4.4	4.3	4.1	4.1	4.0	4.1	3.9	4.0	3.8	3.9	3.8
% Boron Retention	53	-	-	-	-	-	-	-	-	-	-	-	95

Table A.7 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA
Initial Loading	:	0.001
pH	:	9.0
Initial Boron Conc.	:	10ppm
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5kDa
Initial Feed Volume	:	300mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240	260
Feed Volume (mL)	280	260	240	220	200	180	160	140	120	100	80	60	40
Flux ($L/m^2.h$)	20.7	20.5	20.1	19.4	18.1	17.5	15.9	14.1	12.9	10.6	7.1	5.6	2.9
Feed Conc. (ppm)	10.1	-	-	-	-	-	-	-	-	-	-	-	68.6
Perm Conc. (ppm)	0.8	0.7	0.7	0.8	0.9	1.0	0.9	0.8	1.0	1.1	1.0	1.2	1.1
% Boron Retention	92	-	-	-	-	-	-	-	-	-	-	-	98

Table A.7 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA
Loading	:	0.001
pH	:	7.0
Initial Boron Conc.	:	9.1ppm
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5kDa
Initial Feed Volume	:	280mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240
Feed Volume (mL)	260	240	220	200	180	160	140	120	100	80	60	40
Flux ($L/m^2.h$)	20.1	20.4	19.8	17.5	16.1	14.6	14.2	12.3	11.2	7.3	5.8	3.1
Feed Conc. (ppm)	9.1	-	-	-	-	-	-	-	-	-	-	38.8
Perm Conc. (ppm)	4.3	4.6	4.4	4.1	4.2	4.1	4.1	4.0	3.8	4.0	3.9	3.7
% Boron Retention	53	-	-	-	-	-	-	-	-	-	-	90

Table A.7 (continued)

Water : Synthetic
Polymer Name : GPVA
Loading : 0.0006
pH : 7.0
Initial Boron Conc.: 5.2ppm
ΔP : 200 kPa
Membrane : PolyetherSulfone
MWCO : 5kDa
Initial Feed Volume: 280mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240
Feed Volume (mL)	260	240	220	200	180	160	140	120	100	80	60	40
Flux ($L/m^2.h$)	19.8	19.4	19.4	16.5	15.7	13.9	12.8	12.1	11.0	7.1	5.3	2.7
Feed Conc. (ppm)	5.2	-	-	-	-	-	-	-	-	-	-	20.6
Perm Conc. (ppm)	2.1	2.4	2.0	2.3	2.1	2.3	2.3	2.5	2.4	2.3	2.6	2.6
% Boron Retention	60	-	-	-	-	-	-	-	-	-	-	87

Table A.7 (continued)

Water	**:**	Synthetic
Polymer Name	**:**	GPVA4
Initial Loading	**:**	0.001
pH	**:**	9.0
Initial Boron Conc.	**:**	10ppm
ΔP	**:**	200 kPa
Membrane	**:**	PolyetherSulfone
MWCO	**:**	5kDa
Initial Feed Volume	**:**	300mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240	260
Feed Volume (mL)	280	260	240	220	200	180	160	140	120	100	80	60	40
Flux ($L/m^2.h$)	23.1	23.5	23.4	22.7	20.8	19.3	17.5	15.6	13.7	11.4	8.7	5.9	3.2
Feed Conc. (ppm)	10.7	-	-	-	-	-	-	-	-	-	-	-	71.3
Perm Conc. (ppm)	0.8	0.9	0.8	0.8	0.9	0.8	0.9	1.0	1.1	1.2	1.1	1.0	1.2
% Boron Retention	93	-	-	-	-	-	-	-	-	-	-	-	98

Table A.7 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA4
Loading	:	0.001
pH	:	4.0
Initial Boron Conc.	:	9.2ppm
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5kDa
Initial Feed Volume	:	300mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240	260
Feed Volume (mL)	280	260	240	220	200	180	160	140	120	100	80	60	40
Flux ($L/m^2.h$)	23.4	23.2	23.5	22.5	21.3	19.6	17.7	15.3	13.4	10.9	8.4	5.7	2.8
Feed Conc. (ppm)	9.2	-	-	-	-	-	-	-	-	-	-	-	13.3
Perm Conc. (ppm)	8.1	8.3	7.9	8.3	8.0	8.4	8.5	8.1	8.3	8.7	8.6	8.7	8.8
% Boron Retention	12	-	-	-	-	-	-	-	-	-	-	-	34

Table A.7 (continued)

Water	:	Synthetic
Polymer Name	:	GPVA4
Loading	:	0.00017
pH	:	4.0
Initial Boron Conc.	:	1.7ppm
ΔP	:	200 kPa
Membrane	:	PolyetherSulfone
MWCO	:	5kDa
Initial Feed Volume	:	300mL

Total Permeate Collected (mL)	20	40	60	80	100	120	140	160	180	200	220	240	260
Feed Volume (mL)	280	260	240	220	200	180	160	140	120	100	80	60	40
Flux ($L/m^2.h$)	23.8	23.1	23.2	22.6	21.8	20.1	18.4	15.2	13.9	10.8	7.9	5.4	3.3
Feed Conc. (ppm)	1.7	-	-	-	-	-	-	-	-	-	-	-	2.2
Perm Conc. (ppm)	1.3	1.5	1.4	1.7	1.3	1.4	1.4	1.2	1.8	1.6	1.5	1.8	1.7
% Boron Retention	24	-	-	-	-	-	-	-	-	-	-	-	23

APPENDIX B

DETERMINATION OF POLYMER MOLECULAR WEIGHTS

Table B.1. Time of flight data with respect to concentration of Polyvinyl formamide 1 in aqueous solution at 25°C.

Concentration, C (g/L)	Time of flight, t (s)	$(t-t_o)/(t_oC)$
0	105	-
0.215	132	1.20
0.645	200	1.40
0.774	238	1.64

$$[\eta] = 1.15 \text{ dL/g} = KM_V^{\alpha}$$

$$1.15 = 5.43x10^{-4}M_V^{0.715}$$

$M_V \cong 44800\ g/mole$ for Polyvinyl formamide 1.

Table B.2. Time of flight data with respect to concentration of Polyvinyl formamide 2 in aqueous solution at 25°C.

Concentration, C (g/L)	Time of flight, t (s)	$(t-t_o)/(t_oC)$
0	307	-
0.01313	313	1.488
0.0175	315	1.489
0.035	322	1.396
0.0525	328	1.303
0.2625	324	0.211

$$[\eta] = 1.571\ \mathrm{dL/g} = KM_V^{\alpha}$$

$$1.571 = 5.43x10^{-4}M_V^{0.715}$$

$$M_V \cong 69356\ g/mole \text{ for Polyvinyl formamide 2}$$

Table B.3. Time of flight data with respect to concentration of Polyvinyl formamide 3 in aqueous solution at 25°C.

Concentration, C (g/L)	Time of flight, t (s)	$(t-t_o)/(t_oC)$
0	305	-
0.00659	308	1.493
0.0142	311	1.385
0.0407	321	1.289
0.2374	335	0.414

$$[\eta] = 1.482\ \mathrm{dL/g} = KM_V^{\alpha}$$

$$1.482= 5.43x10^{-4}M_V^{0.715}$$

$$M_V \cong 63930\ g/mole \text{ for Polyvinyl formamide 3}$$

APPENDIX C

DETERMINATION OF BORON CONCENTRATION BY DRE-ICP-OES ANALYSIS METHOD AND SAMPLE CALCULATIONS

In order to calibrate the instrument, standards for permeate and feed are prepared with ultrapure water. The permeate standards are prepared with boron and ultrapure water, whereas the feed standards are prepared using additional polymer in the same concentration as that of feed solution. Five standard solutions are introduced to the system for feed and permeate. These standard solutions are pumped into plasma and the intensities of the standards are obtained. Representative intensity data obtained from permeate and feed calibrations are given in Tables C.1 and C.2, respectively. Sample calibration plots for permeate and feed are given in Figures C.1 and C.2, respectively. After the calibrations, samples are introduced and the intensities of the samples are recorded. Using the calibration curve together with the obtained intensity for each sample, the concentrations of the samples are calculated.

Table C.1. Representative intensity data of the standard solutions of borate for permeate.

Permeate Calibration		
Boron Concentration (ppm)	Intensity	Corrected Intensity
0	1929	0
1.5	22264	20335
4.5	55680	53751
7.5	92826	90897
10	115489	113560
12	141105	139176

Table C.2. Representative intensity data of the standard solutions of borate for feed.

