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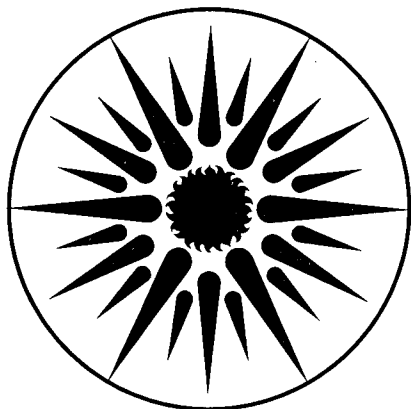
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APPLIED SCIENCE DIVISION

Separation of Glycols from Dilute Aqueous Solutions Via
Complexation with Boronic Acids

L.A. Randel* and C.J. King
(*M.S. Thesis)

July 1991

**APPLIED SCIENCE
DIVISION**

DISCLAIMER

SEPARATION OF GLYCOLS FROM

DILUTE AQUEOUS SOLUTIONS VIA

COMPLEXATION WITH BORONIC ACIDS

by

Lucy A. Randel and C. Judson King

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July 1991

DEDICATION

To Chuck

Belief

is at the beginning

of all accomplishment.

--Joan Walsh Anglund

Separation of Glycols from Dilute Aqueous Solutions
via Complexation with Boronic Acids

By

Lucy Ann Randel

ABSTRACT

This work examines methods for separating low molecular weight glycols from dilute aqueous solution. Extraction into conventional solvents is generally not economical, since, in the literature reviewed, distribution ratios for the two- to four-carbon glycols are all less than one. Distribution ratios can be increased, however, by incorporating into the organic phase an extracting agent that will complex with the solute of interest.

The extracting agent investigated in this work is 3-nitrophenylboronic acid (NPBA). NPBA, a boric acid derivative, reversibly complexes with many glycols. The literature on complexation of borate and related compounds with glycols, including mechanistic data, measurement techniques, and applications to separation processes, provides information valuable for designing experiments with NPBA and is reviewed herein.
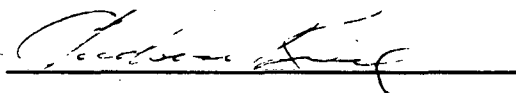
Both aqueous and two-phase measurements are performed with NPBA-glycol systems. Stability constants for the formation in aqueous solution of the anionic complex between NPBA and both 1,2- and 1,3-propanediol are measured potentiometrically at 25, 35 and 44.8°C. Results for 1,2-propanediol at 25°C are comparable to literature values for the 1:1 complex with borate, but the potentiometric method does not appear suitable for the 1,3-diol. Thermodynamic parameters for the 1,2-propanediol complex are derived from the temperature dependence of the stability constant.

In batch extraction experiments at 25°C, distribution ratios for 1,2-propanediol between water and 2-ethyl-1-hexanol are reported for varying concentrations of NPBA paired with Aliquat 336, a quaternary amine that provides a counter-ion for the anionic NPBA$^-$-diol complex in the organic phase. In the absence of NPBA and Aliquat 336, the

measured partition coefficient in 2-ethyl-1-hexanol equals 0.08 +/- 0.007. The distribution ratios do not increase significantly when nearly equimolar mixtures of NPBA and Aliquat 336 in 2-ethyl-1-hexanol are contacted with aqueous diol solutions, unless the mixture is pretreated by base-washing. For an extractant pretreated with base, distribution ratios vary linearly with NPBA¯:diol ratio, ranging from 0.18 for ratio of 0.5:1 to 0.51 for a ratio of 2.5:1. Extraction data are also modeled in terms of complex formation in the organic phase and compared to the accepted model for complex formation in the aqueous phase.

In extraction systems, a complexing agent with low aqueous solubility is desired to minimize losses to the aqueous phase. For NPBA, the measured solubility in water at 25°C is 0.45 +/- 0.02 weight percent. Further, during extraction experiments, losses to aqueous solution were less than 1% at concentrations typically less than 0.1 weight percent.

Implementation of the NPBA-diol complexation reaction in an industrial separation process may be hindered by third phase formation, which is affected by the phase-contacting technique and the ratio of NPBA to Aliquat 336. Immobilization of NPBA or control of these parameters may be useful in minimizing third phase formation.

C. Judson King

Thesis Committee Chair

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Lucy Ann Randel

Berkeley, CA

July, 1991

1 INTRODUCTION

The top 16 oxychemicals in the U.S., including alcohols, glycols, and organic acids, can all be produced from renewable materials. The 1985 market value for these chemicals exceeded $14 billion (Busche, 1985). Examples of high volume products currently produced by bioprocess technology include high fructose corn syrup (16 billion lb/yr), ethanol (850 million gal/yr), citric acid (350 million lb/yr), and glucose (900 million lb/yr) (Jain, Datta, and Zeikus, 1989).

