## Title

Separation of Compounds with Multiple -OH Groups from Dilute Aqueous Solutions via Complexation with Organoboronate



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## ENERGY & ENVIRONMENT DIVISION

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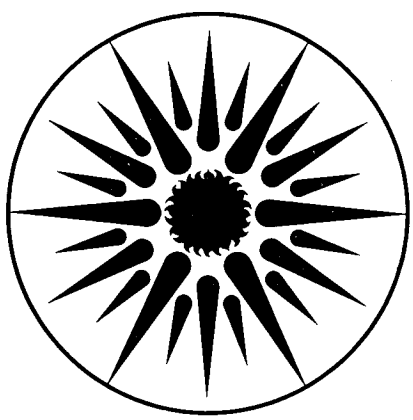
T.K.F. Chow
(M.S. Thesis)

May 1992



**ENERGY & ENVIRONMENT DIVISION**



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LBL-32430

# Separation of Compounds with Multiple -OH Groups from Dilute Aqueous Solutions via Complexation with Organoboronate

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M.S. Thesis

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May 1992

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# SEPARATION OF COMPOUNDS WITH MULTIPLE -OH GROUPS FROM DILUTE AQUEOUS SOLUTIONS VIA COMPLEXATION WITH ORGANOBORONATES

Tina Kuo Fung Chow

## ABSTRACT

This work examines the separation of polar solutes with multiple -OH groups from dilute aqueous solution into an organic phase. The extraction is enhanced by incorporating into the organic phase an agent that complexes reversibly with the solute of interest. The extractant agent investigated in this work is 3-nitrophenylboronic acid (NPBA) in its anionic form ($NPB^-$). The NPBA, together with Aliquat 336, is dissolved into 2-ethyl-1-hexanol, and the extractant is contacted with aqueous NaOH to convert NPBA to $NPB^-$. Aliquat 336 is a quaternary amine which provides the counter-ion ($TOMA^+$) for the anionic $NPB^-$-solute complex in the organic phase.

The solutes investigated were: 1,2-propanediol, glycerol, fructose, sorbitol and lactic acid. Batch extraction experiments were performed at 25°C. Partition coefficients, distribution ratios and loadings are reported for varying concentrations of the solute and the $NPB^-$. All of the solutes investigated showed complexation with $NPB^-$ and all of the complexes appear to consist of only one $NPB^-$ per complex. By fitting the extraction data to a theoretical model, the corresponding complexation equilibrium constants were estimated for some of the solutes investigated.

The 1:1 complexation constants for the solutes glycerol,

fructose and sorbitol follow trends similar to those reported earlier for complexation with $B(OH)_4^-$ in the aqueous phase; i.e. the complexation constants increase with increasing number of -OH groups available for complexation. This supports the postulate that -OH groups are involved in the complexation. The assumption of 1:1 complex appears not to be valid for 1,2-propanediol, which showed overloading (more than one mole of solute complexed to one mole $NPB^-$) at higher equilibrium aqueous solute concentrations. The -OH group on the $NPB^-$ which is left uncomplexed after one solute molecule had bound to the other two -OH groups may be responsible for the overloading. Overloading is also observed in extraction of lactic acid, but through a different mechanism. It was found that $TOMA^+$ can extract lactic acid to an extent comparable to the uptake of lactic acid by $NPB^-$. The complexation is probably through formation of an acid-base ion pair.

Losses of NPBA into the aqueous phase during the initial treatment and during extraction could lead to problems and/or poor economics in an industrial separation process. One way of overcoming this problem would be to incorporate the NPBA onto a solid support.

## ACKNOWLEDGEMENTS

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# 1. INTRODUCTION

Economical recovery of -OH bearing compounds from aqueous solutions is important because they are present in many process streams where either the -OH bearing compound is the product of interest (e.g., fermentation broths), or there is a need to remove them (e.g., aqueous waste streams). However, these streams are typically dilute in the solute of interest and complex in composition, features which make separation processes challenging and costly. For example, typical fermentation broths contain 0.5-5% of the desired product in a complex aqueous mixture of buffering agents, nutrients, cell debris and other components (Busche,1983), and typical downstream processing costs for these streams constitute 40% or more of the final product cost (Stowell, 1986).

Efficient and economical separation methods are needed for these process streams. Such methods should allow direct recovery and selectively remove the desired solute from the complex solution. It is helpful for the separation to remove the solutes of interest, without the need for the large energy expense which would be needed for removal of most or all of the water. As will be seen below, many of these substances are presently isolated from rather dilute aqueous soluions by evaporation of the water, an approach which is energy-intensive and does not provide the wherewithal for separating among the various solutes which may be present. Further

complicating matters is the fact that most -OH bearing substances are difficult to solidify.

Our research has focussed upon separation of -OH bearing solutes from dilute aqueous solutions via reversible chemical complexation. The solutes investigated are lactic acid, glycerol, fructose, sorbitol and propylene glycol. Fig. 1.1 shows the molecular structures of these substances.

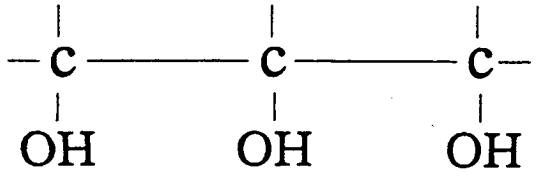
## 1.1 Chemicals from Biomass

Most commodity chemicals are currently produced from petroleum resources. However, fluctuating petroleum costs, uncertainty of supply and concerns relating to the depletion of these non-renewable fossil fuels mean that we need to develop other resources for chemicals. Biomass is an attractive and abundant alternative. Chemicals most attractive for manufacture from biomass are those which can be made by fermentation, are sufficiently valuable, and have substantial existing or potential markets.

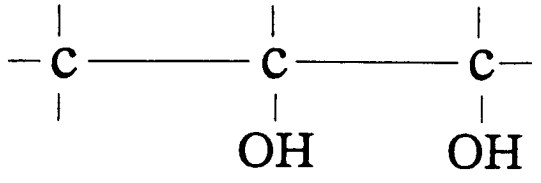
## 1.2 Lactic Acid

One example is lactic acid. About half of the world demand for lactic acid is produced by fermentation (Ward,1989). Lactic acid possesses two functionally active

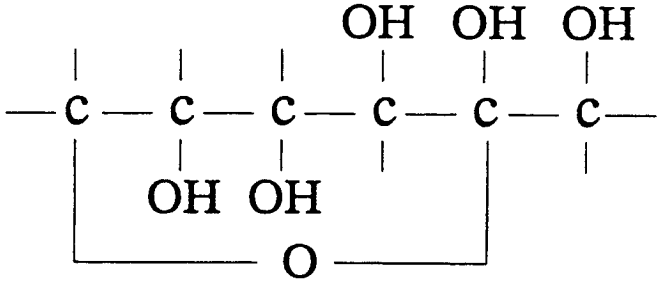
Glycerol



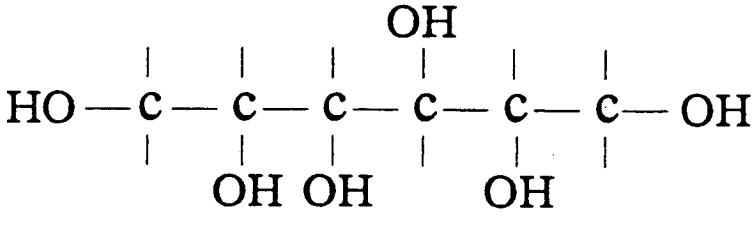
1,2-propanediol



D-Fructose



Sorbitol



Lactic acid

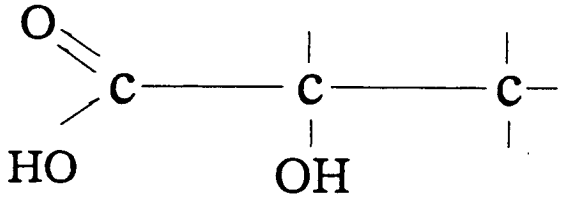


Fig.1.1 Molecular structures of solutes investigated

groups, α-hydroxyl and carboxyl, which make it a potential precursor for numerous value-added chemicals (Ward, 1989). It is also presently receiving much attention as a monomer for production of biodegradable polymers. However, lactic acid is presently relegated to uses in low-volume specialty markets, due to the relatively high costs of production, which are attributable more to recovery and purification than to the fermentation itself (Jain, et al, 1989).

The main industrial uses of lactic acid are as a food acidulant (50% of the market), for manufacture of stearoyl-2-lactylate (20%) and in pharmaceutical and other applications (Ward, 1989). L-(+)-lactic acid is produced by anaerobic fermentation using *Lactobacillus debruckii* and related homofermentative bacteria (Ward, 1989). Concentrations of up to around 10% lactic acid can be achieved. The recovery process has been precipitation with calcium carbonate or calcium hydroxide, followed by acidification of the calcium lactate salt by sulfuric acid. The resultant aqueous acid solution (about 10% lactic acid) is concentrated to 50%, refined over carbon, treated with sodium ferrocyanide, and passed through an ion exchange column for final finishing (Ward, 1989).

### 1.3 Propylene Glycol

Propylene glycol (1,2-propanediol) is another example of

a chemical that can be produced from biomass, although chemical conversion is primarily used. Propylene glycol is used in food and pharmaceutical applications and in unsaturated polyester resins for fiberglass-reinforced products, such as appliances and cars (Chemical Marketing Reporter, February 9,1987).

Racemic propylene glycol is currently produced by hydrolysis of propylene oxide derived from petrochemical sources. The water in the product stream (about 15% propylene glycol) is removed by multiple-effect evaporation, and the product is purified by vacuum distillation (Reiche and Heckman, 1976). R-propylene glycol can be produced by fermentation using the bacterium *Clostridium thermosaccharolyticum*, with glucose as the substrate (Cameron and Cooney, 1986, 1987). Product concentration is about 1% and byproducts such as acetate, lactate and ethanol are formed.

## 1.4 Glycerol

Glycerol was produced by fermentation for explosives (nitroglycerin) manufacture during World Wars I and II. Glycerol is formed by yeast in small amounts along with ethanol in the alcoholic fermentation. Current commercial production of glycerol involves both synthesis from propylene and saponification of glycerides. World production of glycerol is 450-600 x $10^3$ tons/yr, and for the past 20 years synthetic

glycerol has accounted for about one half of the United States annual production (Kirk and Othmer, 1977). Glycerol is used in nearly every industry, with the largest single use being in the manufacture of alkyd resins. It is also used in tobacco processing, drugs, cosmetics and foods.

The product from synthesis from propylene is a dilute aqueous solution containing 5% or less glycerol. This crude glycerol is concentrated to about 80% in multiple-effect evaporators, and salt is removed by centrifuging. Additional concentration of the product, followed by desalting, yields 98% glycerol.

Glycerol from glycerides can be obtained from two sources -- soap manufacture and fat splitting. Both result in aqueous solutions containing about 8 to 20% glycerol. Chemicals such as ferric chloride, caustic soda, calcium chloride, etc., are added to remove impurities. The dilute glycerol liquors, after purification, are concentrated to crude glycerol by evaporation under vacuum, heated by low-pressure steam. The crude glycerol is then refined by distillation, followed by treatment with active carbon.

## 1.5 Sorbitol

Sorbitol belongs to the sugar alcohol family. Annual world production capacity outside the United States is about 159,000 tons, and the production in the United States grew at

an average rate of 6.3% in the 1965-1974 period (Kirk and Othmer). Sorbitol is used to impart body, texture and sweetness to frozen desserts, as a bodying agent in pharmaceutical syrups and elixirs, as a humectant and emollient.in cosmetics and in textile bleaching or scouring solutions.

Sorbitol is synthesized commercially by high pressure hydrogenation of glucose, usually with a nickel catalyst. Corn syrup is the most important raw material. The sorbitol solution produced is purified by passage through an ion-exchange resin bed to remove ions and then treated with activated carbon to remove trace organic impurities. The solution of pure sorbitol is concentrated in a continuous evaporator to a solution containing 70% solids and sold as is, or else it is further concentrated and crystallized.

## 1.6 Fructose

The most common use of sugar is as a sweetener in the food industry. Fructose is popular as a dietary sugar because it is 1.3-1.8 times as sweet as sucrose or glucose ( Kim, et al. 1985). High fructose content syrups are used by the food industries for producing low calorie foods and drinks (Barker, 1983). Previously fructose was obtained from the hydrolysis of inulin, which was very costly. Nowadays, fructose is produced by separation from the enzymatically isomerized mixture

containing fructose and glucose, commercialy called high fructose syrup. The isomerized fructose corn syrup typically contains 42% fructose, 50% glucose, and 8% oligosaccharides on a dry weight basis (Kim, et al. 1985). The mixture is equivalent in sweetness to invert sucrose, the 50-50 mixture of D-glucose and D-fructose obtained on hydrolysis of sucrose by acid or the enzyme invertase, but with a lower selling price (Barker, 1983). The United States now produces more than $2.3 \times 10^6$ metric tons of isomerized syrup annually (Kirk and Othmer, 1977).

In the production of high fructose syrup, corn starch is pasted in a steam jet cooker and then passed over a fixed column of glucoamylase to produce high quality D-glucose. This syrup is passed through a column of fixed isomerase enzyme to give the equlibrium mixture od D-glucose and D-fructose. Either the mixture is sold as a syrup or the D-fructose is concentrated to higher levels by using calcium ion-exchange columns.

In addition to product streams, selective and energy efficient separation methods can also be applied to treatment of aqueous streams to remove fructose commonly found in waste streams from sugar refineries, wineries and distillery. Table 1.1 lists the characteristics of a typical molasses-based distillery spent wash which shows the amount of fructose in the stream and the complexity of the solution.

**TABLE 1.1 Characteristics of Molasses-based distillery system** (Karhadkar, et al, 1990)

| Characteristics | Average conc. (g/l) |
|---|---|
| pH | 4.4 |
| Temperature | 98°c |
| Total solids | 97.0 |
| Ash | 52.4 |
| TVA as acetic acid | 3.2 |
| Nitrogen | 2.1 |
| Sodium | 2.7 |
| Potassium | 9.5 |
| Calcium | 2.2 |
| Phosphorus | 0.15 |
| Sulphate | 2.5 |
| Glucose | 13.5 |
| Fructose | 12.5 |

## 1.7 Purpose of this project

This project investigates the possibility of utilizing reversible chemical complexation for removal and recovery of the aforementioned -OH bearing substances from dilute aqueous solutions. Reversible chemical complexation is one of the few methods capable of direct and selective recovery of the desired solute out of the complex solution. The fact that the complexing agent may react with certain functional groups on solutes can engender high selectivity and uptake capacity.

Moreover, separation based on chemical complexation typically provides a high capacity at low solute concentration, since for low solute concentrations there is a high driving force of free association sites of the complexing agent.

Most of the solutes considered here are very difficult to separate from aqueous solution by ordinary solvent extraction. Diols, for example, are very hydrophilic and have low equlibrium distribution ratios; for ambient conditions no values above 0.7 are reported for propylene glycol (Arenson,1989; Leo, et al, 1971). Lactic acid also has a strong affinity for water due to the presence of a hydroxyl group and a carboxylic acid group. The distribution ratios for common solvents have been reported to range from 0.04 to 0.82 (Short and Eaglesfield, 1952). Therefore, incorporation into the organic phase of an agent that will complex with the solute can potentially increase the economic viability of solvent extraction substantially.

## 2. SELECTION OF EXTRACTANT SYSTEM

The extractant system used in this study is the same as that used by Randel in a precursor project. A brief explanation of how each component was selected is given below. Please refer to Randel (1991) for a more detailed description.

The complexing agent investigated is 3-nitrophenylboronic acid (NPBA), shown in Fig. 2.1. It possesses adjacent -OH groups that serve to complex reversibly with cis-vicinal hydroxyl groups on the solute. It has been found that complex formation takes place only when the NPBA is in its anionic form (Randel, 1991). Fig.2.2 shows how the complex is thought to be formed. The substituted organic ligand on the boron eliminates the capacity for 1:2 complexes, thereby making it easier to study the complexation reactions. Further, NPBA is characteristic of extractants or complexing sorbents that might be used in practice.