Feed Calibration for GPVA L:0.01 pH:9		
Boron Concentration (ppm)	Intensity	Corrected Intensity
0	3205	0
4.5	57181	53976
7.5	97810	94605
10	128785	125580
12	155246	152041

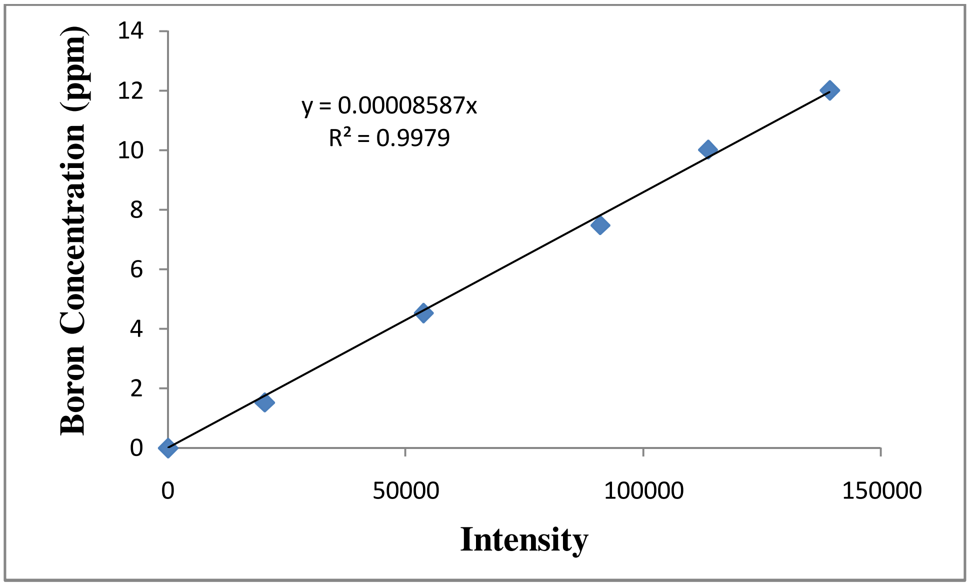


Figure C.1. Calibration curve with the intensity and concentration relation for the corresponding permeate analysis.

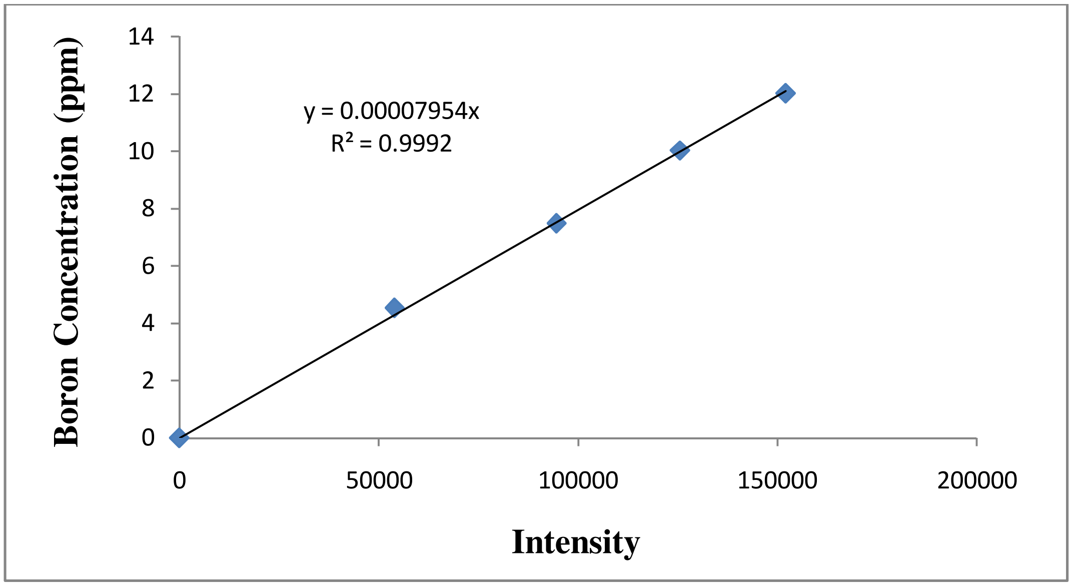


Figure C.2. Calibration curve with the intensity and concentration relation for the corresponding feed analysis.

The concentrations of permeate and feed samples are calculated by the equation given on the calibration curve plots, which relates the intensity to concentration. For a sample run with a loading of 0.01 and pH of 9, permeate and feed intensities and their corresponding concentrations are shown in Tables C.3 and C.4, respectively.

Table C.3. Sample intensity data and the determined concentration values of borate in representative permeate samples.

Time (min)	**Average Intensity**	**Corrected Intensity**	**Concentration (ppm)**
60	63150	61221	5.3
120	63312	61383	5.3
180	64598	62669	5.4
240	64159	62230	5.3

Table C.4. Sample intensity data and the determined concentration values of borate in representative feed samples.

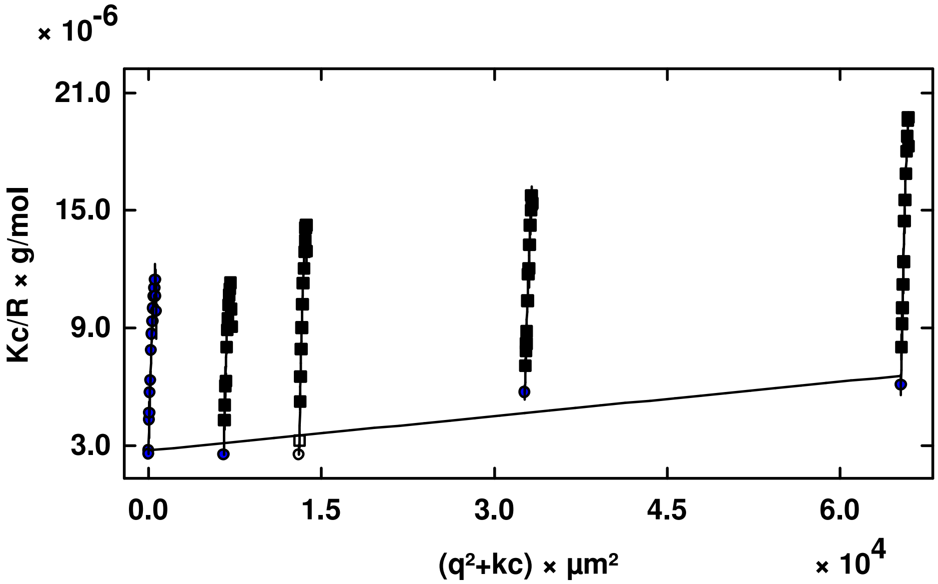
Time (min)	**Average Intensity**	**Corrected Intensity**	**Concentration (ppm)**
0	125327	122122	9.7
60	124983	121778	9.7
120	123294	120089	9.6
180	123269	120064	9.5
240	124610	121405	9.7

APPENDIX D

DYNAMIC AND STATIC LIGHT SCATTERING EXPERIMENTS

Table D.1. Data obtained from guinier plot of polyvinyl amine / water solution at pH 7.

Conc. (g/L)	Rg (nm)
10	97.7
5	110.8
2	130.4
1	192.3
Infinite dilution	183.0



Mw(c): 3.645e+05 g/mol Mw(q²): 3.896e+05 g/mol

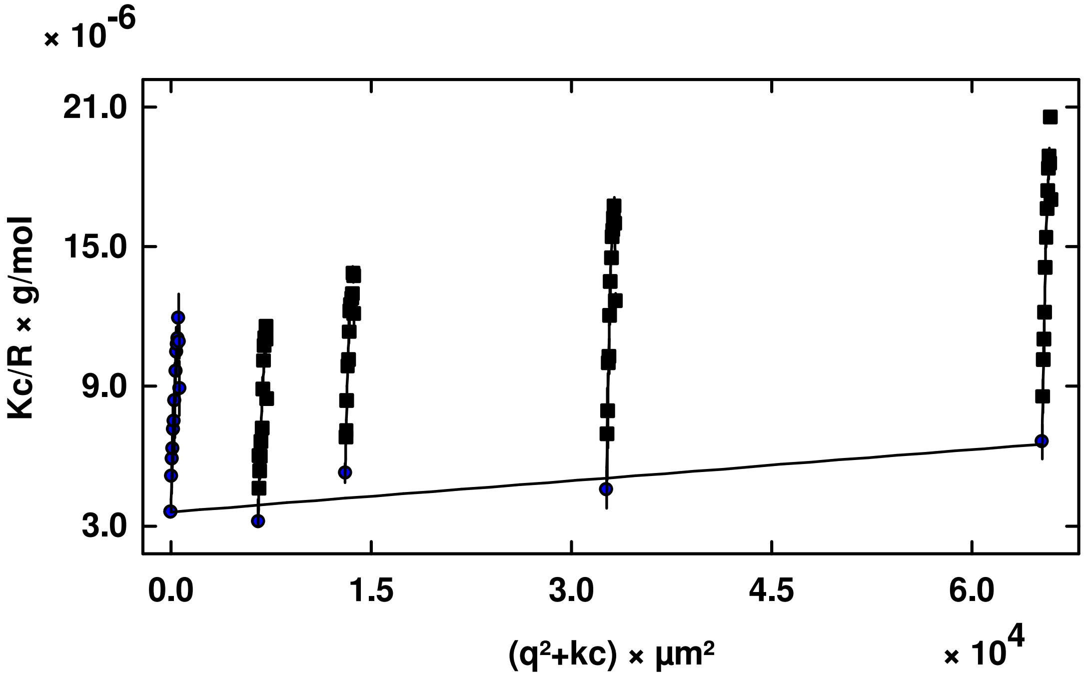
A2: 1.909e-07 mol dm³/g² Rg: 1.830e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\pva\10ph7.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\5ph7.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\2ph7.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\1ph7.STA

Figure D.1. Guinier plot of polyvinyl amine / water solution at pH 7.

Table D.2. Data obtained from guinier plot of polyvinyl amine / water solution at pH 8.