The viability of biotechnology as a source for other commodity chemicals, however, largely depends on improvements in separation processes (National Research Council, 1987). The difficult recovery of products from dilute (typically 1-5%) fermentation broths is a major factor in the cost of these chemicals (Busche, 1985). The low molecular weight diols, such as ethylene glycol, propylene glycol, and the butanediols, are particularly difficult to separate because of their hydrophilicity and high boiling points relative to water. Distillation is prohibitively expensive for such applications since as much as 99 percent of the initial solution would be taken overhead.

Busche (1984) evaluated alternatives to distillation for recovering such high boiling products from dilute fermentation broths. He concluded that, of demonstrated processes, solvent extraction was "the method of choice for high boilers." The choice of extraction solvent is critical to the economics of this technique. The effectiveness of a solvent is largely dependent on its capacity and selectivity for the solute. The selectivity, the ratio of two components in the extraction solvent phase (extract) to that in the feed solvent phase (raffinate), indicates the relative separation. The distribution of the solute between the two immiscible phases determines the solvent to feed ratio needed to achieve the desired separation. Corrections to account for ionization and dimerization can be made to the

experimentally measured distribution ratio, D, to obtain Nernst partition coefficients for the neutral solutes. An extensive listing of Nernst partition coefficients, P, has been compiled by Hansch et al. (Leo, Hansch, and Elkins, 1971; Hansch and Leo, 1979), but that work included very limited data for low molecular weight diols.

Low molecular weight monomeric alcohols, however, have many properties similar to the corresponding diols. Kertes and King (1987) prepared a comprehensive review of the extraction chemistry of low molecular weight alcohols. The highest Nernst coefficients for monomeric alcohols occur with polar solvents having oxygen-containing functional groups. Solvents with the highest distribution ratios for the alcohols typically also had the highest distribution ratios for coextraction of water; the distribution ratio for water increased as a function of equilibrium aqueous alcohol concentration.

Low molecular weight diols are even more hydrophilic than their monomeric analogs and have correspondingly lower distribution ratios. Table 1-1 summarizes available distribution data for these compounds. Near ambient temperature (20 - 30°C) no values above 0.5 are reported for ethylene glycol. No values greater than 1 are reported for any of the two- to four-carbon diols.

Because of the very low distribution ratios, extraction with any of the solvents listed in Table 1-1 does not seem a likely candidate for an economical separation of diols. Extraction can be made more favorable, however, by incorporating into the organic phase an extracting agent that will complex with the solute of interest. The extractant selected should form a reversible chemical complex, typically with a bond energy of 10 - 50 kJ/mol (King, 1987), that can be easily regenerated. These substances, known as solvatropes, increase the solubility in the organic solvent by forming molecular complexes (Korenman, 1973a).

In previous work in our research group dealing with complexing extractants, Tamada et al. (Tamada, Kertes, and King, 1990; Tamada and King, 1990a, 1990b) studied extraction of carboxylic acids with amine extractants, and Arenson et al. (Arenson, 1989; Arenson, Kertes, and King, 1988) studied extraction of alcohols with *m*-cresol. They measured

Table 1-1. Distribution ratios for low molecular weight glycols between water and various solvents.

Solvent	T°C	Solubility of solvent in H$_2$O [a] (g/100g)	Distribution ratio, D (Concentration basis)	Ref.
1,2-ethanediol				
n-butanol	20	7.8 [b]	0.119 [e]	(7)
n-butanol	27	7.2 [b]	0.334 [e]	(10)
n-butanol	40	6.6 [b]	0.318 [e]	(7)
n-amyl alcohol	20	2.7 [22][c]	0.095 [e]	(4)
n-hexanol	20	0.58 [b]	0.226 [e]	(4)
n-octanol	**	0.059 [25][b]	0.012 [e]	(5)
furfural	25	8.3 [20][b]	0.365 [e]	(3)
methyl ethyl ketone	30	27.5 [d]	0.042 [e]	(10)
acrylonitrile	25	7.35 [20][d]	0.025 [e]	(8)
ethyl acetate	20	8.5 [15][c]	0.015	(6)
butyl acetate	20	0.78 [25][b]	0.006	(6)
diethylether	**	7.5 [20][c]	0.005	(5)
1,2-propanediol				
m-cresol (9.5M in m-xylene)	25	0.5 [c]	0.7	(1)
m-cresol (9.5M in chloroform)	25	0.5 [c]	0.7	(1)
diethylether	**	7.5 [20][c]	0.018	(5)
1,3-propanediol				
m-cresol (9.5M in m-xylene)	25	0.5 [c]	0.7	(1)
ethyl acetate	20	8.5 [15][c]	0.028	(6)
butyl acetate	20	0.78 [25][b]	0.014	(6)
diethylether	**	7.5 [20][c]	0.010	(5)
1,4-butanediol				
ethyl acetate	20	8.5 [15][b]	0.065	(6)
butyl acetate	20	0.78 [25][a]	0.035	(6)
diethylether	**	7.5 [20][c]	0.019	(5)