NPBA is slightly soluble in water (0.4 wt%), but very soluble in organic solvents such as alcohols and ethers. Solubility losses could be reduced still further by using an organoboronate with greater aliphatic and/or alkyl weighting. Another reason for the selection of NPBA is that the acid has a $pK_a$ of 7.1 (Barker,et al, 1973), whereas most other organoboronates have much higher values of $pK_a$. The electron-withdrawing nitro group stabilizes the anionic complex. This means that complex formation occurs under near-neutral

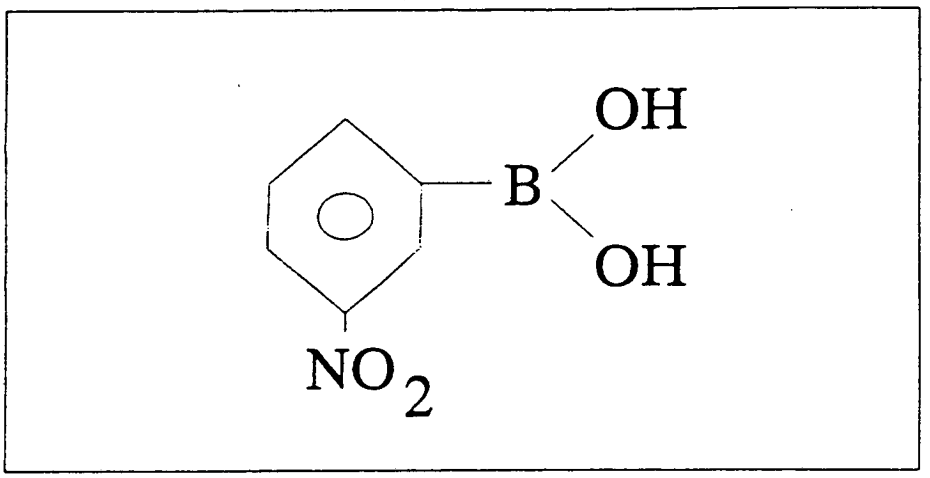



Fig.2.1 Molecular structure of NPBA

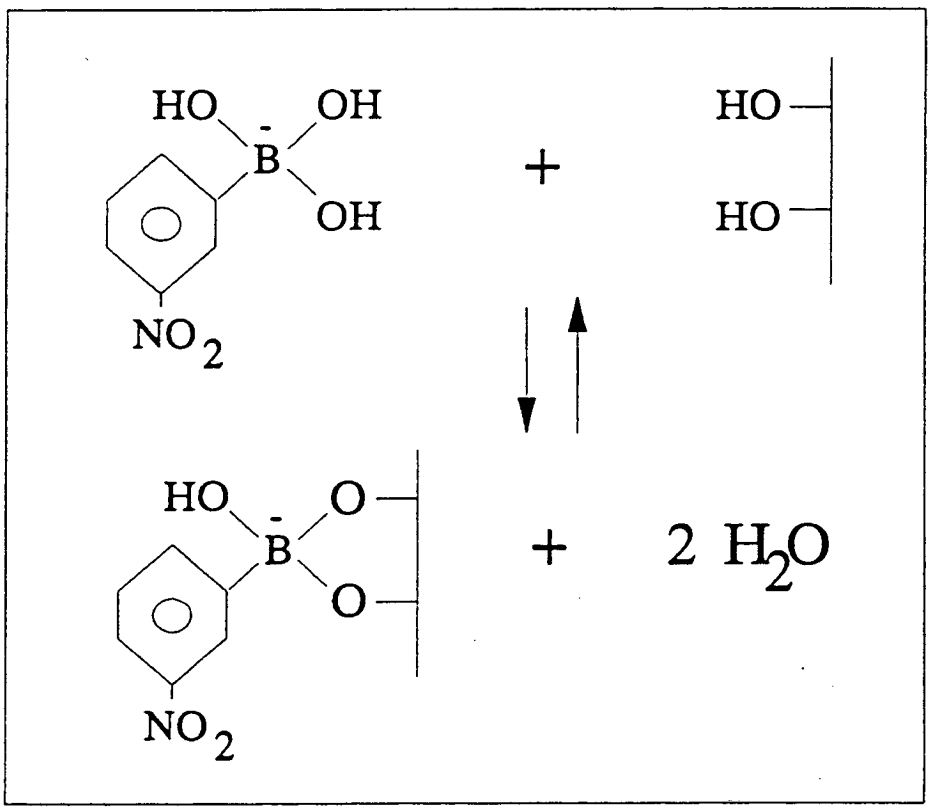



Fig. 2.2 Possible reaction scheme for the complexation

conditions, which are closer to the conditions of fermentation broths and waste streams. Also, for pH close to 7.0, a minimum amount of chemicals will be required for regeneration by pH swing.

Since the NPBA complexes only in its anionic boronate form ($NPB^-$), the solvent system for extraction should consist of the organoboronate anion, organic cation, and probably also a diluent, or co-solvent. Aliquat 336 (Aldrich), a quaternary ammonium compound (primarily trioctylmethylammonium ion, $TOMA^+$) was used as the organic cation (Fig. 2.3). Mixed ionic extractants have been used previously for extraction of inorganic acids and salts from aqueous solution (see, e.g., Grinstead, et al, 1969; Lynn and Charlesworth, 1972)

A diluent is required for the system because NPBA is a solid. The diluent should be able to dissolve NPBA and Aliquat 336 in sufficient concentration and solvate the $TOMA^+NPB^-.S$ complex. 2-Ethyl-1-hexanol was selected as diluent since it meets all these requirements (Randel, 1991). Toluene was also used as diluent in one set of experiments to determine the effect of a different diluent on the solvation of the complex, as well as to reveal any effect of 2-ethyl-1-hexanol competing with the -OH bearing solutes for binding sites on NPBA anions.

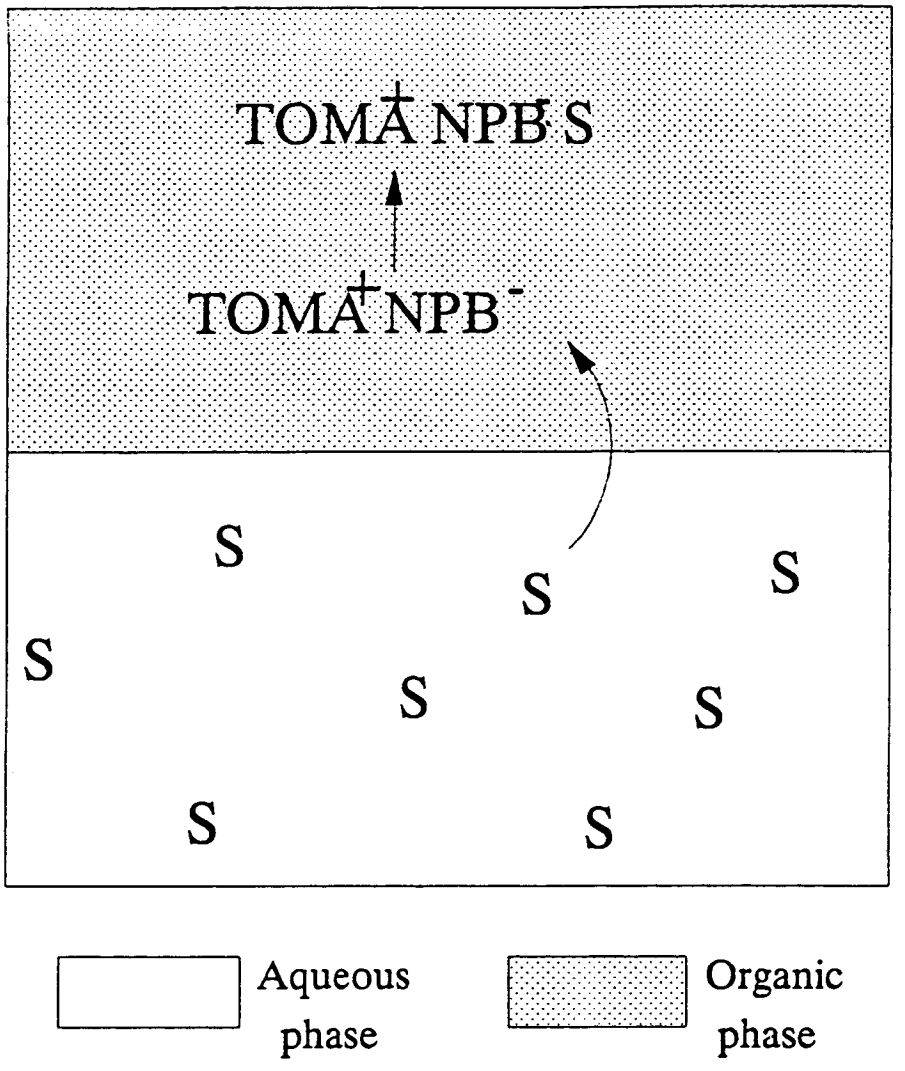



Fig. 2.3 The solute (S) in an aqueous phase is "pulled" into the organic phase via complexation with $NPB^-$ anion paired with $TOMA^+$ cation.

# 3. EXPERIMENTAL

## 3.1 Goals

The purpose of this research was to investigate the feasibility of using the 3-nitrophenylboronate anion as a complexing agent for recovery of compounds with multiple -OH groups from dilute aqueous solution. This study is a continuation of the work of Randel (1991) with propanediols. We aim to devise a better extracting system with a higher capacity and extend the investigation from propanediols to other solutes of interest, as mentioned in Chapter 1.

Data obtained through batch extraction experiments allowed parameters such as the distribution ratio (D) and stoichiometric loading (Z) to be calculated and used as means of comparison of complexation behavior amoung various solutes of interest. We also sought to compare the results obtained in this study with aqueous borate complexation data from the literature.

## 3.2 Materials

The chemicals used are listed in Table 3.1. All of them were used as received, without further purification. Aqueous solutions of known concentrations were prepared by dissolving weighed amounts of the solute of interest in 18-megohm

distilled, deionized water from a Millipore Milli-Q water purification system. Lactic acid was diluted to about 15% w/w and refluxed for 10 hours at atmospheric pressure to ensure that all dimers and multimers were hydrolyzed to monomers. 2-Ethyl-1-hexanol was presaturated with pure distilled water before use. The solubility of water in 2-ethyl-1-hexanol is 2.6% w/w (Flick, 1985).

TABLE 3.1 Chemicals Used

| Chemicals | Purity | Supplier |
|---|---|---|
| 1,2-Propanediol | 99% | Aldrich |
| Glycerol | 99% | Mallinkrodt |
| Fructose | - | Eastman Organic |
| Sorbitol | - | Eastman Organic |
| Lactic Acid | reagent grade | Mallinkrodt |
| 3-Nitrophenyl-boronic acid (NPBA) | - | Aldrich |
| Aliquat 336 | - | Aldrich |
| 2-Ethyl-hexanol | 99% | Aldrich |
| Sulphuric acid | reagent grade | Mallinkrodt |

Standardized 0.1N and 0.01N HCl and NaOH solutions were used for acid-base titrations. Standardized $Cl^-$ solutions (NaCl) were used for $Cl^-$ concentration measurements. Sulfuric acid was diluted to the desired concentration (0.01N) and filtered with Millipore type-HA 0.45 micron filters before use. Compressed gases were obtained in cylinders from the University of California, Berkeley, College of Chemistry.

### 3.3 Purity of materials

Aliquat 336 (primarily trioctylmethylammonium Chloride, $TOMA^+Cl^-$) is a quarternary ammonium compound supplied in the Cl- form. The manufacturer reports that $C_8$ chains predominate in Aliquat 336 and that the formula weight is 404.17. However, an elemental analysis done by the UCB Microanalytical laboratory (Table 3.2) indicates that more carbon was present than expected, and chloride concentration was measured to be 6.63% w/w, compared to 8.77% based on the formula weight. The disagreement may be explained by a predominance of $C_{10}$ chains rather than $C_8$ chains. Alternatively, there may be a significant alkane-like impurity. Moreover, the % wt/wt for the elements in Table 3.2 adds up to about 88%; adding to this the $Cl^-$ concentration (6.63%) increases the sum to about 95%. The "missing" 5% could be due to analytical error, or some other elements might be present. One possible additional element might be oxygen in the form of hydroxide ions, acting

as counterions for the $TOMA^+$ in place of chloride ions. The chloride concentration of 6.63% w/w was used in subsequent calculations.

The manufacturer reports the formula weight for the NPBA as 166.93, but Randel (1991) determined the formula weight to be 148.91, which is the formula weight of the corresponding anhydride, which has the same melting point as that of the NPBA, as reported by the manufacturer.

TABLE 3.2 Analysis of Aliquat 336

| Element | % wt/wt | mols/100g |
|---|---|---|
| Carbon | 71.31 | 5.94 |
| Hydrogen | 13.65 | 13.54 |
| Nitrogen | 2.99 | 0.21 |

* Ratio of C:N = 5.937/0.2131 = 27.85. If all chains were $C_8$, C:N = 25. This indicate that some side chains contain more than eight carbons.

## 3.4 Chemical Analyses

### 3.4.1 Elemental analyses

Chloride : Aqueous samples were analyzed in the laboratory with an Orion Model 96-17B combination chloride electrode.

Boron : Samples were sent to the UCB Microlab for analysis by flame atomic absorption spectrometry.

### 3.4.2 Water

Water concentrations in the organic extractant were determined with a Quintel Computrac MS-1 Karl Fisher Titrator, using the 2mg $H_2O$/ml titer Karl Fischer Reagent from Ericson Instruments.

### 3.4.3 Solutes in aqueous solutions

The solutes investigated were 1,2-propanediol, glycerol, fructose, sorbitol and lactic acid. The concentrations of the solutes in aqueous solutions were determined by HPLC (High Performance Liquid Chromatography). The system consisted of a Perkin Elmer Series 10 Liquid Chromatography pump with a 20$\mu$l Rheodyne injection loop, a Bio-Rad Fast Acid column (packing: sulphonated divinylbenzene-styrene copolymer, 9

micron, 8% crosslinked; mechanism: reverse phase partitioning onto hydrophobic backbone) and a Waters model 401 refractive index detector. The samples were analyzed at 60°C with a mobile phase of 0.01N $H_2SO_4$ at 0.85 ml/min. Lactic acid solutions were also analyzed by titration with a Ross model 8103 combination pH electrode. Titrant solutions of 0.01N and 0.001N NaOH were prepared by dilution of standardized 0.1N NaOH solutions.

### 3.4.4 NPBA

The NPBA concentrations in aqueous extraction samples were determined by HPLC with the same system mentioned above, except that a Waters Model 440 Fixed Wavelength (254nm) UV detector was used instead of the RI detector.

The NPBA concentrations in the aqueous wash solutions during organic phase treatment (Section 3.5) were determined by boron analyses.

## 3.5 Procedure

### 3.5.1 Preparation of the Organic Extractant

The components of the organic phase are listed in Table 3.3. NPBA and Aliquat 336 in approximately equal molar amounts were measured into volumetric flasks, and diluent (2-ethyl-1-

hexanol or toluene) was added to the desired volume to dissolve the NPBA and Aliquat 336. The organic solutions were then washed with one or more equal volumes of NaOH solutions, having the same molar concentration as the NPBA. The purpose of this was to convert the NPBA to its anionic form, since previous work has indicated that NPBA must be in its anionic form to complex.

**TABLE 3.3 Components of Organic Extractant**

| Components | F.W. | Specific Gravity |
|---|---|---|
| 2-Ethyl-hexanol | 130.22 | 0.8339 |
| NPBA | 148.91 | (solid) |
| Aliquat 336 | 500.00 | 0.884 |

Several batches of these organic extractants were made throughout the work. All except the first batch were washed twice with NaOH solution, followed by a final wash with an equal volume of pure distilled water. The first batch was washed five times with successive batches of NaOH solution, and showed a subsequent decrease in the loading capacity, as will be discussed in Chapter 7. The aqueous alkali wash

solutions after the treatment were analyzed for boron and chloride concentrations so as to enable the final anionic $NPB^-$ concentration in the organic phase to be inferred. The goal was to obtain close to 100% ionization.

Another approach for treating the organic phase is to dissolve Aliquat 336 in the diluent first and then mix this solution with the NaOH solution to convert $TOMA^+Cl^-$ to $TOMA^+OH^-$, before NPBA is added. An experiment was done in this way and a comparison of results are shown in Section 5.2.