Conc. (g/L)	Rg (nm)
10	95.4
5	105.7
2	116.8
1	127.1
Infinite dilution	145.7



Mw(c): 2.774e+05 g/mol Mw(q^2): 2.774e+05 g/mol

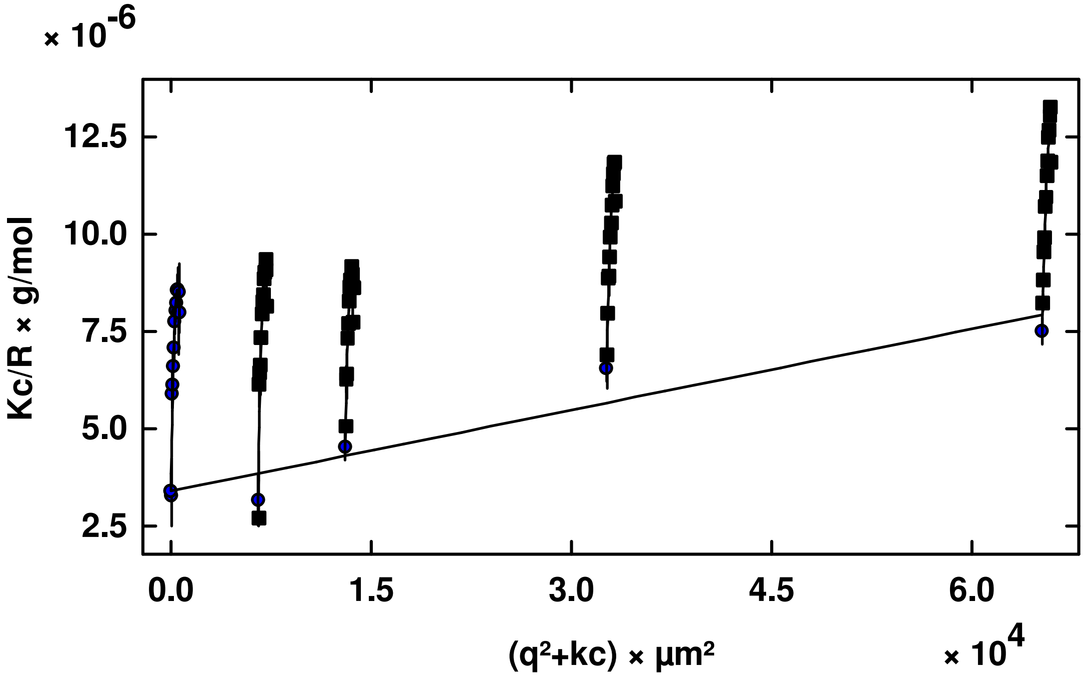
A2: 1.458e-07 mol dm^3/g^2 Rg: 1.457e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\pva\10ph8.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\5ph8.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\2ph8.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\1ph8.STA

Figure D.2. Guinier plot of polyvinyl amine / water solution at pH 8.

Table D.3. Data obtained from guinier plot of polyvinyl amine / water solution at pH 9.

Conc. (g/L)	Rg (nm)
10	7.18
5	76.8
2	109.9
1	102.5
Infinite dilution	137.4



Mw(c): 2.940e+05 g/mol Mw(q^2): 2.940e+05 g/mol

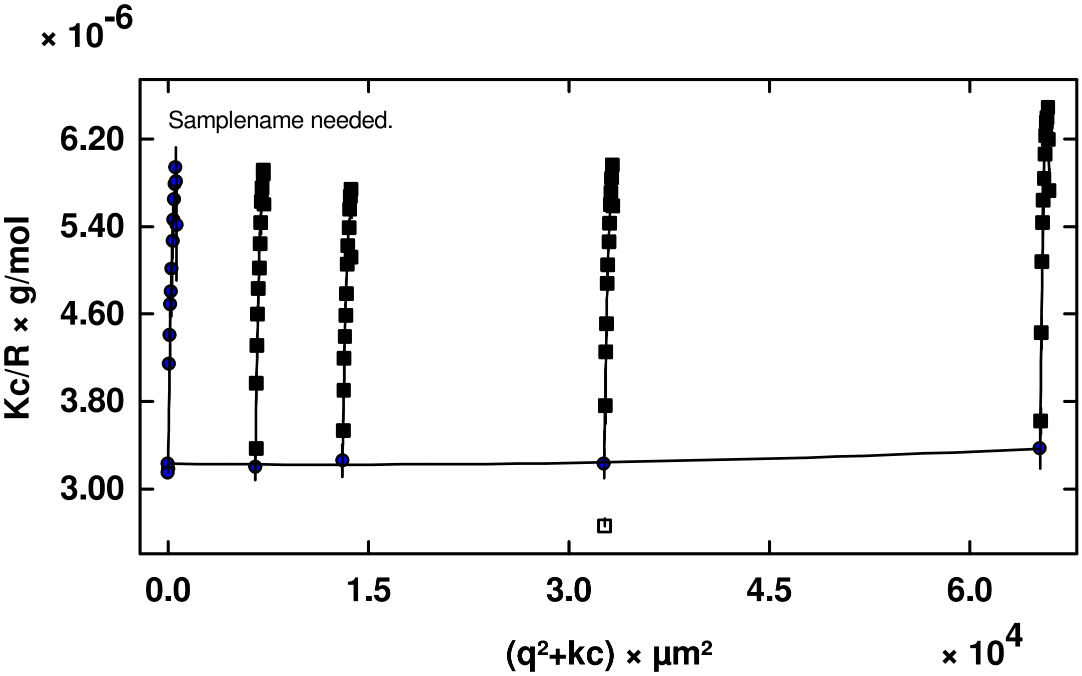
A2: 2.263e-07 mol dm^3/g^2 Rg: 1.374e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\pva\10ph9.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\5ph9.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\2ph9.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\1ph9.STA

Figure D.3. Guinier plot of polyvinyl amine / water solution at pH 9.

Table D.4. Data obtained from guinier plot of polyvinyl amine / water solution at pH 10.

Conc. (g/L)	Rg (nm)
10	68.1
5	74.9
2	73.6
1	86.6
Infinite dilution	94.8



Mw(c): 3.096e+05 g/mol Mw(q²): 3.178e+05 g/mol

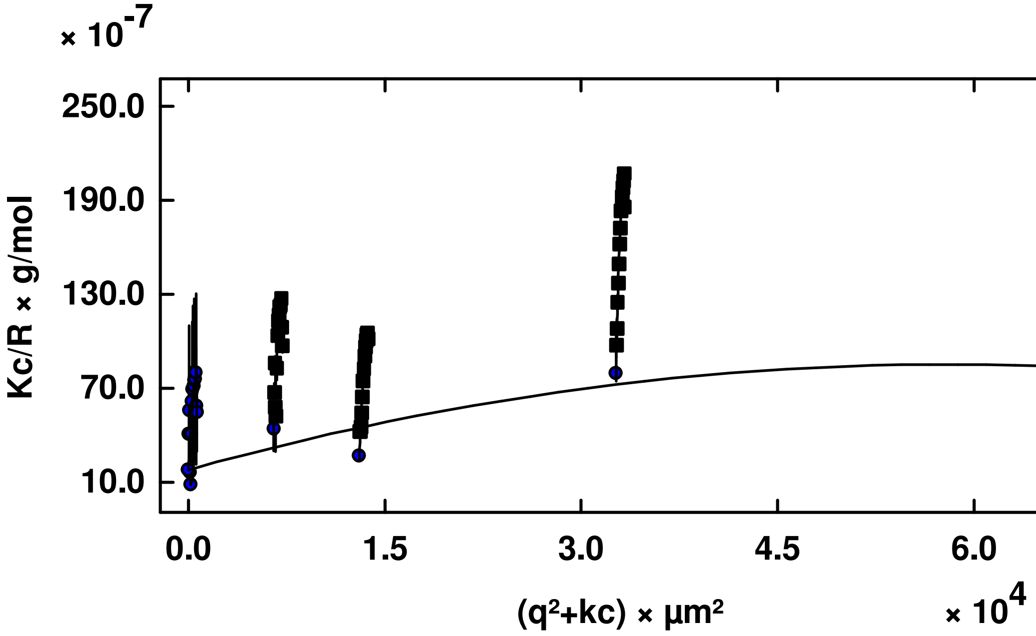
A2: -4.425e-09 mol dm³/g² Rg: 9.478e+01 nm

C:\Program Files\ALV_V3.0\data\Hasan\pva\10ph10.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\5ph10.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\2ph10.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\1ph10.STA

Figure D.4. Guinier plot of polyvinyl amine / water solution at pH 10.

Table D.5. Data obtained from guinier plot of polyvinyl amine / boron / water solution at pH 7.