Table 1-1. (Continued)

Solvent	T°C	Solubility of solvent in H_2O [a] (g/100g)	Distribution ratio, D (Concentration basis)	Ref.
		2,3-butanediol		
n-butanol	26	7.2 [b]	0.484 [e]	(9)
n-butanol	50	6.4 [b]	0.723 [e]	(9)
n-octanol	18	0.059 [25][b]	0.12	(2)
butyl acetate	26	0.78 [25][b]	0.020	(9)
diethylether	**	7.5 [20][c]	0.029	(5)
2,3-butylene glycol diacetate	26	3.62	0.14 [f]	(9)
2,3-butylene glycol diacetate	75	3.7	0.58 [f]	(9)
methyl vinyl carbinol acetate	26	1.32	0.20 [g]	(9)
methyl vinyl carbinol acetate	50	0.8	0.30 [g]	(9)
methyl vinyl carbinol acetate	75	2.0	0.21 [g]	(9)

Notes:

** No temperature was cited. Temperature is believed to be close to 20°C.

[a] Values in parentheses are temperatures at which solubilities were measured, if different from listed temperature.

[b] Flick, 1985.

[c] Perry and Green, 1984.

[d] Windholz, 1983.

[e] The specific gravity (at 20 -25°C) was used to convert D from a mass basis to the molar concentration basis shown here.

[f] The density of 1,3-butanediol diacetate (d ^{20} = 1.028 (Aldrich, 1988)) was used to convert D to a molar concentration basis.

[g] The density of the extract layer at 75°C and the density of water at the listed temperature were used to convert D to a molar concentration basis.

Table 1-1. (Continued)

References

(1) Arenson, 1989.

(2) Collander, 1951.

(3) Conway and Norton, 1951.

(4) Laddha and Smith, 1948.

(5) Leo, Hansch, and Elkins, 1971.

(6) Levina and Zhelezynak, 1975.

(7) Matsumoto and Sone, 1956.

(8) Nikurashina, Gei and Kharitonova, 1976.

(9) Othmer et al, 1945. (Calculated from tie line data for lowest solute concentration reported.)

(10) Rao and Rao, 1957.

distribution ratios significantly higher with the extractant present than for a variety of common solvents.

This study investigates separation of glycols from aqueous solution by reversible chemical complexation. Propylene glycol (1,2-propanediol), in particular, was chosen for experimental study because it has a strong existing market, and can be produced by either chemical or microbial conversion. Trimethylene glycol (1,3-propanediol), which can also be produced by either method, was studied in selected experiments to provide a comparison between the two isomers.

The commercial importance of propylene glycol is illustrated by the 1985 U.S. market value of $220 million - the tenth highest value of all oxychemicals (Busche, 1985). In 1987, the annual U.S. production capacity was 820 million pounds (*Chemical Marketing Reporter*, February 9, 1987).

The market for propylene glycol includes food and pharmaceutical applications, for example as a solvent for flavors, vitamins and preservatives (*Chemical Marketing Reporter*, February 9, 1987). The low toxicity of propylene glycol makes it the preferred antifreeze in breweries and dairies (Brown et al., 1980). Propylene glycol is also used in unsaturated polyester resins. By virtue of strength and light weight, these resins find application in fiberglass reinforced products such as appliances, trucks and passenger cars (*Chemical Marketing Reporter*, February 9, 1987).

Currently racemic propylene glycol is produced by hydrolysis of propylene oxide, derived from petroleum via propylene. At a mole ratio of water to propylene oxide of 15 (about 20 weight percent) propylene glycol can be produced at a yield of 85% with about 13% dipropylene glycol and 1.5% higher adducts produced as byproducts (Brown et al., 1980). The water is removed in multieffect evaporators, typically triple effect (Reiche and Heckman, 1976), and the product purified by vacuum distillation.

Optically active R-propylene glycol can be produced by fermentation at product

concentrations of about 1%. Details of this fermentation, using glucose and other sugars as the substrate for the bacterium *Clostridium thermosaccharolyticum*, have been investigated by several researchers (Cameron and Cooney, 1986; Sánchez-Riera, Cameron and Cooney, 1987; Simon et al., 1987; Cameron, Tong, and Cockrem, 1990). The byproducts included acetate, lactate and ethanol. R-propylene glycol was recovered through a multistep separation including an ether extraction step, with yields from 4 - 8 g/l. In the most recent work, Cameron, Tong, and Cockrem (1990) investigated the potential for substituting ion exchange for the extraction step.