### 3.5.2 Forward Extraction

Batch experiments were performed for each solute separately (Fig. 3.1). Equal volumes (5 ml) of aqueous solution and organic extractant solution of known concentrations were mixed in 20 ml vials and were sealed with foil at the top so as to minimize evaporation. The vials were equilibrated in a temperature-controlled shaker bath at 25°C for at least 15 hours, which preliminary tests demonstrated to be a sufficient time for equilibration. The aqueous and organic phases were then separated, and the aqueous phase was diluted and filtered before being analyzed by HPLC to determine how much of the solute remained. Mass-balance calculations indicated how much solute was extracted into the organic phase, and other useful parameters were then inferred as described in Chapter 4. Partition coefficients were

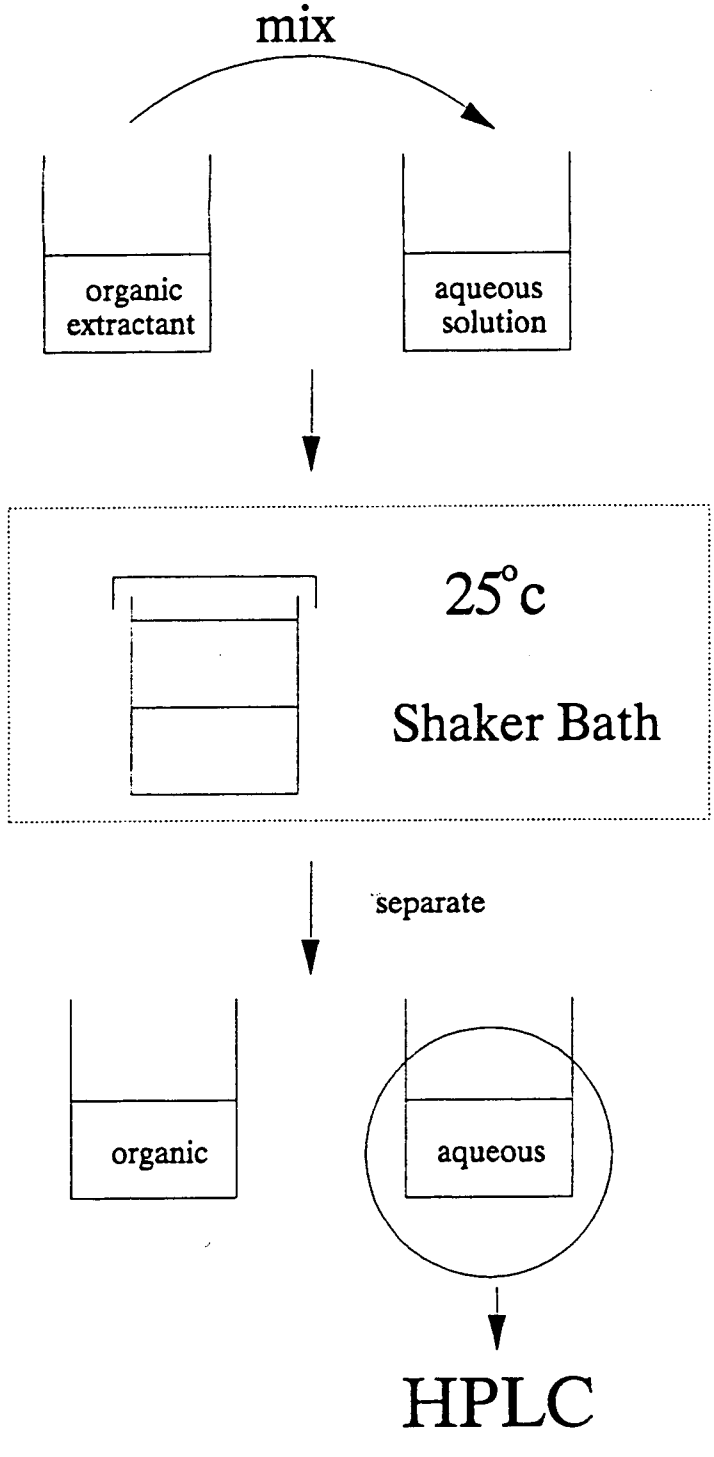



Fig. 3.1 Batch Extraction Procedure

obtained by contacting the aqueous phase with the diluent only instead of with the extractant mixture.

### 3.5.3 Back Extraction

Back extraction experiments were carried out with 1,2-propanediol to assess whether the forward extraction had attained equilibrium before separation of the phases. The organic phase obtained after forward extraction of 1,2-propanediol was mixed with distilled water and equilibrated in the shaker bath again for about 15 hours. The aqueous phase after separation was analyzed in the same way as for the forward extraction.

### 3.5.4 Effect of Diluent

Most experiments were done with 2-ethyl-1-hexanol as the diluent. To check the effect of the polarity and the -OH group of the diluent on the complexation, a less polar diluent, toluene, was used for some experiments with 1,2-propanediol, and the comparison is shown in Section 6.2.3.

### 3.5.5 Extraction by $TOMA^+$ alone

The same procedure as described in Section 3.5.2 was used, except that no NPBA was added to the organic extractant

and only the Aliquat 336 was used as extractant. This was done to check whether and to what extent $TOMA^+$ itself contributes to the extraction. It has been reported that TOMA+ extracts phenols effectively (Katsutoshi, et al, 1984).

# 4. TREATMENT OF THE ORGANIC EXTRACTANT

As mentioned in Section 3.5.1, the organic extractant was washed with aqueous NaOH solutions to ionize the NPBA to $NPB^-$. The wash solutions were then analyzed for $Cl^-$ and boron concentration to infer the final $NPB^-$ concentration of the extractant. Table 4.1 shows the results of these analyses for one typical treatment.

**TABLE 4.1 Results of boron and $Cl^-$ analysis of the wash solutions for one typical batch of extractant**

| | $[Cl^-]$ (M) | [B] (M) |
|---|---|---|
| 1st NaOH wash | 0.102000 | 0.0625 |
| 2nd NaOH wash | 0.021420 | 0.0289 |
| water wash | 0.000306 | 0.0093 |

Fig. 4.1 part a) shows a possible mechanism for the ionization and displacement of $Cl^-$: The $OH^-$ ions from the wash solution enter the organic phase and ionize the NPBA molecules to $NPB^-$ anion. Once an $NPB^-$ anion is formed, it pairs with a $TOMA^+$ cation and a $Cl^-$ ion is displaced into the aqueous wash

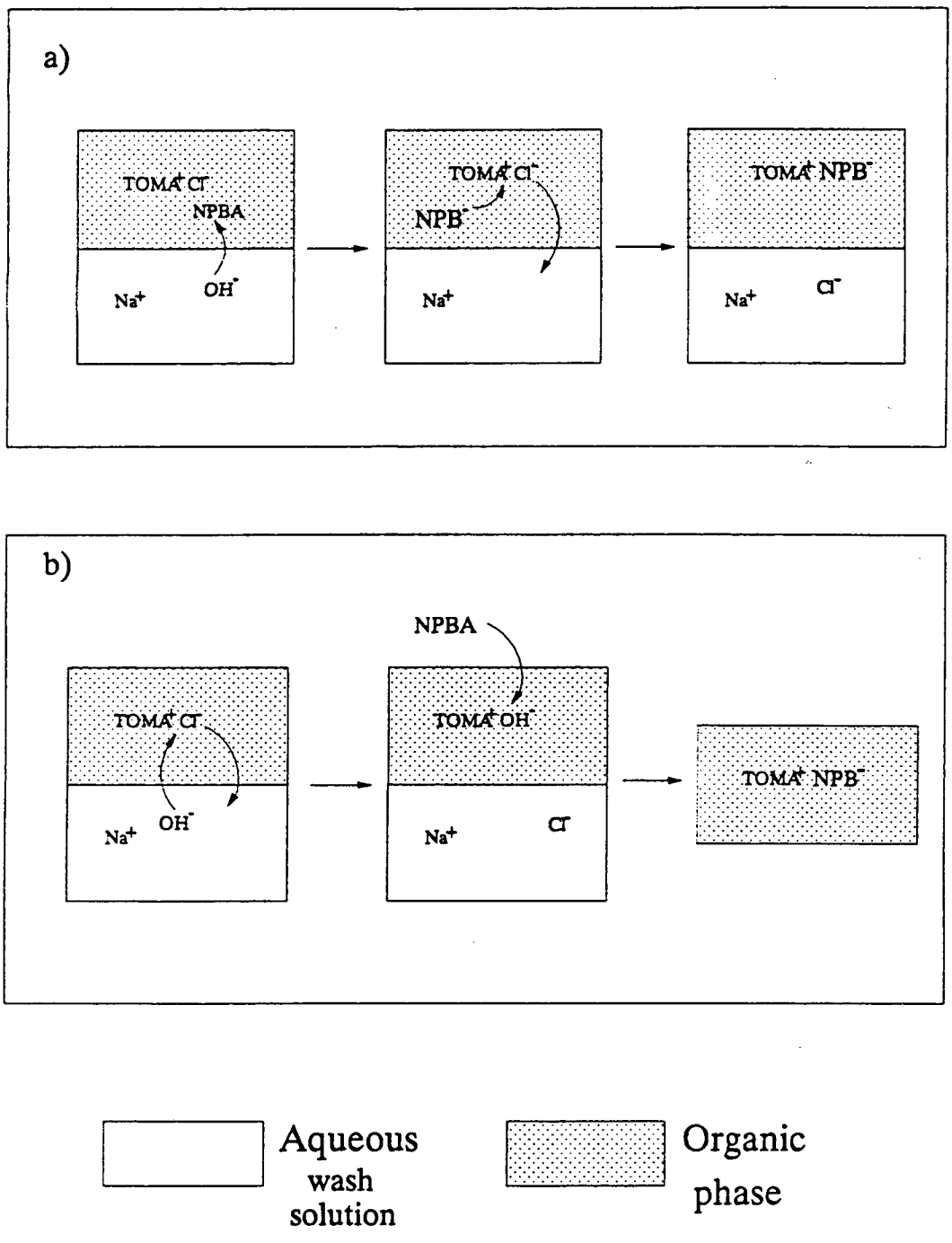



Fig. 4.1 Preparation of the Organic Extractant

solution, because of the requirement for electroneutrality. It is assumed that $TOMA^+$ would not partition into the aqueous phase due to its hydrophobic nature. Therefore, it was assumed that one $Cl^-$ ion displaced corresponded to one NPBA molecule ionized to $NPB^-$ anion.

**4.1 Sample calculation**

Using the data from Table 4.1 above, the concentration of $NPB^-$ ions in the extractant was calculated as follows:

* initial concentration of NPBA = 0.2105M
* initial concentration of $TOMA^+Cl^-$ = 0.1904M

* sum of $Cl^-$ concentrations of all wash solutions
  = (0.102+0.02142+0.000306)M
  = 0.12372M

* sum of boron concentrations of all wash solutions
  = (0.0625+0.0289+0.0093)M
  = 0.1007M

* amount of NPBA left in the organic phase
  = (0.2105-0.1007)M = 0.1098M

Concentrations were used directly without multiplication by

volume because the volumes of each wash solution and organic extractant solution were the same.

Since the amount of $Cl^-$ ions displaced (0.12372M) is greater than amount of NPBA left in the extractant after washing (0.1098M), it was assumed that all NPBA was ionized and that the final $NPB^-$ concentration of the extractant was 0.1098M.

The fact that the amount of $Cl^-$ removed was greater than the amount of NPBA remaining suggests that the excess $TOMA^+$ that was not paired with $NPB^-$ might be paired with $Cl^-$ or $OH^-$. However, since the amount of NPBA initially present in the extractant was estimated by calculation based on the weight and the estimated molecular weight, there could also be error involved in that estimation.

### 4.2 Converting $TOMA^+Cl^-$ to $TOMA^+OH^-$ first

Another approach for treating the extractant is to convert the $TOMA^+Cl^-$ dissolved in the diluent to $TOMA^+OH^-$ before adding in the NPBA, as shown in Fig. 4.1, part b. The results of $Cl^-$ analysis of the wash solutions from treating an organic phase in this way are shown in table 4.2 below.

When compared to the results shown in Table 4.1, it is obvious that the rate of $Cl^-$ displacement is slow using the second method, and more alkali is needed. Therefore, the first method was used for all extractant treatment.

## 4.3 NPBA losses

It can be seen from the data in Table 4.1 that the amount of NPBA lost into the aqueous wash solution during treatment is rather large, since NPBA is more soluble in basic than neutral aqueous solutions. This is probably due to the formation of $NPB^-$, which is more easily dissolved into water than is NPBA. This result indicates that losses of the extractant would increase sharply with increasing pH of the aqueous feed to an extraction using $NPB^-$ as the complexant.

**TABLE 4.2 pH and $Cl^-$ analysis of wash solutions for converting $TOMA^+Cl^-$ to $TOMA^+OH^-$**

Initial concentration of $TOMA^+Cl^-$ = 0.1802 M

| | pH | $[Cl^-]$ (M) |
|---|---|---|
| 1st NaOH wash | 13.04 | 0.03128 |
| 2nd NaOH wash | 13.07 | 0.01104 |
| 3rd NaOH wash | 13.08 | 0.01163 |
| 4th NaOH wash | 13.09 | 0.01010 |
| 5th NaOH wash | 13.11 | 0.00592 |

# 5. NUMERICAL TREATMENT OF DATA

In order to make use of the data obtained experimentally, some numerical manipulation was done to obtain useful parameters such as partition coefficient (P), distribution ratio (D), degree of loading (Z),..., etc., which are useful for evaluating process feasibility.

## 5.1 Experimentally measured quantities

The experimental data available for each extraction sample are:

i) $(S)_i$, the initial concentration of the solute in the aqueous phase (mol/L).

ii) $(S)_f$, the final concentration of the solute in the aqueous phase (mol/L).

iii) $[N]_i$, the total concentration of $NPB^-$ anions in the organic extractant (mol/L).

Parentheses denote aqueous phase concentrations, and brackets denote organic phase concentrations. i) and ii) were obtained by HPLC; iii) was obtained as described in Section 4.1, adjusted for the degree of dilution.

## 5.2 Amount of solute extracted into the organic phase

The difference between $(S)_i$ and $(S)_f$, $(S)_i-(S)_f$, was taken

as the concentration of solute extracted into the organic phase $[S]_{o,f}$. An assumption is made here that the phase volumes remain equal after extraction.

## 5.3 Correction for water co-extraction

The organic phases of the extraction samples were analyzed for water concentration by Karl Fischer titration before and after the extraction. This enabled a determination of whether the effect of water co-extraction on the final phase volumes was significant, i.e., whether the change of phase volumes due to water co-extraction would affect the calculation of the amount of solute in the organic phase.

It was found that the difference in water concentrations in the organic extractant before and after the extraction was typically ± 0.3% wt/wt, which is small and was taken to be negligible. This favorable result was facilitated by the presaturation of the 2-ethyl-1-hexanol with water before making up the extractant mixture.

## 5.4 Distribution ratio, (D)

Solvent extraction equilibria are generally reported as distribution ratio, D, which reflects the capacity of the solvent for extraction of the solute from the aqueous phase into the organic phase. D is defined in terms of the

experimentally measured equilibrium concentrations of the solute in the aqueous and organic phases:

$$D = \frac{C_{org}}{C_{aq}}$$

$C_{org}$ = molar concentration of solute in the organic phase

$C_{aq}$ = molar concentration of solute in the aqueous phase

In terms of the extractant system used here:

$$D = \frac{[N.S]_{org} + [S]_{org}}{(S)_{aq}}$$

$[N.S]_{org}$ = equilibrium concentration of $NPB^-$-solute complex in the organic phase.

$[S]_{org}$ = equilibrium concentration of the uncomplexed solute in the organic phase.

$[N.S]_{org} + [S]_{org} = [S]_{o,f} = (S)_i - (S)_f$

$(S)_{aq}$ = equilibrium concentration of the solute in aqueous phase after contact with the diluent.

$= (S)_f$

D varies with the concentration of NPB- in the organic phase and the concentration of solute in the aqueous phase.

## 5.5 Partition coefficient, (P)

When the organic phase is composed of the diluent only, D becomes P, the partition coefficient, under the assumption that there is no complexation of the solute with either itself or the diluent. P provides information on the degree of extraction of solute by the diluent alone and depends upon the natures of the solute and diluent. This information is needed to distinguish the chemical extraction by the complexing agent (NPB-) from the physical extraction by the diluent alone, as discussed below in Section 5.6. P is defined as

$$P = \frac{[S]_{org}}{(S)_{aq}}$$

The values of P for the solutes investigated using 2-ethyl-1-hexanol as the diluent are listed in Table 7.1 in Chapter 7.

## 5.6 Correction for Extraction by diluent

Physical extraction by the diluent alone was taken into account by subtracting a correction factor from the experimentally determined value of $[S]_{o,f}$. The correction factor at each value of $[S]_{o,f}$ was the concentration of solute extracted by the diluent alone (obtained by separate experiments), multiplied by the volume fraction diluent in the

solvent mixture:

$$\text{corrected } [S]_{o,f} = [S]_{o,f} - P \times [S]_{aq} \times V_f$$

$V_f$ = volume fraction diluent in the organic phase, which was typically large, above 97%.