Conc. (g/L)	**Rg (nm)**
10	108.2
5	109.7
2	138.2
Infinite dilution	173.1

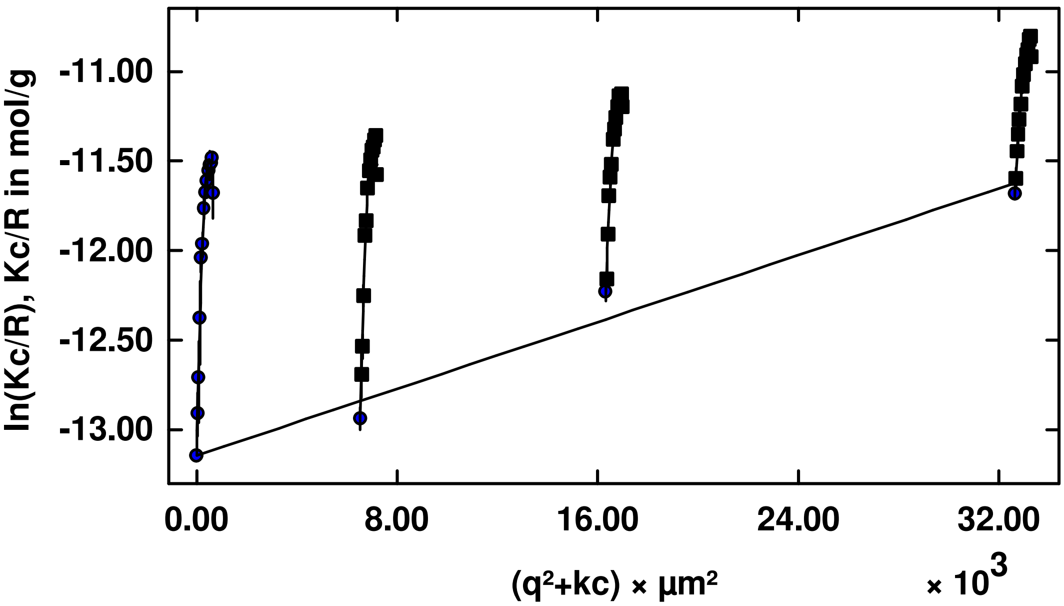


```
Mw(c): 5.631e+05 g/mol          Mw(q²): 5.631e+05 g/mol
A2: 7.576e-07 mol dm³/g²        Rg: 1.731e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\10pH7.STA; C:\Program
Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\5-pH7.STA; C:\Program Files\ALV_V3.0\
data\Hasan\pva\Bor-PVA\2-pH7.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\
Bor-PVA\1-pH7.STA
```

Figure D.5. Guinier plot of polyvinyl amine / boron / water solution at pH 7.

Table D.6. Data obtained from guinier plot of polyvinyl amine / boron / water solution at pH 8.

Conc. (g/L)	Rg (nm)
10	101.7
5	109.0
2	133.5
Infinite dilution	140.8

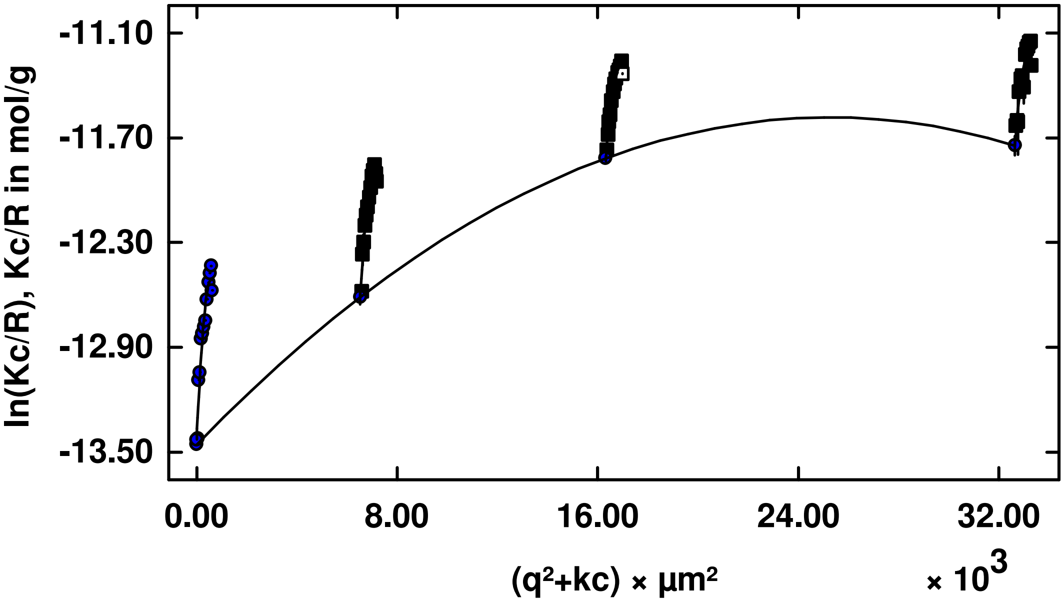


Mw(c): 5.107e+05 g/mol Mw(q^2): 5.107e+05 g/mol
A2: 1.489e-07 mol dm^3/g^2 Rg: 1.408e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\10pH8.STA; C:\Program
Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\5-pH8.STA; C:\Program Files\ALV_V3.0\
data\Hasan\pva\Bor-PVA\2-pH8.STA

Figure D.6. Guinier plot of polyvinyl amine / boron / water solution at pH 8.

Table D.7. Data obtained from guinier plot of polyvinyl amine / boron / water solution at pH 9.

Conc. (g/L)	Rg (nm)
10	81.8
5	84.3
2	94.3
Infinite dilution	97.9



Mw(c): 6.988e+05 g/mol Mw(q²): 6.791e+05 g/mol

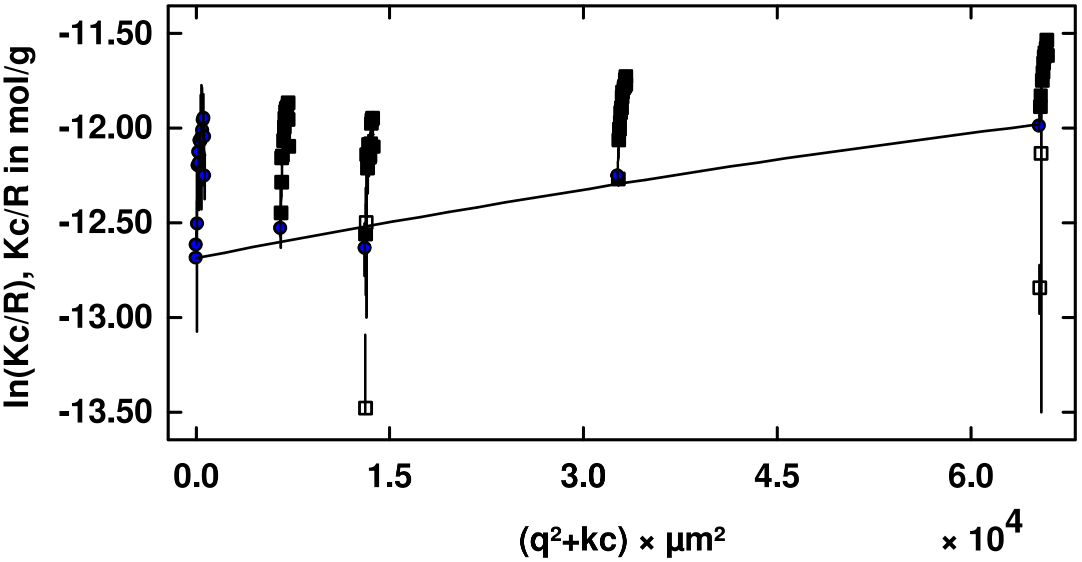
A2: 3.467e-07 mol dm³/g² Rg: 9.785e+01 nm

C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\5-pH9.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\10pH9.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\2-pH9.STA

Figure D.7. Guinier plot of polyvinyl amine / boron / water solution at pH 9.

Table D.8. Data obtained from guinier plot of polyvinyl amine / boron / water solution at pH 10.

Conc. (g/L)	Rg (nm)
10	62.8
5	72.3
2	82.8
1	92.0
Infinite dilution	92.7



Mw(c): 3.232e+05 g/mol Mw(q²): 3.012e+05 g/mol

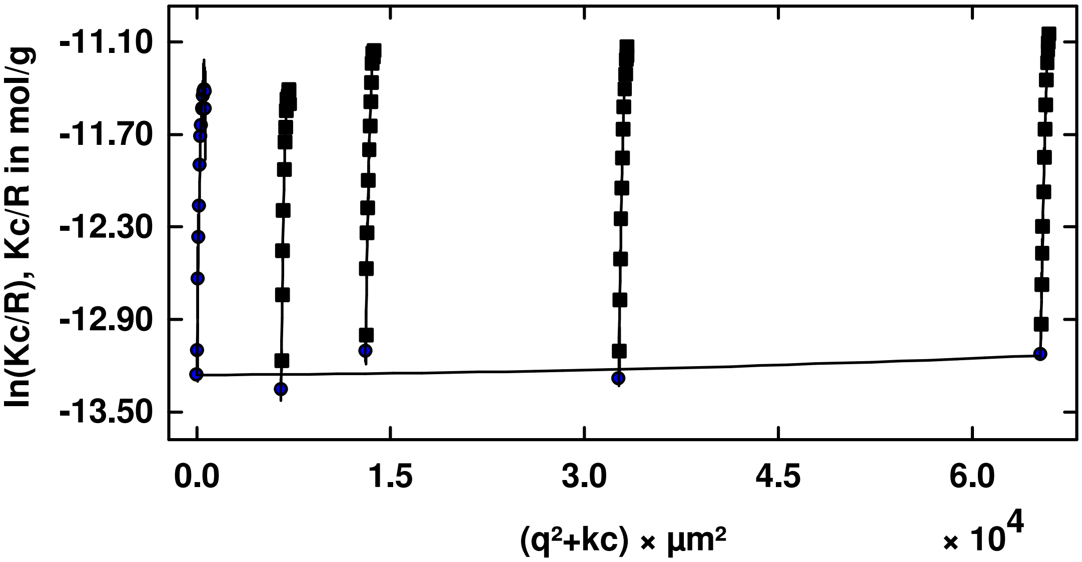
A2: 1.323e-07 mol dm³/g² Rg: 9.268e+01 nm

C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\2-pH10.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\10pH10.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\5-pH10.STA; C:\Program Files\ALV_V3.0\data\Hasan\pva\Bor-PVA\1-pH10.STA

Figure D.8. Guinier plot of polyvinyl amine / boron / water solution at pH 10.