Optically active S-propylene glycol can be produced by reduction of S-lactic acid, while yeast catalyzed reduction of hydroxyacetone (acetol) yields R-propylene glycol (Cameron, Tong, and Cockrem, 1990). S-propylene glycol isomers are available in research quantities from the Aldrich Chemical Company.

Trimethylene glycol (1,3-propanediol) is currently produced chemically from acrolein, but can also be produced by fermentation of glycerol. It is used as an intermediate in organic synthesis and as a chain extender in polymers (Cameron, Tong, and Cockrem, 1990).

2 SELECTION OF COMPLEXING AGENT

The literature was reviewed to identify potential complexing agents. Both phenols and borates have been shown to complex with glycols.

2.1 Phenol-glycol complexes

Ethylene glycol and diethylene glycol form 1:1 and 1:2 phenol:glycol complexes with xylenols, naphthols and halogenophenols in aqueous solution. 1:1 complexes also form with other water-miscible substances like glycerol and acetone. The complexes exhibit hydrotropic effects, increasing the solubility of the phenolic compounds in water. The reported complexes are almost non-extractable into nonpolar solvents, such as benzene (Korenman, 1972, 1973b, 1974a, 1974b).

Arenson (1989) measured distribution ratios for the propanediols between water and *m*-cresol in various organic diluents. As shown in Figure 2-1, distribution ratios for 1,2- and 1,3-propanediol were approximately equal for extraction into a given concentration of *m*-cresol in *m*-xylene. Higher distribution ratios were obtained for 1,2-propanediol when chloroform was the diluent. When the ethanol stabilizer was washed from the chloroform prior to extraction, even larger distribution ratios were observed. Arenson attributed this to competition of the diol with ethanol for interactions with *m*-cresol. Even at extractant:diol ratios approaching 20, however, the distribution ratios did not exceed 1 for any of the diluents studied.

2.2 Borate-glycol complexes

There are extensive data to support complexation of glycols with borates. In fact, this
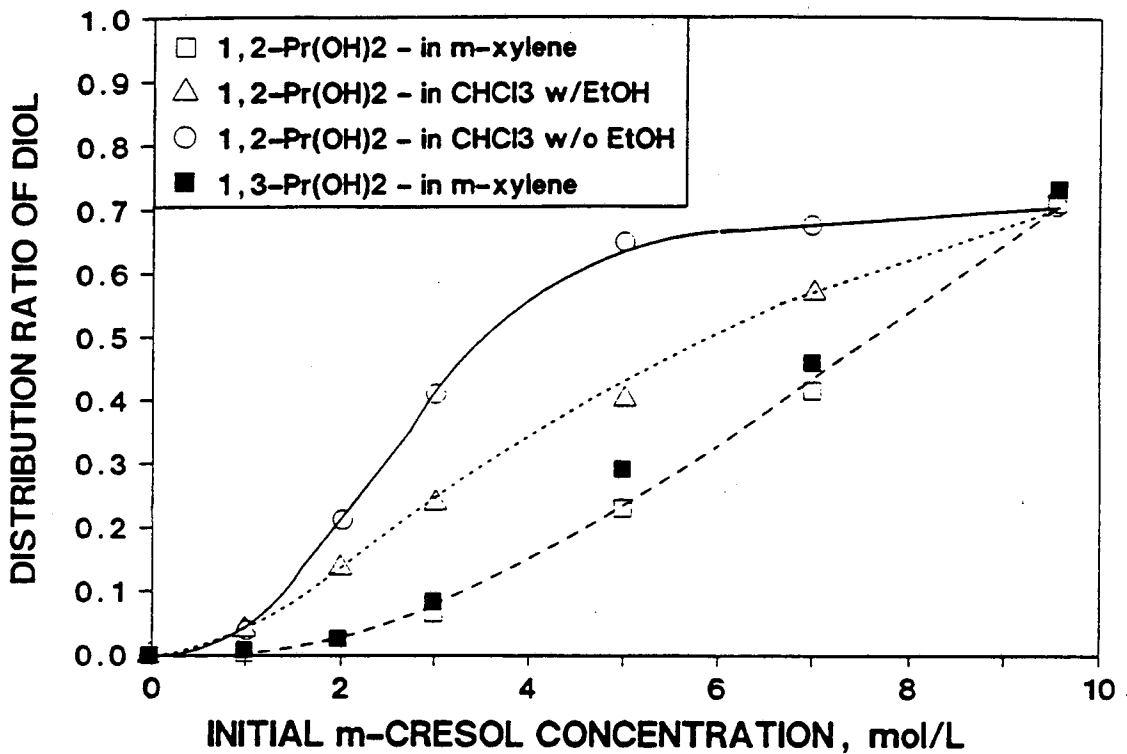
Source: Arenson, 1989. (Two typographical errors have been corrected.)