The corrected $[S]_{o,f}$ corresponds to the amount of extraction by the complexing agent ($NPB^-$) alone. It is needed for calculating the degree of loading of the extractant, as described below.

**5.7 Degree of loading, (Z)**

The stoichiometric loading of the extractant, Z, is the number of molecules of solute that are complexed per $NPB^-$ anion. Z is defined as the equilibrium molar ratio of the solute extracted by the extractant to the total extractant in the organic phase :

$$Z = \frac{[N.S]_{org}}{[N]_i}$$

$[N]_i$ = concentration of $NPB^-$ anion in the extractant.

Z gives information on the capacity of the system and the

stoichiometry of the complex.

# 6. CHEMICAL MODELING OF EXTRACTION DATA

An equilibrium description of the complexation system can be written as :

$$nN + mS \rightleftharpoons N_n.S_m$$

where n molecules of $NPB^-$ anions, N, are complexed with m molecules of solute, S, to form a complex $N_n.S_m$.

The relationship can be expressed in terms of a heterogeneous equilibrium constant, $\beta_{nm}$ :

$$\beta_{n,m} = \frac{[N_n.S_m]_{org}}{[N]_{org}^{\ n}\ (S)_{aq}^{\ m}} \qquad \text{(Eq.6-1)}$$

Theoretically, activities of the species should be used, but for practicality the activities of the species are assumed to be proportional to the concentrations, and the constants of proportionality are taken up in the equilibrium constant. For a 1:1 complex, the expression would be:

$$\beta_{1,1} = \frac{[N.S]_{org}}{[N]_{org}\ (S)_{aq}} \qquad \text{(Eq.6-2)}$$

From the definitions for distribution ratio and partition coefficient in Chapter 4:

$$D = \frac{[N.S]_{org} + [S]_{org}}{(S)_{aq}}$$

$$P = \frac{[S]_{org}}{(S)_{aq}}$$

From Eq.6-2,

$$\beta_{1,1}\ [N]_{org} = \frac{[N.S]_{org}}{(S)_{aq}}$$

$$= D - P \times V_f$$

$V_f$ = volume fraction diluent in the organic phase.

therefore, $$D = \beta_{1,1}[N]_{org} + P \times V_f \qquad \text{(Eq. 6-3)}$$

Theoretically, by knowing D, $[N]_{org}$ and P from the experimentally obtained data, values of $\beta_{1,1}$ can be obtained graphically.

The loading of the extractant, Z, as defined in Section 5.7, could be expressed as follows for a 1:1 complex (Tamada, 1989) which is derivable from Eq.6-2:

$$Z = \frac{\beta_{1,1}(S)_{aq}}{1 + \beta_{1,1}(S)_{aq}} \qquad \text{(Eq.6-4)}$$

This equation suggests that loading increases rapidly with increasing $(S)_{aq}$ in proportion to $\beta_{1,1}$ at low solute concentration and asymptotically approaches unity at high $(S)_{aq}$, as the available extractant is exhausted. The experimental extraction results for the various solutes are presented as loading curves [plots of Z vs $\log(S)_{aq}$], which are shown in the following chapter. The theoretical expression of Z (Eq.6-4) was also used to "calculate" the theoretical loading curve and was compared to the corresponding experimental curve to test the degree of agreement of experimental data with theory for some of the solutes investigated.

# 7. RESULTS AND DISCUSSION

## 7.1 Partition Coefficients and Distibution Ratios

The values of P measured for the solutes investigated using 2-ethyl-1-hexanol as the diluent are listed in Table 7.1

**TABLE 7.1 Partition coefficients into 2-ethyl-1-hexanol for the solutes Investigated**

| Solutes | (P) |
|---|---|
| 1,2-propanediol | 0.010 |
| glycerol | 0.013 |
| fructose | 0.033 |
| sorbitol | 0.035 |
| lactic acid | 0.078 |

The fact that P increases as the number of -OH groups increases on the solute suggests that there is, in fact, some complexation or preferential solvation between the solute and 2-ethyl-1-hexanol.

The values of distribution ratios for the various

experimental measurements are listed in the Appendix.

## 7.2 Glycerol

The experimental results for glycerol extraction are presented in the form of a loading curve in Fig.7.1 (loading plotted against the logarithm of the equlibrium aqueous concentration of solute). The different symbols correspond to different concentrations of $NPB^-$ used during extraction. It can be seen that the points tend to group into a single curve instead of forming different curves for different total $NPB^-$ concentrations. The fact that there is no apparent dependence of loading on total $NPB^-$ concentration suggests that there is only one molecule of $NPB^-$ per complex, since the loading would increase with increasing $NPB^-$ concentration if there were more than one $NPB^-$ per complex (Tamada, 1989).

Fig. 7.2 shows the loading curve measured for glycerol extraction by the first batch of extractant, which was washed five times with NaOH solution as described in Section 3.5.1, compared to the loading curve for extractant washed only twice (Fig. 7.1). It is obvious that extractant washed twice had a higher capacity than extractant washed more extensively. It may be that excessive washing causes greater NPBA losses than were calculated from the aqueous boron analyses. It was shown in Chapter 5 that two consecutive washes appear to be enough to ionize the NPBA in the organic phase nearly completely, and

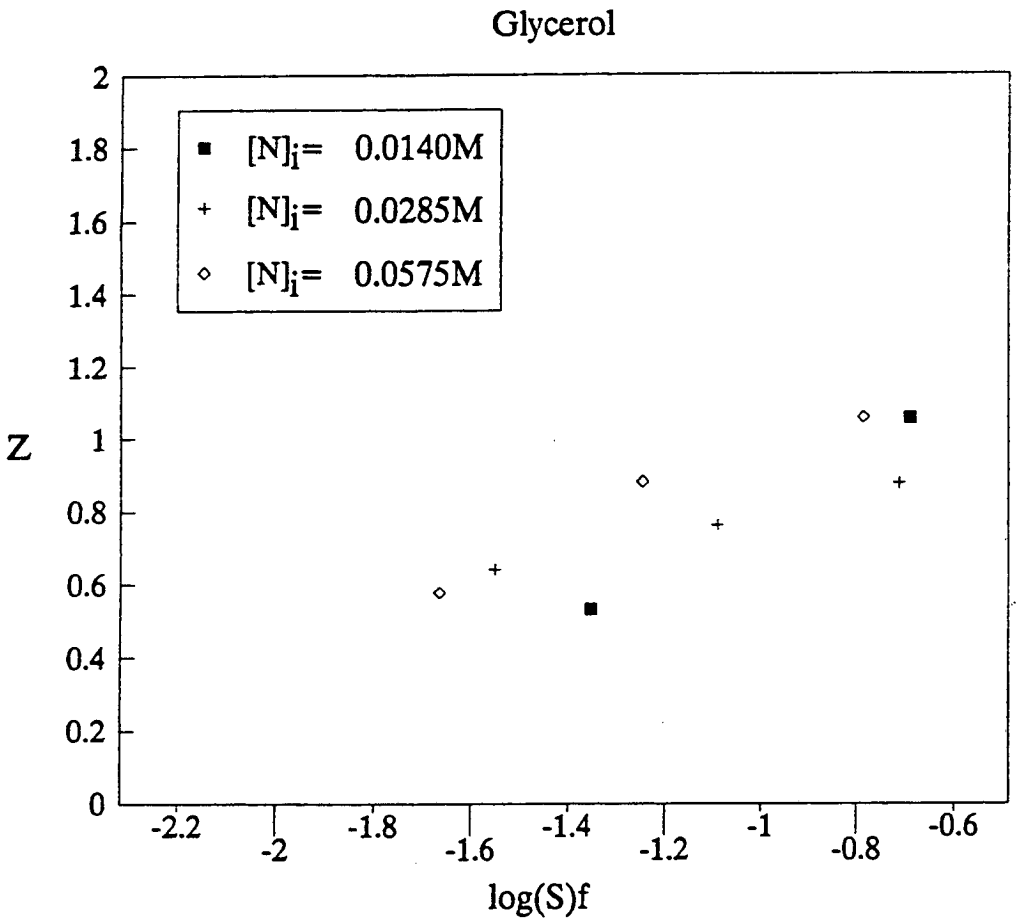



Fig. 7.1 Glycerol extraction results expressed in the form of a loading curve

Z = loading

$(S)_f$ = aqueous solute concentration at equlibrium

$[N]_i$ = total NPB concentration in the organic extractant during extraction

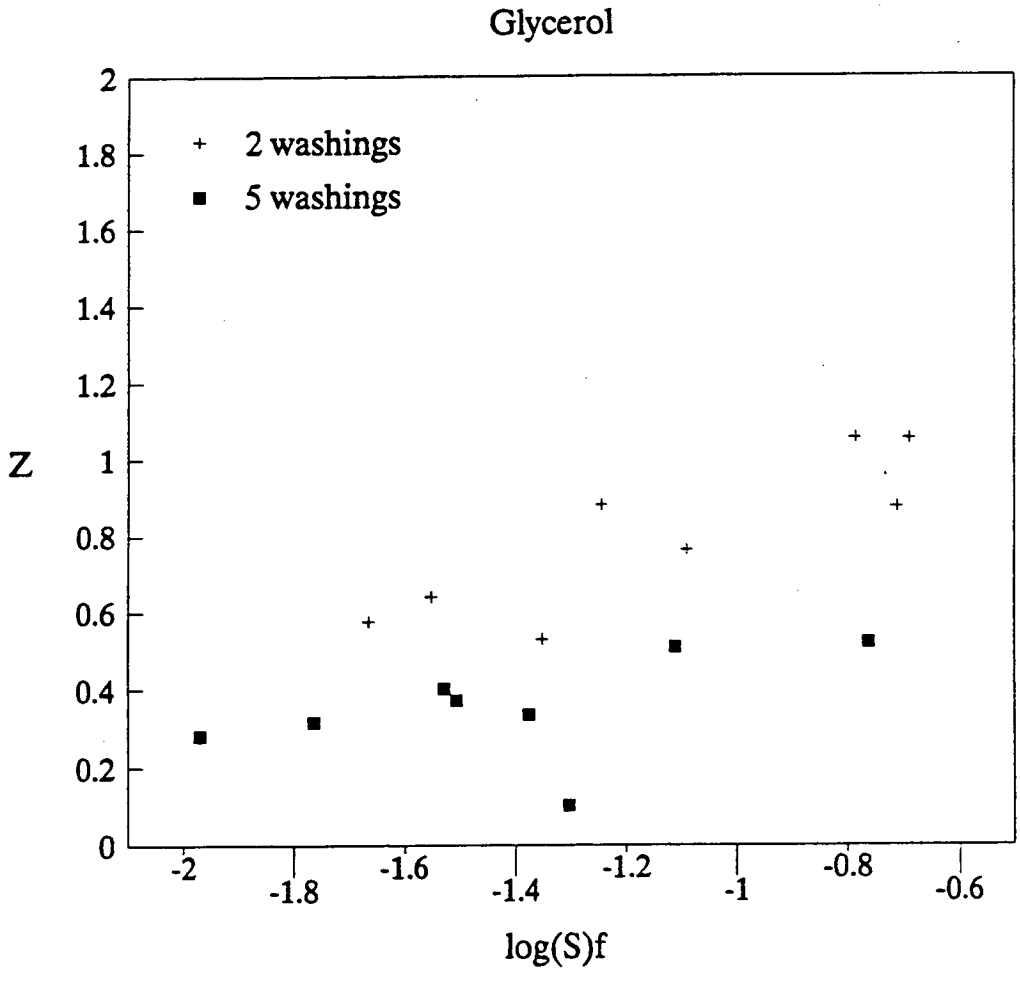



Fig. 7.2 Comparison of capacities of two extractants with different degrees of initial treatment by alkali.

this was therefore the procedure adopted for all the extractants used in the remainder of this work.

Since there is no overloading apparent from Figure 7.1, it was concluded that formation of a 1:1 complex was an appropriate basis for modeling. A test of this postulate was made by fitting the theoretical loading curve (Eq.6-4) to the experimental data, and the results are shown in Fig.7.3. The value of $\beta_{1,1}$ used was obtained by plotting D vs $[N]_{org}$ (Fig.7.4). Following Eq. 6-3, $\beta_{1,1}$ = 64 was obtained as the slope of the straight line best fitted to the data points by linear regression. It can be seen from Fig.7.4 that the data points do not correspond to a straight line very well. Linear regression analysis of the data is subject to uncertainty because of this and because the slope of the line is strongly affected by the single point with the highest D value. Nonetheless, the value of $\beta_{1,1}$ obtained this way does seem to fit the experimental data well, as can be seen in Fig.7.3.

The effect of $TOMA^+$ on the extraction was investigated as described in Section 3.5.5. It was found that the amount of glycerol extracted by $TOMA^+$ ions alone is negligible when compared with that extracted by the $NPB^-$ extractant. In fact, the amount of extraction is comparable to the partition coefficient of glycerol into 2-ethyl-hexanol, so the observed extraction could be caused by the diluent and not the $TOMA^+$.

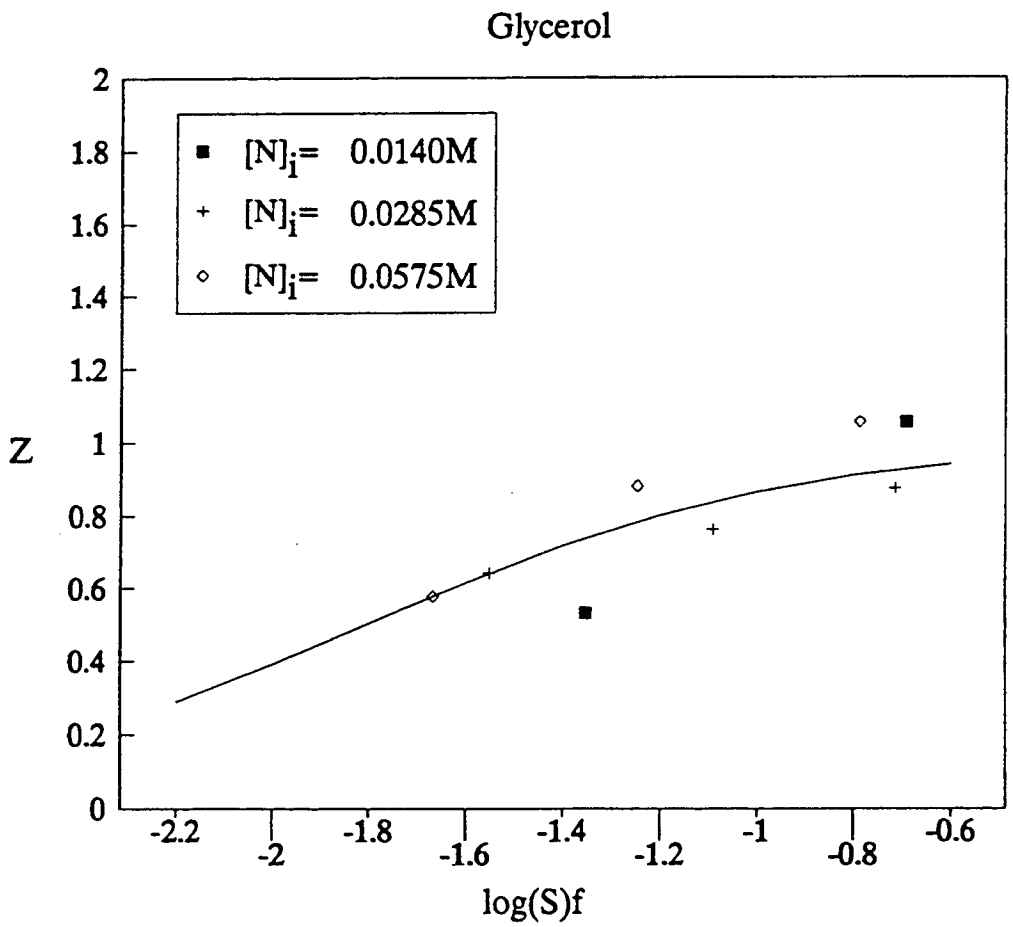



Fig. 7.3 Experimental loading curve for glycerol compared to theoretical loading curve calculated by using Eq. 6-4