Table D.9. Data obtained from guinier plot of GPVA / water solution at pH 8.

Conc. (g/L)	Rg (nm)
10	122
5	132
2	127
1	149
Infinite dilution	148



Mw(c): 5.732e+05 g/mol Mw(q²): 5.732e+05 g/mol

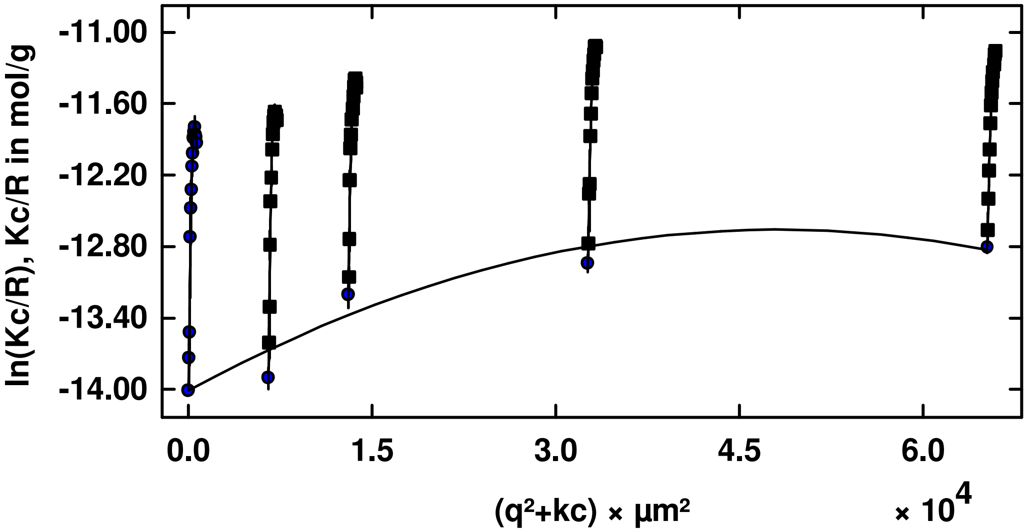
A2: 1.708e-09 mol dm³/g² Rg: 1.481e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh8-10g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh8-5g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh8-2g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh8-1g-L.STA

Figure D.9. Guinier plot of GPVA / water solution at pH 8.

Table D.10. Data obtained from guinier plot of GPVA / water solution at pH 9.

Conc. (g/L)	**Rg (nm)**
10	121
5	133
2	145
1	162
Infinite dilution	167



Mw(c): 1.215e+06 g/mol Mw(q^2): 1.215e+06 g/mol

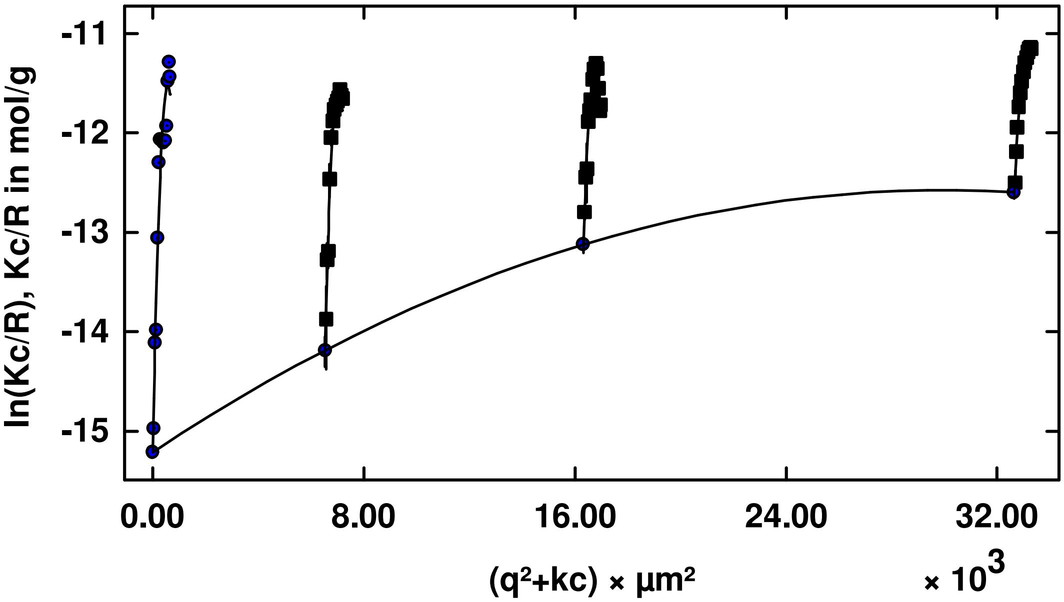
A2: 1.509e-07 mol dm^3/g^2 Rg: 1.668e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh9-10g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh9-5g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh9-2g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh9-1g-L.STA

Figure D.10. Guinier plot of GPVA / water solution at pH 9.

Table D.11. Data obtained from guinier plot of GPVA / water solution at pH 10.

Conc. (g/L)	Rg (nm)
10	122
2	150
1	176
Infinite dilution	198

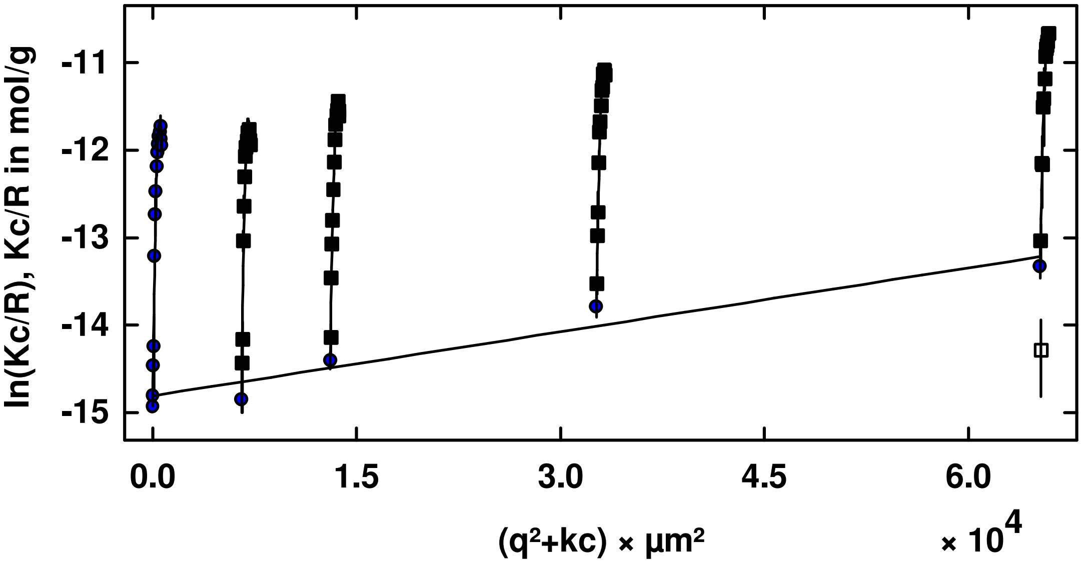


Mw(c): 4.047e+06 g/mol Mw(q²): 4.047e+06 g/mol
A2: 7.105e-08 mol dm³/g² Rg: 1.979e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh10-10g-L.STA; C:\
Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh10-5g-L.STA; C:\Program
Files\ALV_V3.0\data\Hasan\27ocak2011\GPVAPh10-2g-L.STA

Figure D.11. Guinier plot of GPVA / water solution at pH 10.

Table D.12. Data obtained from guinier plot of GPVA / boron / water solution at pH 8.