Figure 2-1. Distribution ratios, as a function of extractant concentration, for 0.5 mol/l 1,2-propanediol and 1,3-propanediol extracted by *m*-cresol in *m*-xylene and in chloroform (CHCl3), both with and without ethanol (EtOH) stabilizers, at 25°C.

phenomenon has been known for more than 100 years, with several applications in analytical chemistry. Extraction of these complexes into an organic solvent, however, remains essentially unexplored. In this study, information on aqueous borate:glycol complex formation is correlated with data for the extraction of the complex into an interactive diluent (2-ethyl-1-hexanol).

The literature relevant to this complexation process is first reviewed to provide the necessary background and context for the proposed separation.

2.2.1 Structure and chemistry

The structure and chemistry of the borate-diol complexes have been studied by numerous researchers using varied techniques (Weser, 1967; Zittle, 1951). Mechanistic and stereochemical data have been obtained through chromatography, electrophoresis, polarimetry, and spectroscopy, with B^{11} NMR spectroscopy recently gaining popularity (Dawber and Green, 1986; Dawber et al., 1988; Oertel, 1972; Onak et al., 1959; van Duin et al., 1984, 1985; Weser, 1967). Significant results of these studies follow.

Diols with cis-hydroxyl groups separated by no more than one carbon rapidly and reversibly form ring structures with boric acid or borate in aqueous solution (Figures 2-2 and 2-3). Stereochemical considerations favor formation of boric esters with cis-1,3-diols and formation of anionic borate complexes with cis-1,2-diols. The 1,3-diols form an unstrained planar six-membered ring with the trigonal boric acid and a nonplanar ring in puckered chair form with the tetrahedral borate anion. The 1,2-diols, however, form only an unstrained five-membered ring with the borate anion. When excess diol is present, 1:2 complexes may form. Since significant borate formation does not occur below the pK_a of the acid (9.2 for boric acid), the anionic complex is formed primarily in basic solution (Böeseken, 1949; Henderson et al., 1973; Weser, 1967).

Raman, C^{13}, and B^{11} NMR spectroscopy have confirmed the formation of anionic
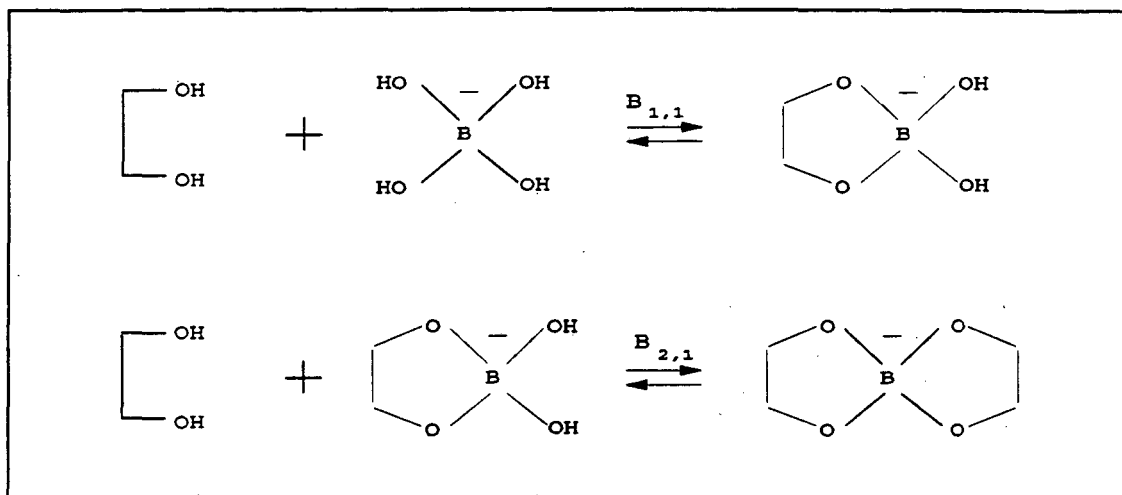
Figure 2-2. 1,2-Diols form 5-membered rings with borate anions in aqueous solution.
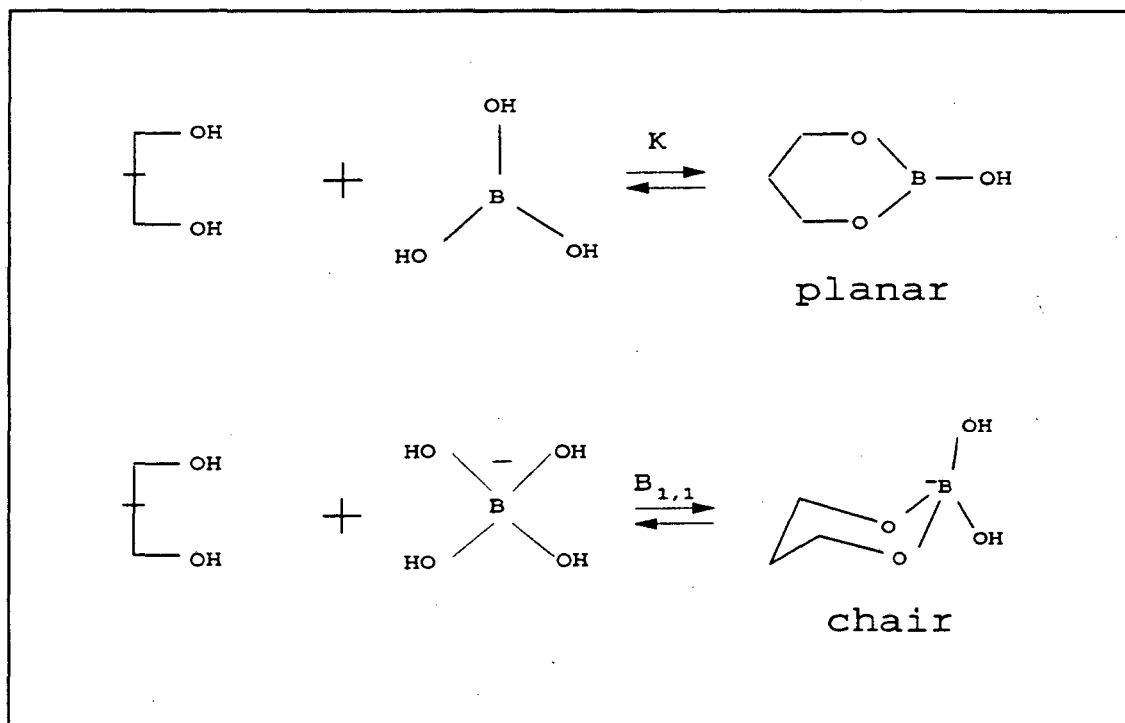
Figure 2-3. 1,3-diols from both anionic and neutral 6-membered rings with boric acid/borate in aqueous solution.