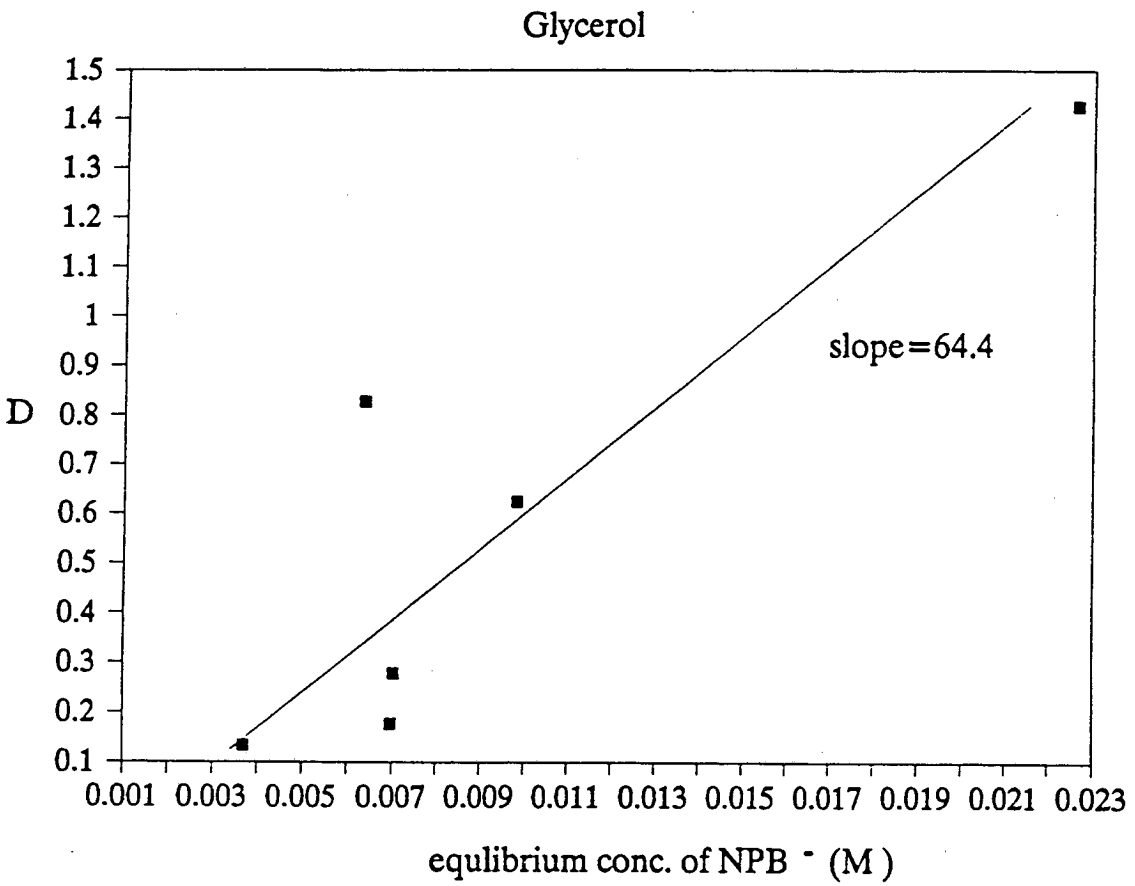



Fig. 7.4 Glycerol extraction results expressed as distribution ratio (D) plotted against equilibrium concentration of $NPB^-$ in the organic phase

## 7.3 Literature data

Dawber, et al. (1988) derived equilibrium constants from NMR data for complexation of the various solutes used in this work with borate ion in aqueous solution. Table 7.2 lists pertinent values.

**TABLE 7.2 Equlibrium constants of complexation ($dm^3mol^{-1}$) with borate ion, $B(OH)_4^-$, in aqueous solution (Dawber, et al., 1988)**

| | $K_1^*$ | $K_2^*$ |
|---|---|---|
| 1,2-propanediol | 4.7 | 0.8 |
| glycerol | 37 | 3.9 |
| fructose | 235 | 111 |
| sorbitol | 540 | 68 |

* $K_1$ = equlibrium constant of 1:1 complex (borate:solute)

$K_2$ = equlibrium constant of 1:2 complex

( data obtained by $^{11}B$ N.M.R. )

From this information, the complexation constants for

glycerol and 1,2-propanediol are small compared to those for some other sugars and sugar alcohols. It was felt to be instructive to see if the complexation of these solutes with $NPB^-$ anion in organic solutions follows the same trends as the aqueous data. If this is the case, then there could be a correlation between the system we used and the aqueous borate system which has been studied extensively. Therefore we proceeded to do experiments with fructose and sorbitol, which have higher complexation constants with borate in aqueous solution.

### 7.4 Fructose and Sorbitol

Fig. 7.5 shows experimentally observed loadings for fructose extraction. Again no dependence of loading upon total $NPB^-$ concentration and no overloading are observed. A theoretical loading curve for a 1:1 complex was fitted to the experimental data as shown in Fig. 7.6, with the value of $\beta_{1,1}$ = 89.5 obtained through the distribution ratio graph, Fig.7.7. The shortcomings of the linear regression are similar to those for glycerol. Nonetheless, the theoretical curve agrees quite well with the experimental data from Fig. 7.6. However, a comparison of these data with the glycerol data, Fig. 7.3, show that fructose is not much stronger as a complexant than glycerol, contary to what is predicted from the aqueous borate data.

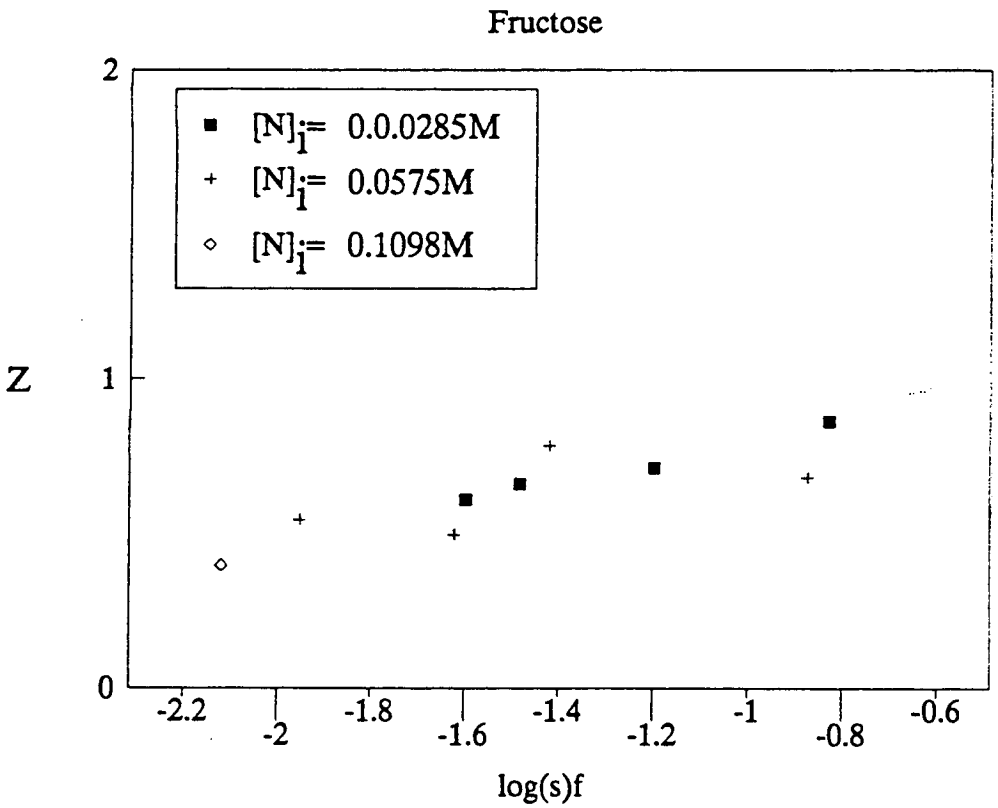



Fig. 7.5 Extraction results for fructose

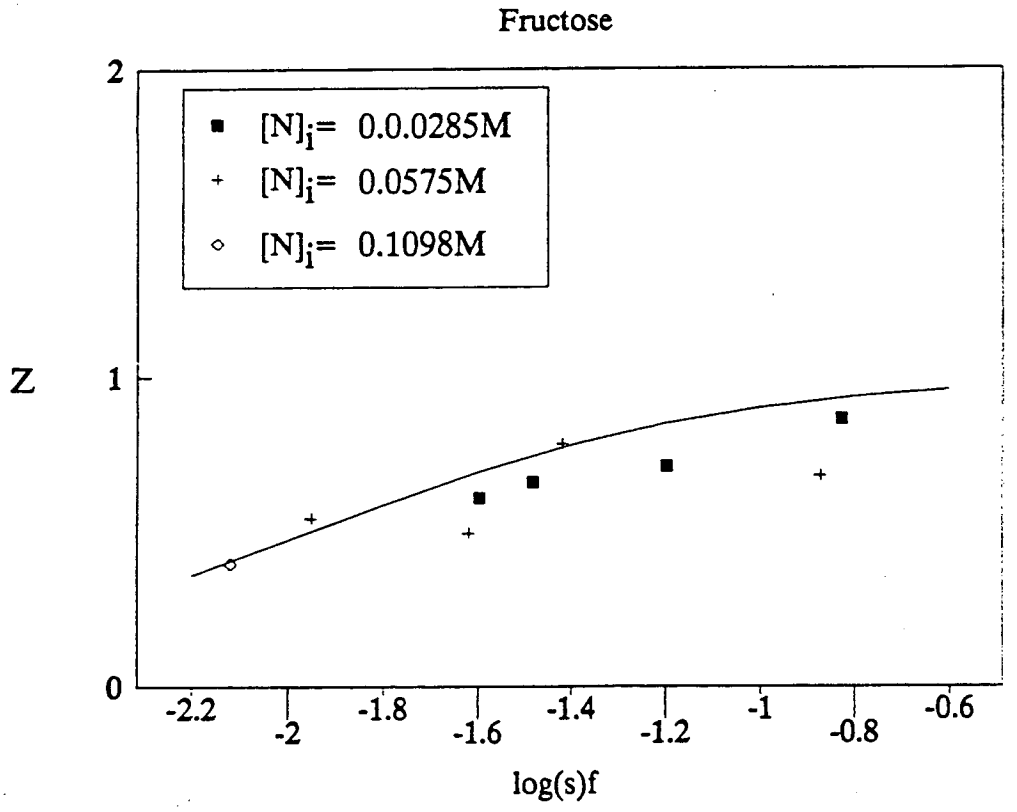



Fig. 7.6 Experimental loading curve for fructose compared to theoretical loading curve calculated by using Eq. 6-4

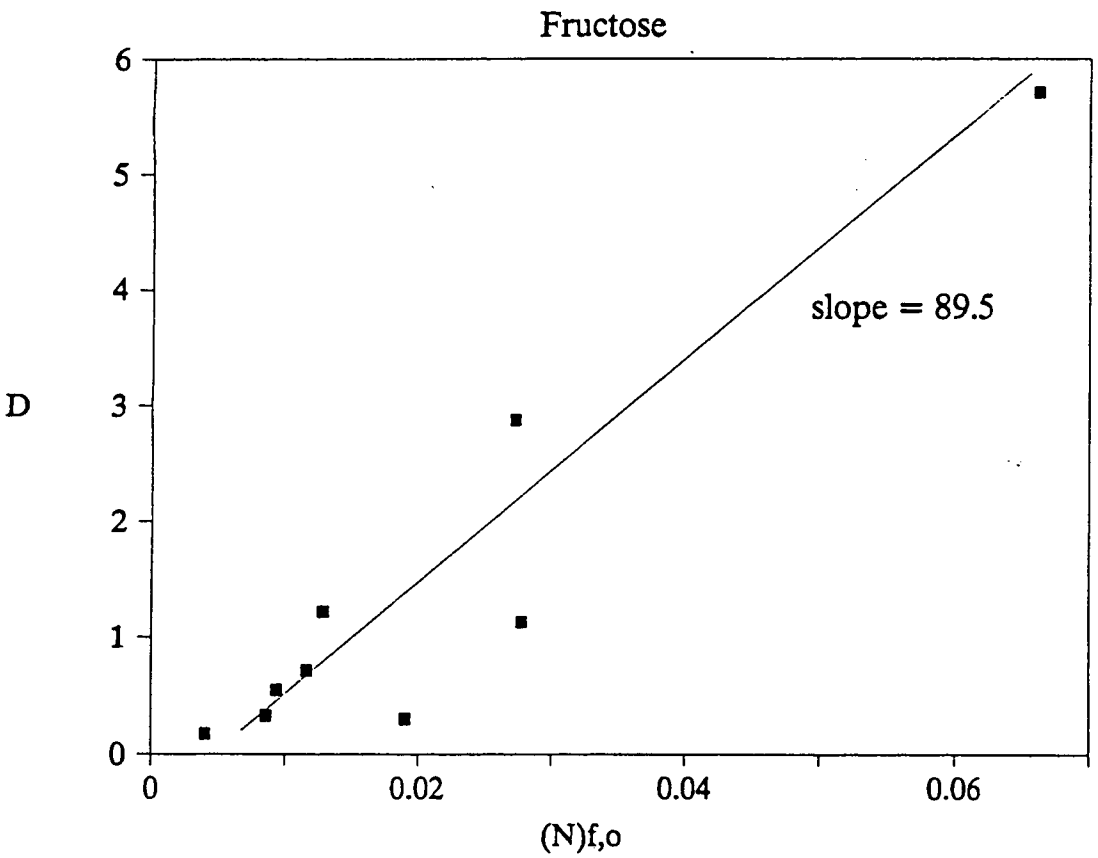



Fig. 7.7 Fructose extraction results expressed as distribution ratio (D) plotted against the equlibrium concentration of NPB in the organic phase

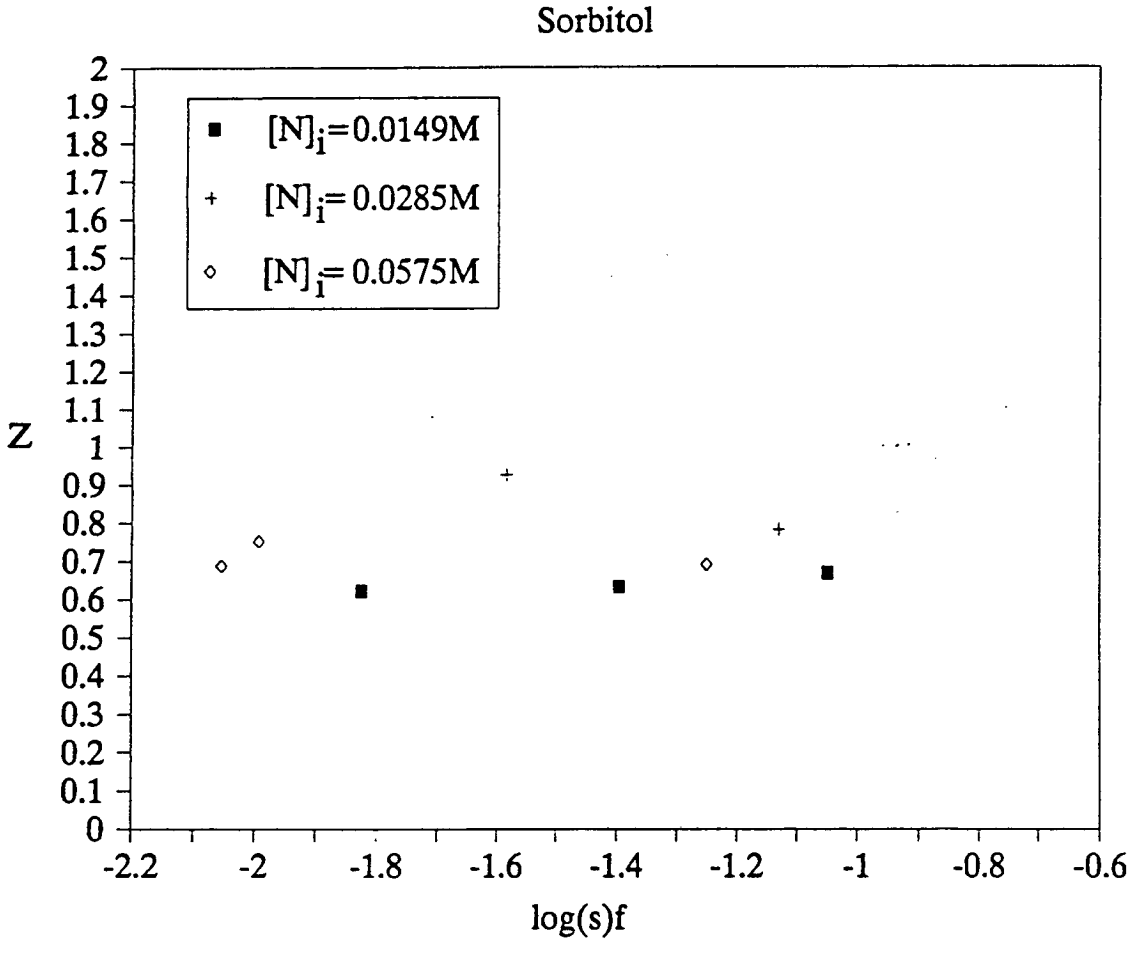



Fig. 7.8 Extraction results for sorbitol expressed in the form of loading curve

The loading curve for sorbitol is presented in Fig. 7.8, which again suggests that sorbitol may form a 1:1 complex with $NPB^-$. The value of $\beta_{1,1}$ = 220 was obtained from Fig. 7.9 as before and the experimental data are compared with the theoretical loading curve in Fig. 7.10. It can be seen that the theoretical curve does not fit the experimental data as well as is the case for the other solutes. The data are flatter at a value of Z>1 than the 1:1 complex model suggests. By fitting other values for $\beta_{1,1}$ in the theoretical loading curve, it was found that $\beta_{1,1}$ = 162.5 fits the experimental data better (Fig. 7.11).