Conc. (g/L)	**Rg (nm)**
10	163
5	173
2	180
1	193
Infinite dilution	199



Mw(c): 2.698e+06 g/mol Mw(q^2): 3.046e+06 g/mol

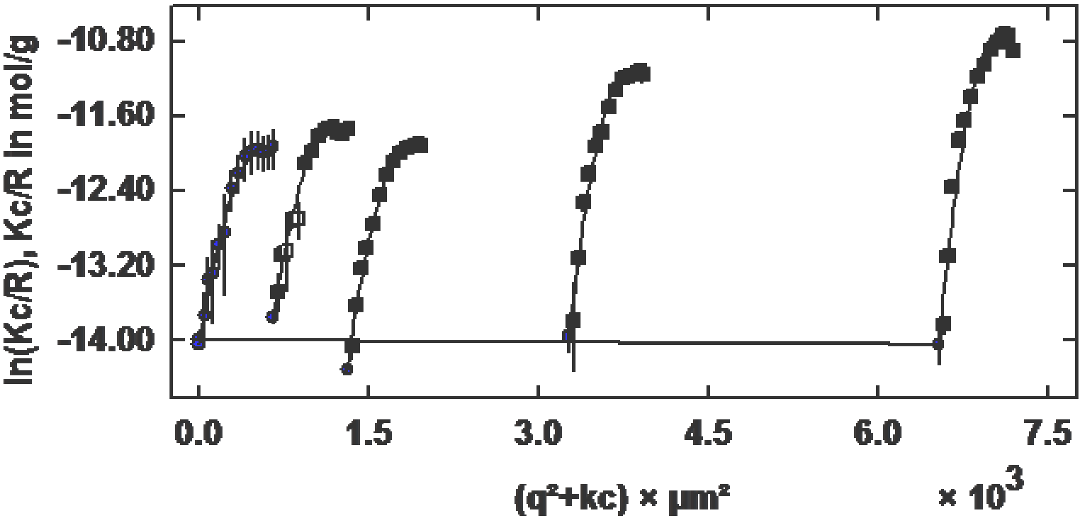
A2: 2.948e-08 mol dm³/g² Rg: 1.994e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-10g-L-pH8.STA; C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-5g-L-pH8.STA; C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-2g-L-pH8.STA; C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-1g-L-pH8.STA

Figure D.12. Guinier plot of GPVA / boron / water solution at pH 8.

Table D.13. Data obtained from guinier plot of GPVA / boron / water solution at pH 9.

Conc. (g/L)	Rg (nm)
10	196
5	180
2	162
1	151
Infinite dilution	121

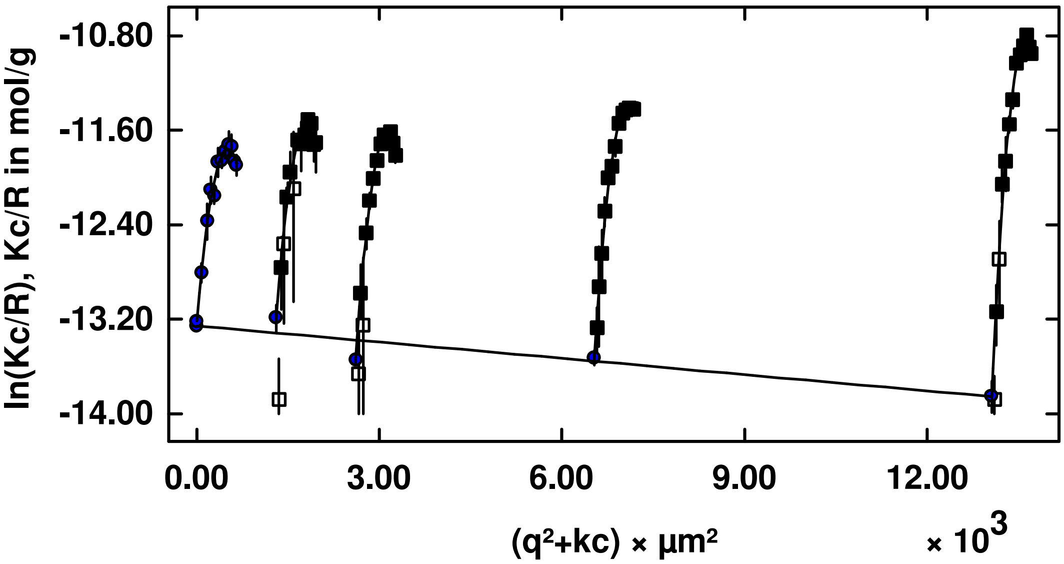


```
Mw(c): 1.192e+06 g/mol                Mw(q²): 1.244e+06 g/mol
A2: -2.042e-09 mol dm³/g²             Rg: 1.207e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-1g-L-pH9.STA; C:\
Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-2g-L-pH9(T2).STA;
C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-5g-L-pH9(T3).STA;
C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-10g-L-pH9(T2).STA
```

Figure D.13. Guinier plot of GPVA / boron / water solution at pH 9.

Table D.14. Data obtained from guinier plot of GPVA / boron / water solution at original pH (pH=10.3).

Conc. (g/L)	**Rg (nm)**
10	181
5	153
2	149
1	140
Infinite dilution	131

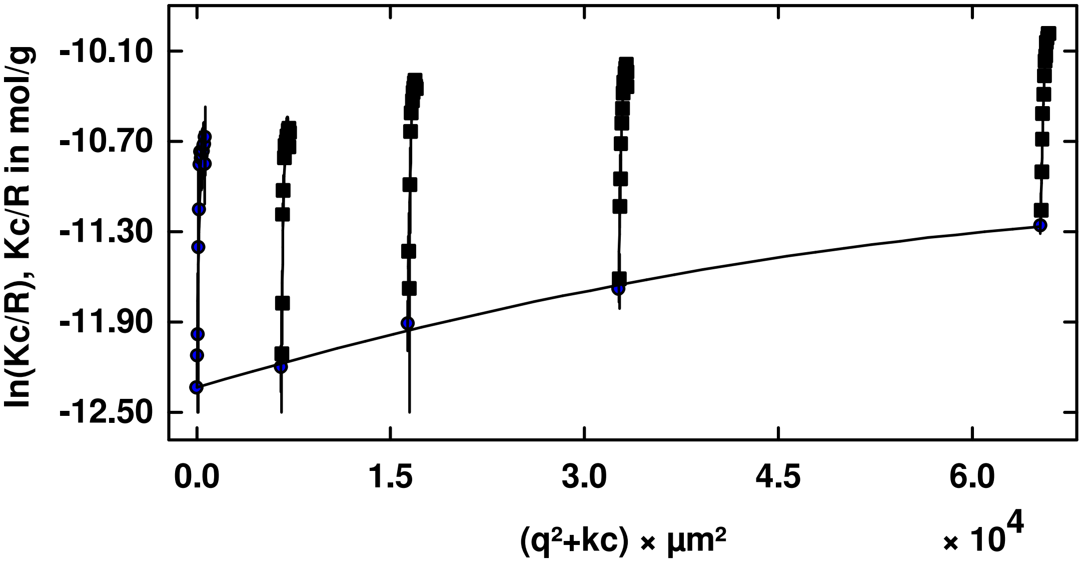


Mw(c): 5.717e+05 g/mol Mw(q²): 5.498e+05 g/mol
A2: -5.229e-08 mol dm³/g² Rg: 1.313e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-1g-L(T4).STA; C:\
Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-2g-L(T3).STA; C:\
Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-10g-L(T3).STA; C:\
Program Files\ALV_V3.0\data\Hasan\5Temmuz2011\GPVA-Bor-5g-L.STA

Figure D.14. Guinier plot of GPVA / boron / water solution at original pH (pH=10.3).

Table D.15. Data obtained from guinier plot of GPVA-co-5%DADMAC / water solution at pH 8.

Conc. (g/L)	Rg (nm)
20	118
10	134
5	136
2	146
Infinite dilution	148



Mw(c): 2.276e+05 g/mol Mw(q^2): 2.276e+05 g/mol

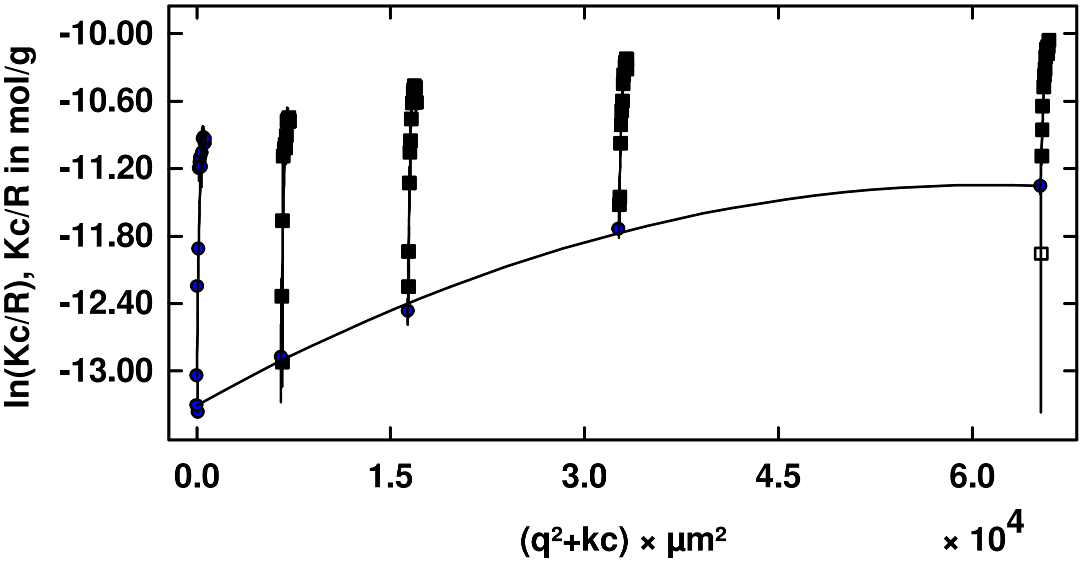
A2: 1.821e-07 mol dm^3/g^2 Rg: 1.477e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph8-20g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph8-10g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph8-5g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph8-2g-L.STA

Figure D.15. Guinier plot of GPVA-co-5%DADMAC / water solution at pH 8.

Table D.16. Data obtained from guinier plot of GPVA-co-5%DADMAC / water solution at pH 9.