complexes for both 1,2- and 1,3-diols (Dawber and Green, 1986; Dawber et al., 1988; Henderson et al., 1973; Oertel, 1972; van Duin et al., 1984, 1985). Further, Oertel's Raman data give direct evidence for the chair conformation for the 1,3-diol-borate complex. Extraction data, on the other hand, confirm the existence of the neutral complex with 1,3-diols (Paál, 1980a). Van Duin et al. (1984) have established a "charge rule" for determining pH stability of the different complexes. The rule states, in essence, that neutral complexes with diols form at low pH and anionic complexes at high pH. α-Hydroxy- and di-carboxylic acids can also complex with borates. However, the optimal pH for complex formation with α-hydroxycarboxylic acids and dicarboxylic acids depends on the pK_a of the acid.

2.2.2 Measurement

Potentiometry has, until recently, been the most common method for determining stoichiometry and stability of the complexes. The model developed by Antikainen (1954) has been widely accepted for studying the anionic complexes in aqueous solution. The stability constant, β_n, measured is the equilibrium constant for formation of the anionic complex, AD_n^-, from the borate anion, A^-, and the neutral diol, D:

$$A^- + nD \rightleftharpoons AD_n^-$$ (2-1)

$$\beta_n = \frac{[AD_n^-]}{[A^-][D]^n}$$ (2-2)

n represents the stoichiometry of the complex. β_n can be obtained from the equilibrium constants for complex formation from the neutral acid and for ionization of the acid,

$$\beta_n = \frac{K_n}{K_a}$$ (2-3)

with K_n and K_a represented by the following relationships:

$$HA + nD \rightleftharpoons H^+ + AD_n^- \qquad (2-4)$$
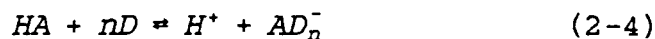
$$K_n = \frac{[H^+] [AD_n^-]}{[HA] [D]^n} \qquad (2-5)$$

$$K_a = \frac{[H^+] [A^-]}{[HA]} \qquad (2-6)$$

Where: [HA] = concentration of neutral acid

The formation of the complex between borate and diols results in a lowering of the observed pK_a of the boric acid. The apparent ionization constant, K_a^*, can be expressed as

$$K_a^* = \frac{[H^+]\left([AD_n^-] + [A^-]\right)}{[HA]} \qquad (2-7)$$

Equation 2-7 is valid when the diol is a considerably weaker acid than the boric acid. (See Sienkiewicz and Roberts, 1980, for extension of the model to the case where dissociation of the diol is significant.) Antikainen correlated this change in apparent ionization constant for boric acid, as a function of diol concentration, to the strength of the anionic complex. The relationship in general form is:

$$K_a^* = K_n [D]^n + K_a \qquad (2-8)$$

or in logarithmic form:

$$p(K_a^* - K_a) = pK_n - nLog [D] \qquad (2-9)$$

Where: n = Average number of ligands bound per acid
[D] = Diol concentration (present in excess)
p( ) = -log( )