## 7.5 1,2-Propanediol

### 7.5.1 Forward extraction

The experimental results for 1,2-propanediol extraction are shown in Fig. 7.12 as a loading curve. There are a few observations worth discussing: 1) The degree of loading is much higher than those obtained in previous work under the same conditions (Randel, 1991); 2) there is no dependence of loading upon total $NPB^-$ concentration; 3) there is overloading, i.e., more than one mole of 1,2-propanediol is complexed to one mole of NPB- ions.

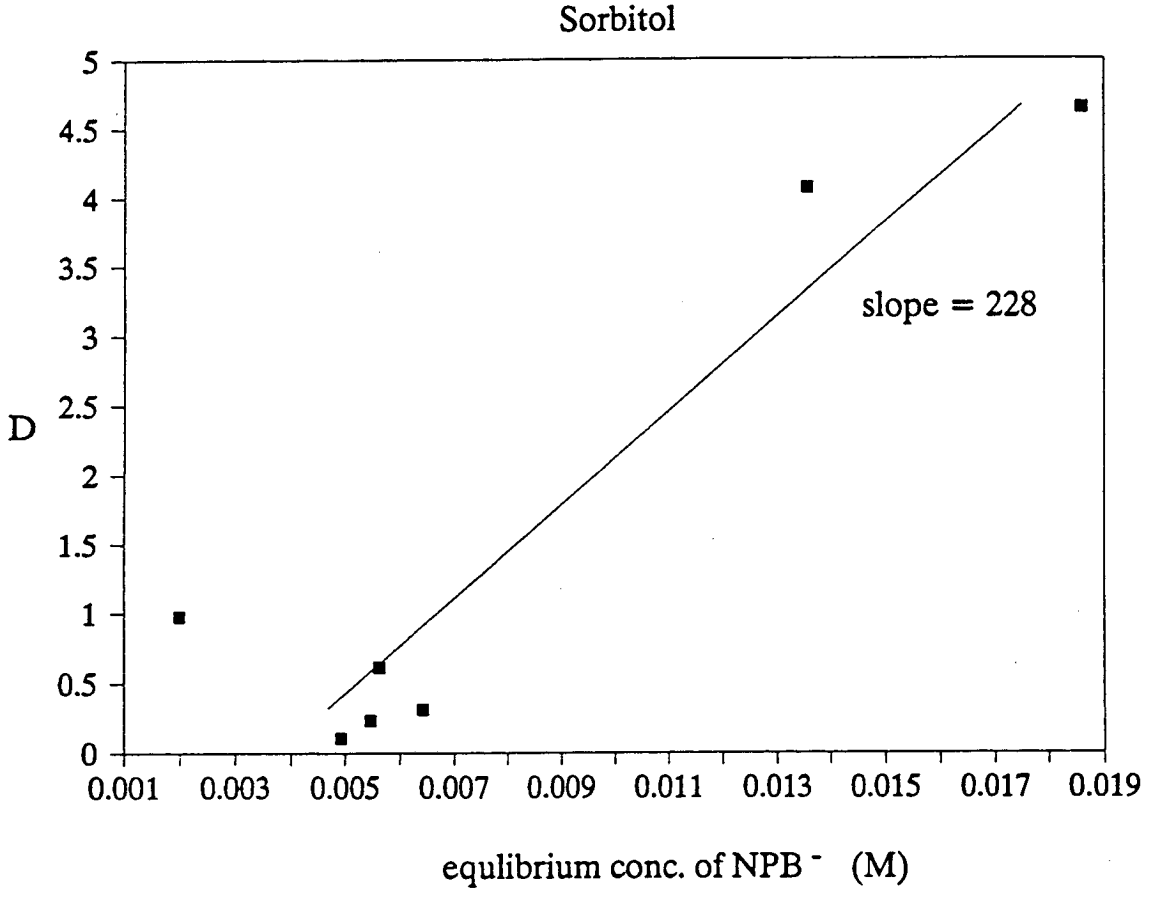



Fig. 7.9 Sorbitol extraction results expressed as distribution ratio (D) plotted against the equlibrium concentration of $NPB^-$ in the organic phase

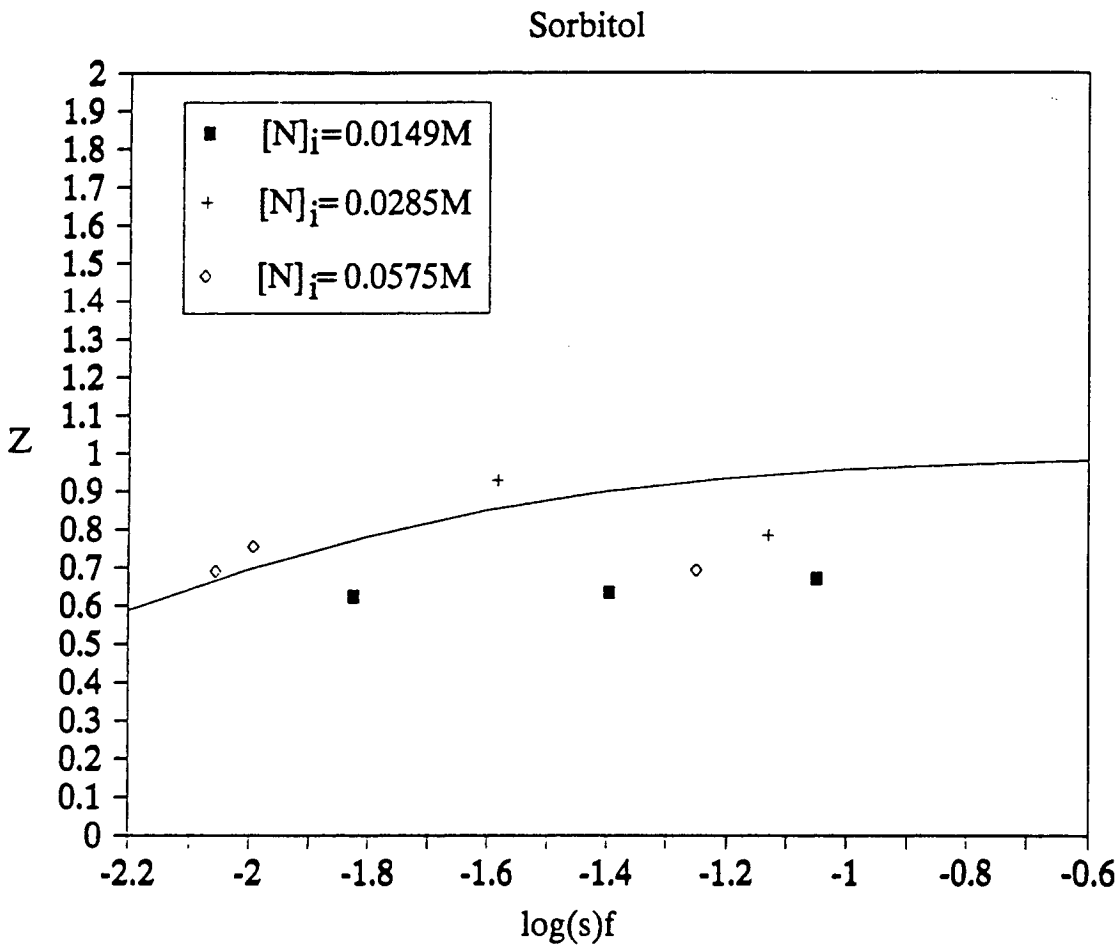



Fig. 7.10 Experimental loading curve for sorbitol compared to theoretical loading curve calculated by using Eq. 6-4

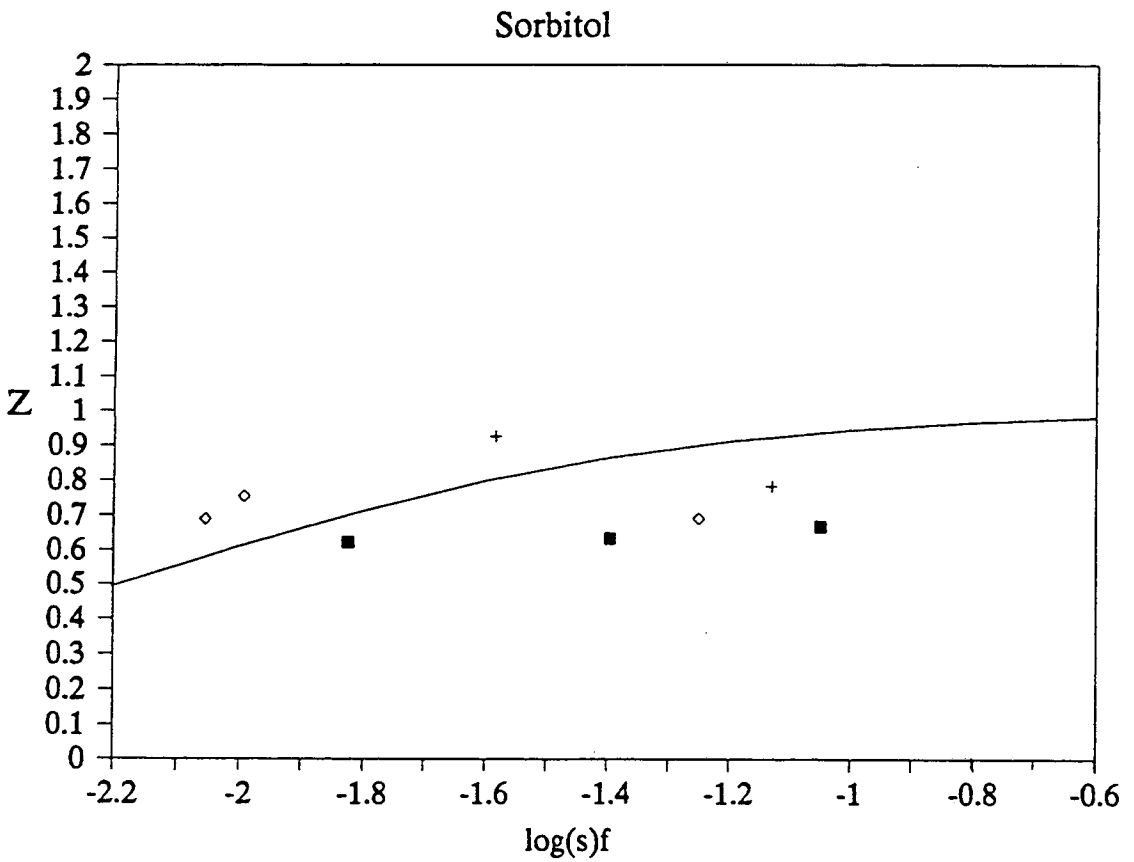



Fig. 7.11 Fitting theoretical loading to experimental data ( equlibrium constant = 162.5 $dm^3 mol^{-1}$ )

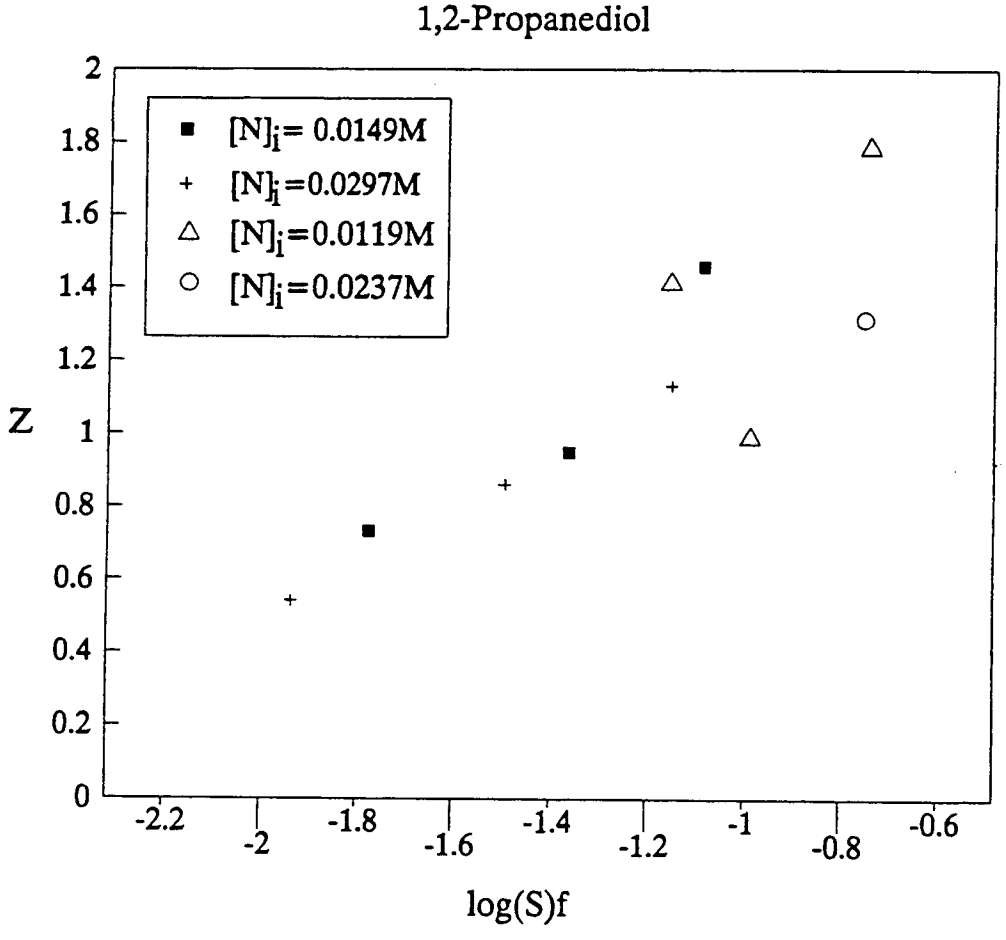



Fig. 7.12 Extraction results for 1,2-propanediol expressed in the form of a loading curve

Higher loading

The loadings from the results of Randel (1991) for 1,2-propanediol range from 0.15 to 0.25 for $\log(S)_{aq}$ equals -1.0 to -1.5. This is very much lower than the present data. The higher capacity of the extractant used in this work appears to be due to a more severe initial treatment with NaOH solution (see Chapter 5), resulting in a higher degree of NPBA ionization to $NPB^-$ which is believed to be responsible for the complexation. This higher loading after more intense treatment by NaOH further confirms that it is $NPB^-$, not NPBA, that is effective in the complexation reaction.

No dependence upon $[N]_i$

It can be seen from Fig. 7.12 that the points do not separate into different curves due to different initial $NPB^-$ concentrations. For systems with only one $NPB^-$ per complex, there should be no effect of total $NPB^-$ concentration on the loading (Tamada, 1989). Therefore, we believe that the complexes formed between 1,2-propanediol and NPB- anions involve just a single molecule of $NPB^-$ per complex.

Overloading

Loading greater than unity is observed at higher

equilibrium aqueous concentrations of 1,2-propanediol. This may be due to the use of the third "uncomplexed" -OH group on the $NPB^-$ anion after the other two -OH groups are used in complexation with one molecule of 1,2-propanediol. Self-association between the 1,2-propanediol molecules by hydrogen bonding would not be a likely explanation since each 1,2-propanediol molecule must use both of its -OH groups to complex with $NPB^-$ ion, and there is no excess -OH group for hydrogen bonding. Based on the above explanation, it would also be possible for the other solutes investigated to overload. The fact that they did not show this property may be due to steric hindrance since $TOMA^+$ and $NPB^-$ are large molecules which form a bulky ion pair, and it would be difficult to load more than one molecule of the solute on the ion pair if the solute is large. Since 1,2-propanediol is the smallest among the solutes investigated, its overloading property supports the postulated explanation.