Conc. (g/L)	Rg (nm)
20	146
10	130
5	159
2	165
Infinite dilution	166



Mw(c): 6.001e+05 g/mol Mw(q²): 4.617e+05 g/mol

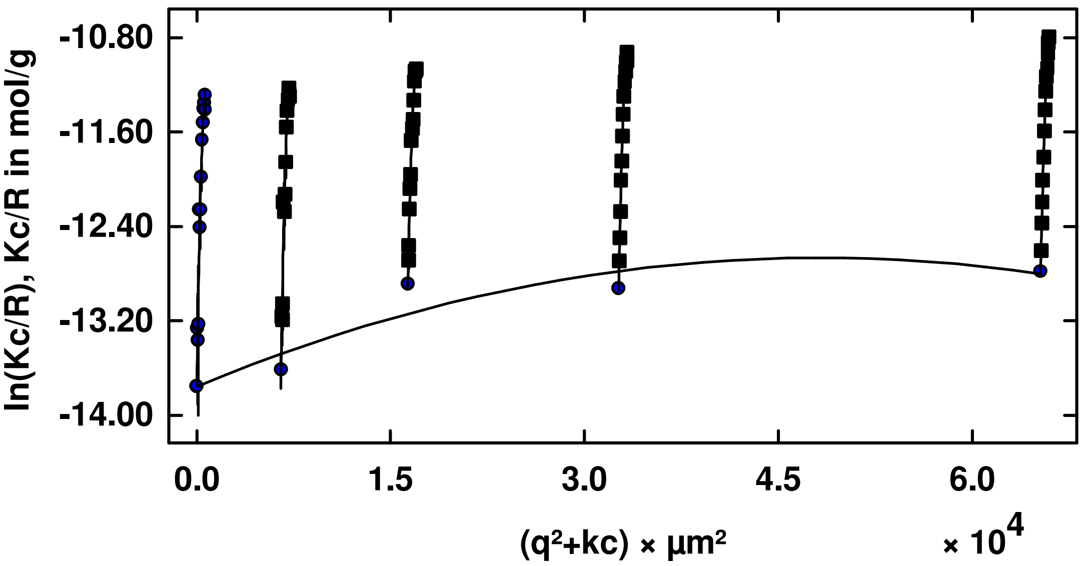
A2: 1.739e-07 mol dm³/g² Rg: 1.658e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph9-10g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph9-20g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph9-5g-L.STA; C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-ph9-2g-L-r.STA

Figure D.16. Guinier plot of GPVA-co-5%DADMAC / water solution at pH 9.

Table D.17. Data obtained from guinier plot of GPVA-co-5%DADMAC / water solution at pH 10.

Conc. (g/L)	**Rg (nm)**
20	122
10	130
5	122
2	145
Infinite dilution	146

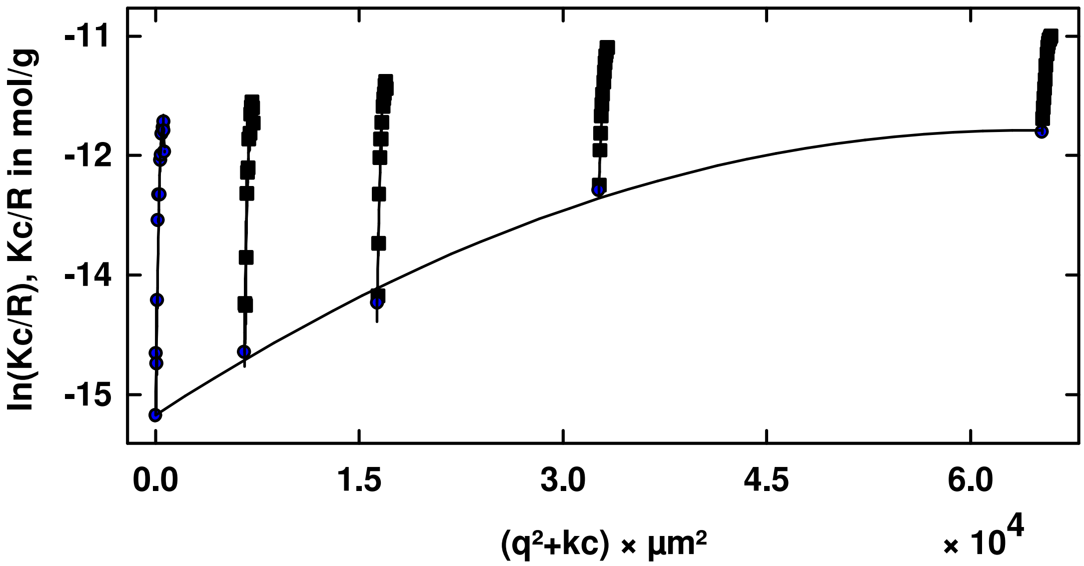


```
Mw(c): 9.411e+05 g/mol              Mw(q²): 9.411e+05 g/mol
A2: 7.838e-08 mol dm³/g²            Rg: 1.464e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-20g-L.STA; C:\
Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-10g-L.STA; C:\
Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-5g-L.STA; C:\Program
Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-2g-L.STA
```

Figure D.17. Guinier plot of GPVA-co-5%DADMAC / water solution at pH 10.

Table D.18. Data obtained from guinier plot of GPVA-co-5%DADMAC / boron / water solution at original pH (pH = 10.1).

Conc. (g/L)	**Rg (nm)**
20	106
10	129
5	175
2	185
Infinite dilution	205



Mw(c): 4.224e+06 g/mol Mw(q^2): 4.224e+06 g/mol

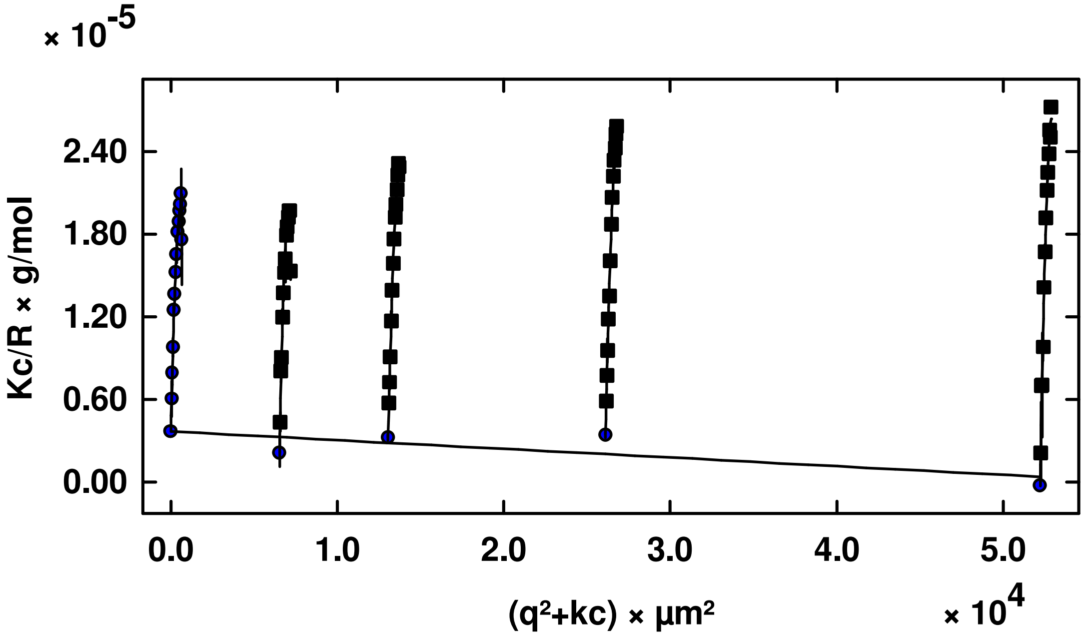
A2: 4.327e-08 mol dm^3/g^2 Rg: 2.050e+02 nm

C:\Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-B-20g-L.STA; C:\
Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-B-10g-L.STA; C:\
Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-B-5g-L.STA; C:\
Program Files\ALV_V3.0\data\Hasan\27ocak2011\GPVA-co5-B-2g-L-r.STA

Figure D.18. Guinier plot of GPVA-co-5%DADMAC / boron / water solution at original pH (pH = 10.1).

Table D.19. Data obtained from guinier plot of GPVA-co-10%DADMAC / boron / water solution at original pH (pH = 10.1).