When diol concentration is much greater than the boric acid concentration, the amount of diol

complexed is small and [D] can be replaced by C_D, the total diol concentration. Further, when diol is present in excess, Antikainen has shown that the apparent ionization constant is independent of boric acid concentration. He verified this for initial boric acid concentrations from 0.005 M to 0.1 M . Dilute solutions of boric acid are required to minimize polyborate formation, which is not included in the model. When plotted as a function of log diol concentration, this relationship gives a straight line with slope, n, and intercept, pK_n. These can be used to calculate β_n as described above.

The Antikainen method, unlike other potentiometric methods, does not make any assumptions about the stoichiometry of the complexes. Other techniques assume certain equilibria, generally similar to those above, and calculate the equilibrium constants numerically rather than graphically. Further, Weser (1967) cites the differential potentiometric method used by Antikainen as eliminating many inconsistencies of other pH depression methods.

In Table 2-1, selected results for stability constants are compared for the different methods. For all entries in Table 2-1, $\beta_{1,1}$ is defined by Equation 2-2. For the two entries from Dawber and Matusin (1982), the Antikainen model was used and n equaled 0.67 and 1.25 for 1,2-ethanediol and glycerol, respectively. For all other entries, n was set equal to 1. $\beta_{1,2}$ was also calculated from Equation 2-2, with n equal to 2, for most entries. In some of the NMR studies, where the complexed species could be measured directly, however, $\beta_{1,2}$ was calculated according to:

$$\beta_{1,2} = \frac{[AD_2]}{[AD^-]\,[D]}$$

The pH depression upon complex formation, as described by Equation 2-7, is the basis of the pH and Emf methods listed in Table 2-1. For both 1,2-ethanediol and 1,2-propanediol, stability constants obtained by Paál (1975, 1976, 1977) and Roy et al. (Roy, Laferriere, and Edwards, 1957) are very similar, with deviations most likely attributable to effects such as differing ionic strengths. (See Paál, 1976, for a discussion of effects of ionic

Table 2-1. Stability constants for 1:1 and 1:2 borate:diol complexes.
(a) 1,2-ethanediol

T°C	Stability Constant		Method	Reference
	$\beta_{1,1}$ $(mol/l)^{-1}$	$\beta_{1,2}$ $(mol/l)^{-2}$		

				1,2-ethanediol
0	3.29	1.38	pH (1)	Conner and Bulgrin, 1967
13	2.9	1.19	pH (1)	Conner and Bulgrin, 1967
25	2.15	1.15	pH (1)	Conner and Bulgrin, 1967
35	1.87	0.893	pH (1)	Conner and Bulgrin, 1967
20	1.48 (n=0.67)		pH (2)	Dawber and Matusin, 1982.
25	1.78	0.12	pH (3)	Paál and Barcza, 1975.
25	1.86	0.18	Emf (3)	Paál, 1976.
25	1.82	0.19	Emf (3)	Paál, 1976.
25	1.70	0.14	Emf (3)	Paál, 1976.
25	1.83	0.17	pH (3)	Paál, 1977.
25	1.85	0.1	pH (4)	Roy, Laferriere, and Edwards, 1957.
30	1.80	0.65	Raman (5)	Oertel, 1952.
--	0.74	0.29 [a]	^{11}B-NMR (6)	Dawber and Green, 1986.
--	3.0	0.4 [a]	^{11}B-NMR (7)	Dawber et al., 1988.
33	1.00	0.1	^{11}B-NMR (6)	Henderson et al., 1973.
20	1	0.16 [a]	^{11}B-NMR (6)	van Duin et al., 1984.
--	1.3	--	Ion exchange (8)	Sargent and Rieman, 1956.

Table 2-1. (Continued) (b) propane di-and triols.