### 7.5.2 Back Extraction

Back extraction experiments were performed as described in Section 3.5.3, where the 1,2-propanediol from loaded organic phase was back-extracted into an aqueous phase consisting of pure water. The results are presented in Fig. 7.13 together with the forward extraction results. Back extraction was carried out to check whether the samples had

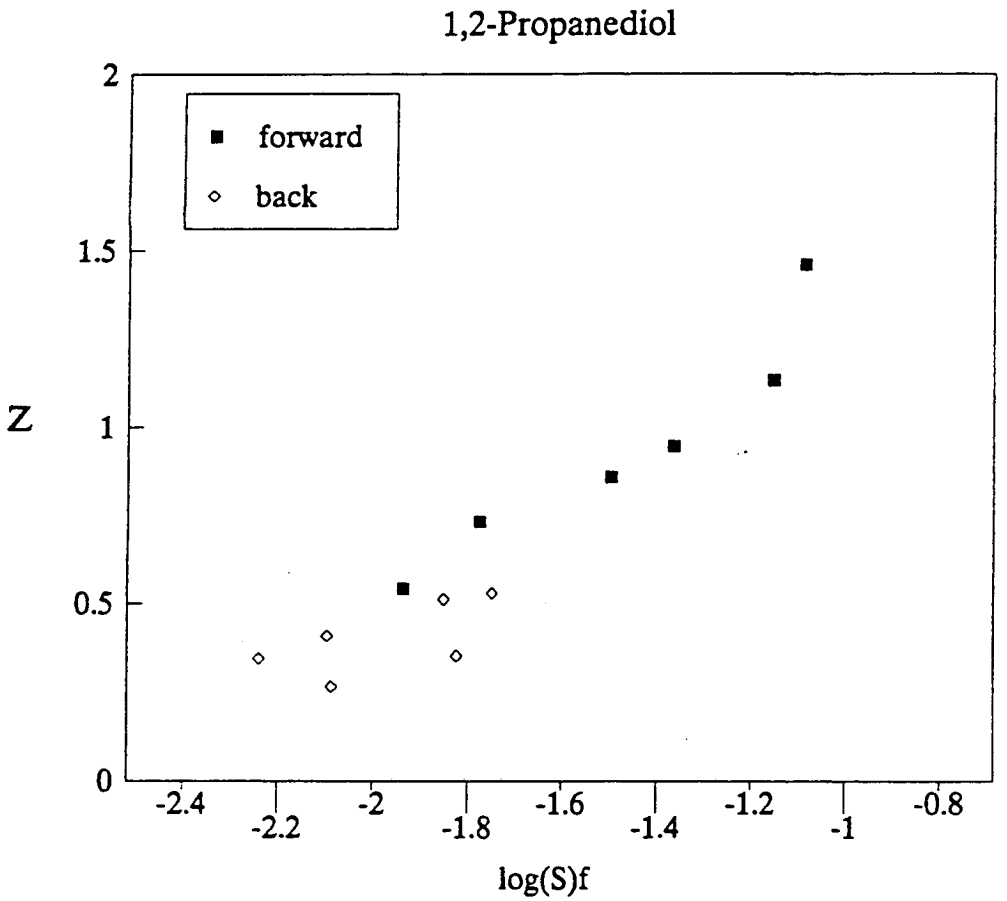



Fig.7.13 Comparing results of forward extraction with back extraction for 1,2-propanediol

reached equlibrium within the time of contact allowed. If equlibrium had been reached, then the conditions would be the same regardless of from which direction the equlibrium had been approached, and the data points from both the forward and back extraction on the loading graph should lie on the same curve. The fact that the data points from back extraction do lie on or even somewhat below the same curve as those obtained from forward extraction in Fig. 7.13 suggests that the extractions investigated had reached equilibrium, and that the data obtained are therefore useful.

### 7.5.3 Effect of diluent

As described in Section 3.5.4, the effect of 2-ethyl-1-hexanol as a diluent on the complexation reaction was tested by changing the diluent to toluene. The extraction experiments were then repeated with all conditions kept the same. It was thought that the 2-ethyl-1-hexanol might compete with the solute for reaction sites on the $NPB^-$ anion since the diluent itself is an alcohol which possesses -OH groups. Fig. 7.14 compares the loading curves obtained using the two diluents. It is obvious that the degree of extraction using toluene as the diluent is less than that when 2-ethyl-1-hexanol is used. This shows that the ability of 2-ethyl-1-hexanol to solvate the complex more than overcomes any competition for reaction sites. Therefore, 2-ethyl-1-hexanol appears to be a reasonably

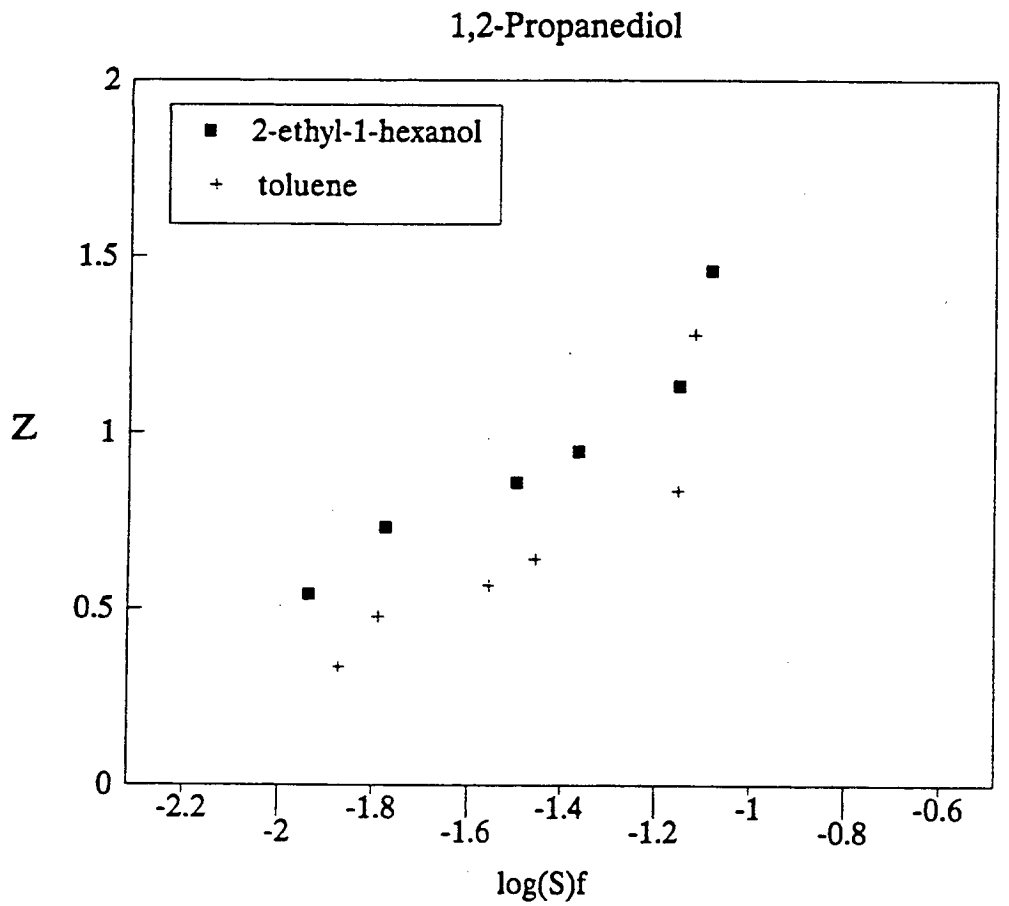



Fig. 7.14 Comparing extraction results for 1,2 propanediol obtained by using two different diluents

good diluent, and it was used for all other extraction experiments.

## 7.6 Lactic acid

Lactic acid was the final solute investigated. Fig. 7.15 shows the extraction results in the form of a loading curve. It can be seen that very high loading was achieved and that overloading was observed for the entire range of solute concentration investigated. It is known that lactic acid has a very high complexation constant with aqueous borate anion (Friedman, et al., 1974). The necessary -OH groups are thought to be supplied by hydration of -COOH to $-C(OH)_3$ (Zittle, 1951).

There are several possible explanations for the consistent overloading behavior of lactic acid.

1. It is known that lactic acid self-associates very well due to fairly strong hydrogen bonding between the molecules, which could be one of the causes of overloading. However, after an acid molecule has complexed with the $NPB^-$ anion, association of its -COOH group with another lactic acid molecule may no longer be as facile.
2. Another possible reason would be ester formation between the third uncomplexed -OH on the NPB- molecule

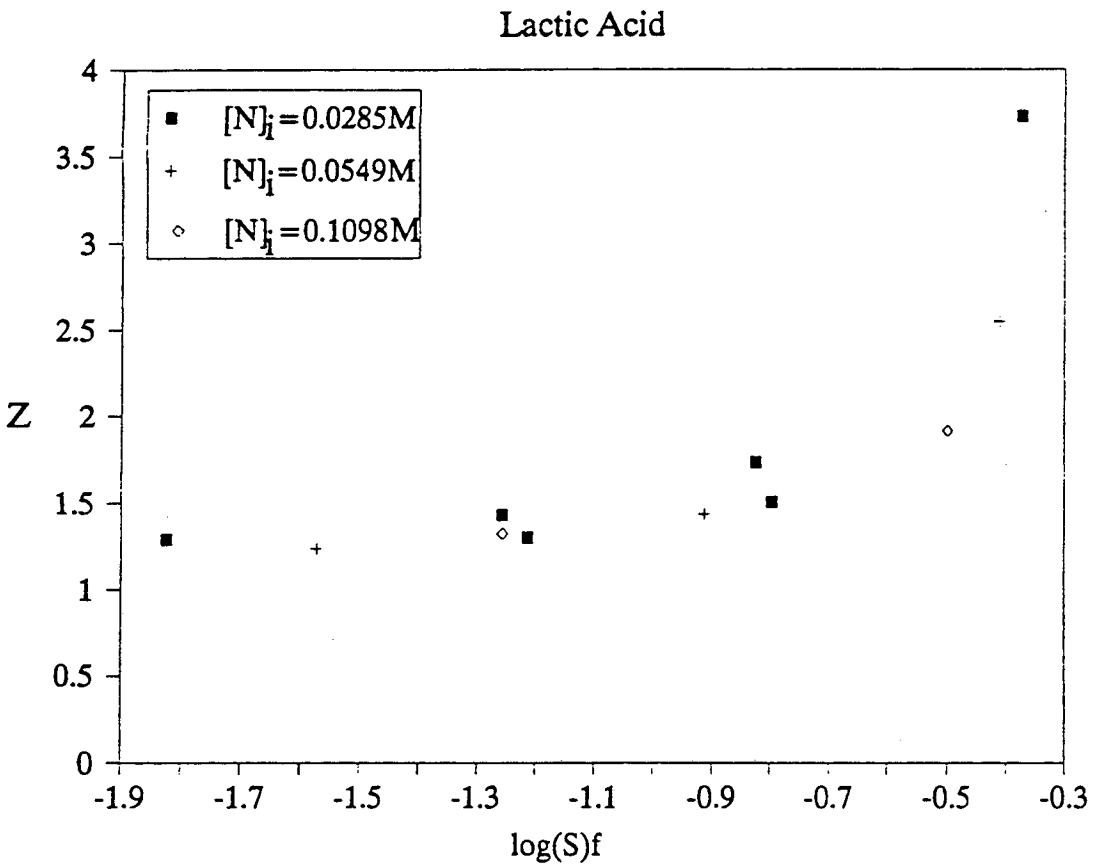



Fig.7.15 Lactic acid extraction results expressed in the form of a loading curve

and the carboxyl group of the lactic acid molecule. However, it is known that 2-ethyl-1-hexanol stabilizes the 1,1 complex in preference to the 2,1 complex in amine-carcoxylic acid systems (Tamada,1989). This is because 2-ethyl-1-hexanol is capable of donating protons, which compete with the carboxyl protons of the second acid for the carboxylate binding site on the first acid complexed to the $NPB^-$. This competition tends to destabilize the 2,1 complex.

3. The most probable reason for overloading would be a high degree of extraction by something other than $NPB^-$ present in the extractant. This leads to the concept that the excess $TOMA^+$ ions left unpaired with $NPB^-$ anions in the extractant are also participating in the extraction, since quaternary ammonium compounds are known to be highly effective in strong base anionic exchange resins for separation of organic acids.

Experiments as described in Section 3.5.5 were done, and the results obtained proved complexation of lactic acid with $TOMA^+$. Table 7.3 shows some sample results for lactic acid extraction by $TOMA^+$ ions. These results show that, under the same extraction condition, $TOMA^+Cl^-$ contributes 30-50% of the extraction by the $TOMA^+NPB^-$ ion-pair extractant. The lactic acid molecules can give up the $H^+$ ions readily to form lactate

anion, which then pairs with the $TOMA^+$, i.e., a strong acid-base interaction.

TABLE 7.3 Comparison of results for lactic acid extraction by $NPB^-$ extractant and $TOMA^+Cl^-$ only

| | initial [S]=0.2M | | initial [S]=0.1M | |
|---|---|---|---|---|
| | [S]i-[S]f | % extrac. | [S]i-[S]f | % extrac. |
| $NPB^-$ extractant | 0.0514 | 25.53 | 0.0387 | 38.73 |
| $TOMA^+Cl^-$ only | 0.0148 | 14.80 | 0.0260 | 12.90 |

For extraction by $TOMA^+Cl^-$ alone, it was found that at lower solute concentrations, approximately 1:1 solute to $TOMA^+$ ratio was obtained and at higher solute concentrations, overloading was observed. Loading of more than one mole of lactic acid per mole of $TOMA^+Cl^-$ present was probably due to self-association between the lactic acid molecules. However, it is hard to separate the lactic acid extraction by $TOMA^+$ from the extraction by $NPB^-$ for modeling purposes, because of unreliable assumptions. Since the $pK_a$ of lactic acid is 3.85 compared to 7.1 for NPBA, the $TOMA^+$ ions in the organic

extractant should preferentially bind to lactic acid rather than $NPB^-$. Therefore, we can presume that at low solute concentrations lactic acid binds to the $TOMA^+$ ions in a 1:1 ratio. Using this assumption, the loadings of lactic acid extracted by $NPB^-$ alone were calculated. The new loading curve is shown in Fig. 7.16. The new loading curve retains the shape of the loading curve in Fig. 7.15 but the plateau has shifted to a value of loading around 1.

## 7.7 Discussion

The theoretical complexation model fits the experimental results reasonably well, and the order of complexation constants for the solutes follows trends similar to those found for complexation with borate anions in aqueous conditions (Table 7.4). The results also showed that by incorporating $NPB^-$ into the diluent, extraction of the solutes is significantly enhanced. Distribution ratios as high as 5.7 were achieved (fructose).