Conc. (g/L)	Rg (nm)
20	139
10	157
5	183
2	194
Infinite dilution	212

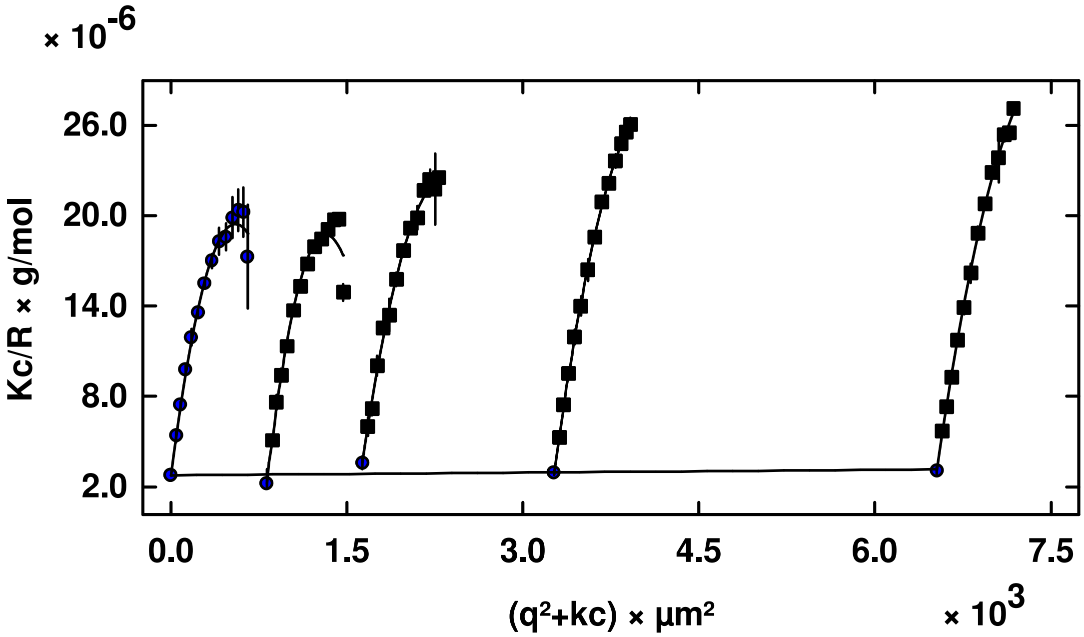


```
Mw(c): 2.715e+05 g/mol               Mw(q²): 2.715e+05 g/mol
A2: -8.210e-08 mol dm³/g²            Rg: 2.117e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer10%\Bor20gL.STA;
C:\Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer10%\Bor10gL.STA;
C:\Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer10%\Bor5gL.STA;
C:\Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer10%\Bor2.5gL.STA
```

Figure D.19. Guinier plot of GPVA-co-10%DADMAC / boron / water solution at original pH (pH = 10.1).

Table D.20. Data obtained from guinier plot of GPVA-co-2%DADMAC / boron / water solution at original pH (pH = 10.1).

Conc. (g/L)	**Rg (nm)**
20	141
10	149
5	184
2	208
Infinite dilution	257



```
Mw(c): 3.615e+05 g/mol              Mw(q²): 3.615e+05 g/mol
A2: 9.861e-09 mol dm³/g²            Rg: 2.570e+02 nm
C:\Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer2%\Bor10gL.STA;
C:\Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer2%\Bor5gL.STA; C:\
Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer2%\Bor2.5gL.STA; C:\
Program Files\ALV_V3.0\data\Hasan\14mart2012\copolymer2%\Bor20gL.STA
```

Figure D.20. Guinier plot of GPVA-co-2%DADMAC / boron / water solution at original pH (pH = 10.1).

CURRICULUM VITAE

Personal Information:

Gender: Male

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Marital Status: Married

Nationality: Turkish Republic

Educational Information:

Ph.D. on B.Sc.: Middle East Technical University-Turkey
Chemical Engineering Department (2007-2012)
Dissertation Title: Boron Removal from Aqueous Solutions via Polymer Enhanced Ultrafiltration Using Novel Imino-Bis-Propane Diol Functional Polymers
Supervisor: Prof. Dr. H. Onder Ozbelge
Co-supervisor: Prof. Dr. Levent Yilmaz

Undergraduate: Middle East Technical University-Turkey
Chemical Engineering Department (2002-2007)

High School : Bursa Nuri Erbak High School (1998-2002)

Computer Skills:

- FORTRAN
- CHEMCAD chemical engineering design software
- POLYMATH
- MATLAB Simulink Tools
- CHEMDRAW

Academic Experiences:

Teaching assistance to the courses:

- ChE327: Heat and Mass Transfer Operations
- ChE222: Fluid Mechanics
- ChE204: Thermodynamics I
- ChE305: Thermodynamics II
- ChE352: Mathematical Modelling in Chemical Engineering
- Chem112: Chemistry Laboratory II
- ChE320, ChE410 & ChE420: Chemical Engineering Laboratory I, II & III
- ChE510: Transport Phenomena

Work Experiences:

Ankara Sugar Plant-Internship in Laboratory and Production Site (Jan.-Feb.2007)

National Organik (Adhesive Manufacturer), Istanbul-Sales Assistant (June-August 2006 and July-September 2005)

Organik Kimya (Manufacturer of a wide range of polymers), Istanbul-Internship (June-July 2005)

Journal Articles:

1. Zerze, H.; Karagoz, B.; Ozbelge, H.O.; Bicak, N.; Aydogan, N.; Yilmaz, L. (2013) Imino-bis-propane diol functional polymer for efficient boron removal from aqueous solutions via continuous PEUF process. *Desalination*, 310: 158-168.
2. Zerze, H.; Karagoz, B.; Ozbelge, H.O.; Bicak, N.; Aydogan, N.; Yilmaz, L. (2013) Novel boron specific copolymers with quaternary amine segments for efficient boron removal via PEUF. *Desalination*, 310: 169-179.

Oral Presentations:

1. H. Zerze, B. Karagöz, H. Önder Özbelge, N. Bıçak, L. Yılmaz, "*Effect of Operating Parameters and Coanions on Boron Removal from Water via Continuous Polymer Enhanced Ultrafiltration*", Book of Abstracts, p. 20, PERMEA (Membrane Science and Technology Conference of Visegrad Countries), Tatranske Matliare, Slovakia, 04-08 September 2010.

2. H. Zerze, C. Oktar Doğanay, H. Önder Özbelge, N. Bıçak, L. Yılmaz, "*Continuous Boron Removal From Water By Specially Synthesized Polymers Via Polymer Enhanced Ultrafiltration*", Book of Abstracts, p. 65, PERMEA (Membrane Science and Technology Conference of Visegrad Countries), Prague, 07-11 June 2009.

Poster Presentations:

1. Hasan Zerze, Levent Yılmaz, H. Önder Özbelge, Niyazi Bıçak, Bünyamin Karagöz, Nihal Aydoğan, *"Aqueous Boron Removal via Continuous Polymer Enhanced Ultrafiltration"*, 12th Mediterranean Congress of Chemical Engineering, Barcelona, 15-18 November 2011.

2. Hasan Zerze, Levent Yılmaz, H. Önder Özbelge, Niyazi Bıçak, Bünyamin Karagöz, *"Boron Removal from Geothermal Water by Polymer Enhanced Ultrafiltration"*, 12th Mediterranean Congress of Chemical Engineering, Barcelona, 15-18 November 2011.

3. Ceren Oktar Doğanay, H. Önder Özbelge, Niyazi Bıçak, Hasan Zerze, Levent Yılmaz, "*Kromat Anyonunun Suda Çözünebilen Bir İşlevsel Polimer Kullanılarak Polimer Komplekslemeli Ultrafiltrasyon ile Sulu Çözeltiden Ayırılmasi*", Book of Abstracts, p. 481, 8th National Congress on Chemical Engineering, Inonu University, 26-29 August 2008.

Conference Proceedings:

1. H. Zerze, C. Oktar Doğanay, B. Karagöz, H. Önder Özbelge, N. Bıçak, L. Yılmaz, "*Removal and Recovery of Anionic Contaminants from Aqueous Solutions by Polymer Enhanced Ultrafiltration (PEUF)*", Book of Abstracts, p. 38, EMCC-6 (6th Chemical Engineering Conference for Collaborative Research in Eastern Mediterranean Countries), Antalya, 07-12 March 2010.

2. H. Zerze, C. Oktar Doğanay, H. Önder Özbelge, N. Bıçak, L. Yılmaz, "S*eparation Of Chromate Anion from Aqueous Solutions By A Water Soluble Functional Polymer Via Polymer Enhanced Ultrafiltration*", Book of Abstracts, p. 67, PERMEA (Membrane Science and Technology Conference of Visegrad Countries), Prague, 07-11 June 2009.

3. Ceren Oktar Doğanay, H. Önder Özbelge, Niyazi Bıçak, Hasan Zerze, Levent Yılmaz, "*Borat Anyonunun Özel Olarak Sentezlenmiş Polimerler Kullanılarak Polimer Komplekslemeli Ultrafiltrasyon ile Sulu Çözeltiden Ayırılması*", Book of Abstracts, p. 458, 8th National Congress on Chemical Engineering, Inonu University, 26-29 August 2008.

Projects Completed:

1. Polimer Komplekslemeli Ultrafiltrasyon Yöntemi ile Sulu Çözeltilerden Borat Ayırımı ve Rakip Anyonların Etkisi, METU- Scientific Research Project Code: BAP-03-04-2010-002 (2010-2011).

2. Polimer Komplekslemeli Ultrafiltrasyon Yöntemi İle Sulu Çözeltilerden Boratın Ayrılmasında Özel Polimerler Kullanılması, METU-Scientific Research Project Code: BAP-2008-03-04-04 (2008-2009).

Degrees, Awards & Scholarships:

- Presentation Award in PERMEA (Membrane Science and Technology Conference of Visegrad Countries) held in Prague on June 2009.
- In all semesters, honor or high honor degrees throughout the undergraduate years in the University (2003-2007).
- Third rank in the Math Contest among high school students in Bursa organized by Istanbul Technical University (2002).
- Second rank in the Chess Tournament among high school students in Yıldırım, Bursa (2001).
- Fourth rank in the Chess Tournament among high school students in Bursa (2001).
- Scholarship from Turkish Research Council of Science and Technology during Ph.D (2007-2012)