For all of the solutes investigated, there appears to be only one $NPB^-$ per complex. For glycerol, fructose and sorbitol, the ratio of solute molecules to $NPB^-$ in the complexes appears to be 1:1. For 1,2-propanediol, more than one molecule of solute binding to one $NPB^-$ was observed. This could be due to the use of the free -OH on the $NPB^-$. The other solutes did not overload this way, a fact which may be due to

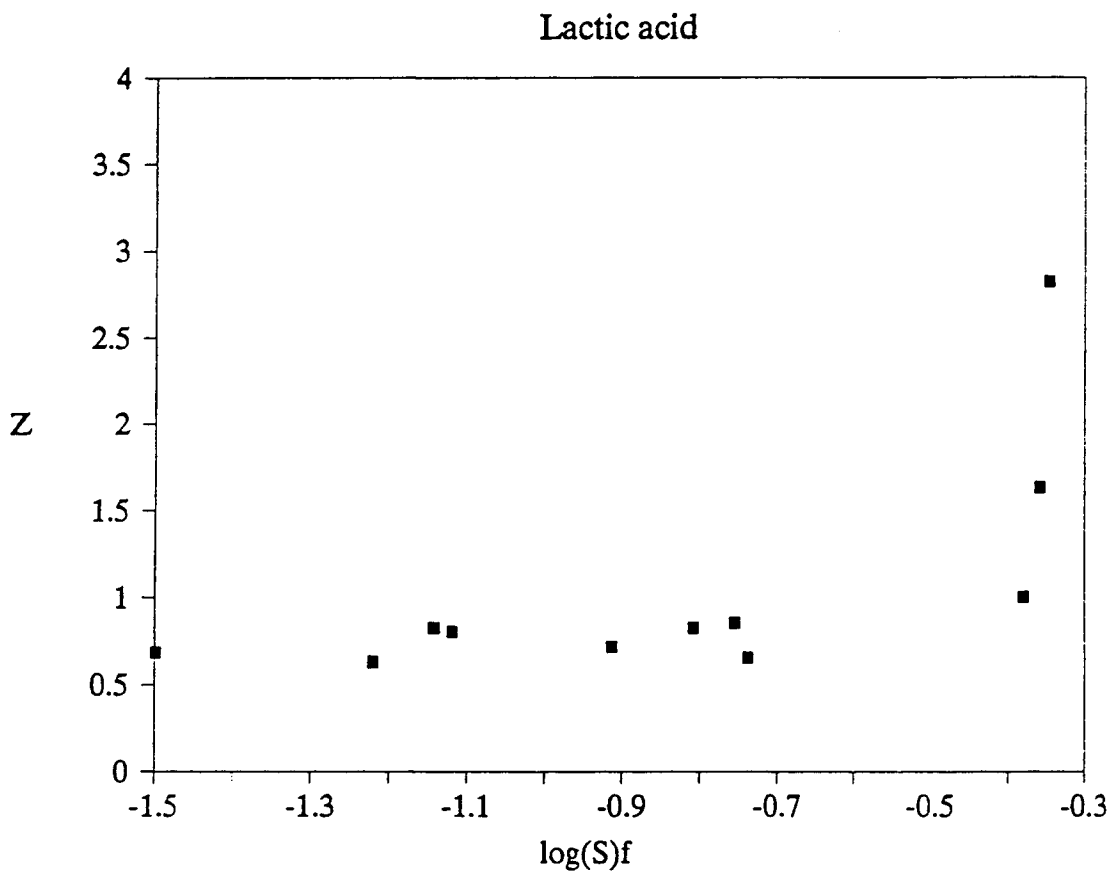



Fig. 7.16 Lactic acid extraction results after effect of $TOMA^+$ has been removed

steric hindrance since $TOMA^+$ and $NPB^-$ are large molecules which form a bulky ion pair. It would be difficult to load more than one molecule of the solute on the ion pair if the solute is large. 1,2-Propanediol is the smallest among the solutes.

**TABLE 7.4 Equlibrium constants of complexation ($dm^3mol^{-1}$)of solutes with borate in aqueous conditions (Dawber, et al, 1988) and with NPB- in organic conditions**

| | $B(OH)_4^-$, aqueous | $NPB^-$, organic |
|---|---|---|
| glycerol | 37 | 64.3 |
| fructose | 235 | 89.5 |
| sorbitol | 540 | 162.5 |

## 7.8 Recovery

It is known that for complexes with borate ions under aqueous conditions, the reaction can be reversed very easily (Zittle, 1951). A preliminary experiment was done whereby a sorbitol-loaded organic extractant was contacted with equal volumes of 0.01N sulfuric acid, and the results showed 50% to 90% recovery (Table 7.5).

TABLE 7.5 Results for sorbitol recovery experiments

| $[S]_{i,o}$ | $(S)_{f,aq}$ | % recovered |
|---|---|---|
| 0.050 | 0.025 | 49.7 |
| 0.041 | 0.022 | 53.1 |
| 0.026 | 0.024 | 94.0 |

$[S]_{i,o}$ = initial sorbitol concentration in the organic phase

$(S)_{f,aq}$ = equlibrium sorbitol concentration in the aqueous phase

## 7.9 Implementation

This is part of an early stage of investigation of the process feasibility using NPBA for extraction of -OH bearing solutes from dilute aqueous solutions. More data are required before making any important conclusions regarding process implementation. However, the data obtained in this work showed a substantial loss of NPBA to the aqueous phase during initial treatment with alkali solutions, which would not be economical in an industrial process. One approach for overcoming this problem could be to incorporate the NPBA onto a solid support, such as an adsorbent.

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# APPENDIX. TABULATION OF EXPERIMENTAL RESULTS

Results of the batch extraction experiments for each solute are tabulated separately below in Tables A-1 to A-6.

List of symbols:

$(S)_{f,aq}$ = equilibrium concentration of the solute in the aqueous phase

$(S)_{i,aq}$ = initial concentration of the solute in the aqueous phase

$(N)_{i,o}$ = initial concentration of $NPB^-$ ions in the organic extractant

(N)/(S) = initial ratio of $NPB^-$ to solute

% extrac. = Amount of solute extracted in terms of percentage

$(N)_{f,o}$ = equilibrium concentration of free NPB- in the organic extractant

D = distribution ratio (see Section 5.4)

Z = loading (see Section 5.7)

TABLE A-1 Experimental data for glycerol extraction experiments

| | (s)f,aq | (s)i,aq | (N)i,o | (N)/(s) | %extrc. | (N)f,o | D | Z |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| G-1 | 0.0259 | 0.0458 | 0.0270 | 0.5895 | 43.4352 | 0.0071 | 0.7679 | 0.7368 |
| G-2 | 0.0339 | 0.0458 | 0.0137 | 0.2998 | 26.0760 | 0.0018 | 0.3527 | 0.8698 |
| G-3 | 0.0282 | 0.0458 | 0.0275 | 0.5993 | 38.4792 | 0.0098 | 0.6255 | 0.6420 |
| G-4 | 0.0569 | 0.1040 | 0.0535 | 0.5143 | 45.3099 | 0.0064 | 0.8285 | 0.8810 |
| G-5 | 0.0216 | 0.0525 | 0.0535 | 1.0185 | 58.7900 | 0.0226 | 1.4266 | 0.5772 |
| G-6 | 0.1640 | 0.2205 | 0.0535 | 0.2426 | 25.6480 | -0.0031 | 0.3450 | 1.0572 |
| G-7 | 0.0814 | 0.1040 | 0.0297 | 0.2855 | 21.7822 | 0.0070 | 0.2785 | 0.7630 |
| G-8 | 0.1945 | 0.2205 | 0.0297 | 0.1347 | 11.7977 | 0.0037 | 0.1338 | 0.8760 |
| G-9 | 0.0446 | 0.0525 | 0.0149 | 0.2836 | 15.0662 | 0.0070 | 0.1774 | 0.5312 |
| G-10 | 0.2048 | 0.2205 | 0.0149 | 0.0676 | 7.1300 | -0.0008 | 0.0768 | 1.0552 |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |

TABLE A-2 Experimental data for fructose extraction experiments

| | (s)f,aq | (s)i,aq | (N)i,o | (N)/(s) | %extrc. | (N)f,o | D | Z |
|---|---|---|---|---|---|---|---|---|
| F-1 | 0.0112 | 0.0434 | 0.0595 | 1.3700 | 74.2040 | 0.0273 | 2.8766 | 0.5416 |
| F-2 | 0.0382 | 0.0848 | 0.0595 | 0.7016 | 54.9785 | 0.0129 | 1.2212 | 0.7836 |
| F-3 | 0.1346 | 0.1750 | 0.0595 | 0.3400 | 23.1102 | 0.0191 | 0.3006 | 0.6797 |
| F-4 | 0.0254 | 0.0434 | 0.0297 | 0.6838 | 41.5683 | 0.0116 | 0.7114 | 0.6079 |
| F-5 | 0.0637 | 0.0848 | 0.0297 | 0.3502 | 24.8671 | 0.0086 | 0.3310 | 0.7100 |
| F-6 | 0.1494 | 0.1750 | 0.0297 | 0.1697 | 14.6396 | 0.0041 | 0.1715 | 0.8626 |
| F-7 | 0.0331 | 0.0512 | 0.0275 | 0.5365 | 35.2657 | 0.0094 | 0.5448 | 0.6573 |
| F-8 | 0.0240 | 0.0512 | 0.0549 | 1.0730 | 53.0051 | 0.0278 | 1.1279 | 0.4940 |
| F-9 | 0.0076 | 0.0512 | 0.1098 | 2.1459 | 85.0940 | 0.0663 | 5.7087 | 0.3965 |
| F-10 | 0.0422 | 0.0888 | 0.0545 | 0.6137 | 52.4606 | 0.0079 | 1.1035 | 0.8548 |
| | | | | | | | | |
| | | | | | | | | |

TABLE A-3 Experimental data for sorbitol extraction experiments

| | (s)f,aq | (s)i,aq | (N)i,o | (N)/(s) | % extrc. | (N)f,o | D | Z |
|---|---|---|---|---|---|---|---|---|
| S-1 | 0.0740 | 0.0973 | 0.0297 | 0.3053 | 23.9155 | 0.0064 | 0.3143 | 0.7833 |
| S-2 | 0.0562 | 0.0973 | 0.0595 | 0.6117 | 42.2646 | 0.0184 | 0.7320 | 0.6910 |
| S-3 | 0.0088 | 0.0497 | 0.0595 | 1.1972 | 82.2873 | 0.0186 | 4.6457 | 0.6873 |
| S-4 | 0.0000 | 0.0242 | 0.0595 | 2.4576 | 100.0000 | 0.0353 | - | 0.4069 |
| S-5 | 0.0894 | 0.0993 | 0.0149 | 0.1495 | 9.9857 | 0.0049 | 0.1109 | 0.6680 |
| S-6 | 0.0403 | 0.0497 | 0.0149 | 0.2988 | 18.8871 | 0.0055 | 0.2328 | 0.6321 |
| S-7 | 0.0150 | 0.0242 | 0.0149 | 0.6134 | 38.1154 | 0.0056 | 0.6159 | 0.6214 |
| S-8 | 0.0498 | 0.0515 | 0.0000 | 0.0000 | 3.2706 | -0.0017 | 0.0338 | - |
| S-9 | 0.0260 | 0.0515 | 0.0275 | 0.5330 | 49.4287 | 0.0020 | 0.9774 | 0.9273 |
| S-10 | 0.0102 | 0.0515 | 0.0549 | 1.0660 | 80.2745 | 0.0136 | 4.0696 | 0.7530 |
| S-11 | 0.0000 | 0.0515 | 0.1098 | 2.1321 | 100.0000 | 0.0583 | - | 0.4690 |

TABLE A-4 Experimental data for 1,2-propanediol extraction experiments

Forward extraction:

| | (s)f,aq | (s)i,aq | (N)i,o | (N)/(s) | % extrc. | (N)f,o | D | Z |
|---|---|---|---|---|---|---|---|---|
| P-1 | 0.0168 | 0.0277 | 0.0149 | 0.5378 | 39.3207 | 0.0040 | 0.6480 | 0.7311 |
| P-2 | 0.0434 | 0.0575 | 0.0149 | 0.2590 | 24.5290 | 0.0008 | 0.3250 | 0.9471 |
| P-3 | 0.0827 | 0.1044 | 0.0149 | 0.1427 | 20.8333 | -0.0069 | 0.2632 | 1.4597 |
| P-4 | 0.0116 | 0.0277 | 0.0297 | 1.0721 | 58.0731 | 0.0136 | 1.3851 | 0.5417 |
| P-5 | 0.0320 | 0.0575 | 0.0297 | 0.5162 | 44.3266 | 0.0042 | 0.7962 | 0.8587 |
| P-6 | 0.0708 | 0.1044 | 0.0297 | 0.2845 | 32.2031 | -0.0039 | 0.4750 | 1.1320 |
| P-7 | 0.0274 | 0.0277 | 0.0000 | 0.0000 | 0.9855 | 0.0000 | 0.0100 | - |

Back extraction:

| | (s)f,aq | (s)i,aq | (N)i,o | (s)i,o | % recovery | Z |
|---|---|---|---|---|---|---|
| P-1 | 0.0058 | 0.0000 | 0.0149 | 0.0109 | 53.1108 | 0.3428 |
| P_2 | 0.0080 | 0.0000 | 0.0149 | 0.0141 | 56.9072 | 0.4081 |
| P-3 | 0.0141 | 0.0000 | 0.0149 | 0.0217 | 65.0117 | 0.5107 |
| P-4 | 0.0082 | 0.0000 | 0.0297 | 0.0161 | 50.9115 | 0.2659 |
| P-5 | 0.0150 | 0.0000 | 0.0297 | 0.0255 | 59.0068 | 0.3520 |
| P-6 | 0.0179 | 0.0000 | 0.0297 | 0.0336 | 53.2819 | 0.5288 |

TABLE A-5 Experimental data for 1,2-propanediol extraction using toluene as diluent

| | (s)f,aq | (s)i,aq | (N)i,o | (N)/(s) | % extrc. | (N)f,o | D | Z |
|---|---|---|---|---|---|---|---|---|
| P-T1 | 0.0937 | 0.0952 | 0.0000 | - | 1.6228 | - | 0.0165 | - |
| P-T2 | 0.0215 | 0.0234 | 0.0000 | - | 8.0962 | - | 0.0881 | - |
| P-1 | 0.0163 | 0.0234 | 0.0149 | 0.6374 | 30.3855 | 0.0078 | 0.4365 | 0.4767 |
| P-2 | 0.0351 | 0.0446 | 0.0149 | 0.3338 | 21.4372 | 0.0053 | 0.2729 | 0.6422 |
| P-3 | 0.0762 | 0.0952 | 0.0149 | 0.1565 | 19.9947 | -0.0041 | 0.2499 | 1.2780 |
| P-4 | 0.0134 | 0.0234 | 0.0297 | 1.2705 | 42.4708 | 0.0198 | 0.7382 | 0.3343 |
| P-5 | 0.0278 | 0.0446 | 0.0297 | 0.6654 | 37.6472 | 0.0129 | 0.6038 | 0.5658 |
| P-6 | 0.0705 | 0.0952 | 0.0297 | 0.3119 | 26.0154 | 0.0049 | 0.3516 | 0.8342 |

TABLE A-6 Experimental data for lactic acid extraction experiments

| | (s)f,aq | (s)i,aq | (N)i,o | (N)/(s) | % extrc. | (N)f,o | D | Z |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| L-1 | 0.4792 | 0.5276 | 0.0000 | 0.0000 | 0.0916 | 0.0000 | P=0.101 | - |
| L-2 | 0.4250 | 0.5276 | 0.0275 | 0.0520 | 0.1944 | -0.0751 | 0.2413 | 3.7357 |
| L-3 | 0.3878 | 0.5276 | 0.0549 | 0.1041 | 0.2650 | -0.0849 | 0.3606 | 2.5468 |
| L-4 | 0.3172 | 0.5276 | 0.1098 | 0.2081 | 0.3989 | -0.1006 | 0.6635 | 1.9164 |
| L-5 | 0.0467 | 0.0505 | 0.0000 | 0.0000 | 0.0745 | 0.0000 | P=0.08 | - |
| L-6 | 0.0150 | 0.0505 | 0.0275 | 0.5436 | 0.7027 | -0.0080 | 2.3633 | 1.2927 |
| L-7 | 0.0000 | 0.0505 | 0.0549 | 1.0871 | 1.0000 | 0.0044 | ERR | 0.9199 |
| L-8 | 0.0000 | 0.0505 | 0.1098 | 2.1743 | 1.0000 | 0.0593 | ERR | 0.4599 |
| L-9 | 0.0000 | 0.0347 | 0.0275 | 0.7911 | 1.0000 | -0.0073 | ERR | 1.2641 |
| L-10 | 0.0554 | 0.0948 | 0.0275 | 0.2896 | 0.4153 | -0.0119 | 0.7103 | 1.4342 |
| L-11 | 0.0268 | 0.0948 | 0.0549 | 0.5791 | 0.7174 | -0.0131 | 2.5391 | 1.2388 |
| L-12 | 0.0000 | 0.0948 | 0.1098 | 1.1583 | 1.0000 | 0.0150 | ERR | 0.8633 |
| L-13 | 0.1596 | 0.2010 | 0.0275 | 0.1366 | 0.2057 | -0.0139 | 0.2590 | 1.5066 |
| L-14 | 0.1222 | 0.2010 | 0.0549 | 0.2731 | 0.3920 | -0.0239 | 0.6447 | 1.4352 |
| L-15 | 0.0555 | 0.2010 | 0.1098 | 0.5463 | 0.7241 | -0.0358 | 2.6249 | 1.3256 |
| L-16 | 0.1501 | 0.2015 | 0.0297 | 0.1474 | 0.2553 | -0.0217 | 0.3427 | 1.7320 |
| L-17 | 0.0613 | 0.1000 | 0.0297 | 0.2970 | 0.3873 | -0.0090 | 0.6320 | 1.3039 |

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