T°C	Stability Constant		Method	Reference
	$\beta_{1,1}$ $(mol/l)^{-1}$	$\beta_{1,2}$ $(mol/l)^{-2}$		
			1,2-propanediol	
0	6.35	8.29	pH (1)	Conner and Bulgrin, 1967
13	4.35	6.06	pH (1)	Conner and Bulgrin, 1967
25	4.05	3.85	pH (1)	Conner and Bulgrin, 1967
35	3.40	2.36	pH (1)	Conner and Bulgrin, 1967
25	2.88	1.26	Emf (3)	Paál, 1976.
25	3.24	1.55	Emf (3)	Paál, 1976.
25	3.17	1.48	pH (3)	Paál, 1977.
25	3.1	1.6	pH (4)	Roy, Laferriere, and Edwards, 1957.
--	2.2	0.55 [a]	^{11}B-NMR (6)	Dawber and Green, 1986.
--	4.7	0.8 [a]	^{11}B-NMR (7)	Dawber et al., 1988.
33	1.8	1.5	^{11}B-NMR (6)	Henderson et al., 1973.
--	2.12	--	Ion exchange (8)	Sargent and Rieman, 1956.
			1,3-propanediol	
0	2.81	0.20	pH (1)	Conner and Bulgrin, 1967.
13	1.77	0.12	pH (1)	Conner and Bulgrin, 1967.
25	1.27	0.11	pH (1)	Conner and Bulgrin, 1967.
35	0.95	0.06	pH (1)	Conner and Bulgrin, 1967.
25	1.15	--	pH (4)	Lorand and Edwards, 1959.
--	1.10	0.08 [a]	^{11}B-NMR (6)	Dawber and Green, 1986.
--	2.90	--	^{11}B-NMR (7)	Dawber et al., 1988.
33	1.2	0.05	^{11}B-NMR (6)	Henderson et al., 1973.
			glycerol (1,2,3-propanetriol)	
20	67.6 (n=1.25)		pH (2)	Dawber and Matusin, 1982.
25	23.6	41.69	pH (3)	Paál, 1977.
--	6.7 [b]	1.3 [a,b]	^{11}B-NMR (6)	Dawber and Green, 1986.
--	37 [b]	3.9 [a,b]	^{11}B-NMR (7)	Dawber et al., 1988.
25	25 [b]	3 [b]	^{11}B-NMR (6)	van Duin et al., 1984.
--	14.8	--	Ion exchange (8)	Sargent and Rieman, 1956.

Table 2-1. (Continued) (c) butanediols.

T°C	Stability Constant		Method	Reference
	$\beta_{1,1}$ $(\text{mol}/l)^{-1}$	$\beta_{1,2}$ $(\text{mol}/l)^{-2}$		

1,4-butanediol

T°C	$\beta_{1,1}$	$\beta_{1,2}$	Method	Reference
33	no complex		^{11}B-NMR (6)	Henderson et al., 1973.

1,3-butanediol

T°C	$\beta_{1,1}$	$\beta_{1,2}$	Method	Reference
25	1.38	--	pH (3)	Paál, 1980a.
33	>1.2	--	^{11}B-NMR (6)	Henderson et al., 1973.

2,3-butanediol (mixed isomers)

T°C	$\beta_{1,1}$	$\beta_{1,2}$	Method	Reference
25	3.45	4.85	pH (4)	Roy, Laferriere, and Edwards, 1957.

d,l-2,3-butanediol

T°C	$\beta_{1,1}$	$\beta_{1,2}$	Method	Reference
--	8.41	--	Ion exchange (8)	Sargent and Rieman, 1956.

l-2,3-butanediol

T°C	$\beta_{1,1}$	$\beta_{1,2}$	Method	Reference
0	62	399	pH (1)	Conner and Bulgrin, 1967.
13	43	281	pH (1)	Conner and Bulgrin, 1967.
25	37	164	pH (1)	Conner and Bulgrin, 1967.
35	25	125	pH (1)	Conner and Bulgrin, 1967.

meso-2,3-butanediol

T°C	$\beta_{1,1}$	$\beta_{1,2}$	Method	Reference
0	5.1	12.8	pH (1)	Conner and Bulgrin, 1967.
13	3.2	7.6	pH (1)	Conner and Bulgrin, 1967.
25	2.7	4.6	pH (1)	Conner and Bulgrin, 1967.
35	2.3	2.7	pH (1)	Conner and Bulgrin, 1967.
--	1.18	--	Ion exchange (8)	Sargent and Rieman, 1956.

Table 2-1. (Continued)

Notes

[a] $\beta_{1,2}$ calculated for formation of 1,2 complex from 1,1 complex.

[b] Values shown are for complexes across adjacent carbons only. Values for complexes across alternate carbons are: $\beta_{1,1} = 3.5$ (Dawber et al. 1988); $\beta_{1,1} = 3.7$, $\beta_{1,2} = 0.05$ (van Duin et al., 1984).

Calculation methods

Unless otherwise stated, all methods used a model assuming complexation with the anionic borate species only.

(1) Calculated from pH depression data with pH adjusted for "medium" effect.

(2) Antikainen graphical method using pH depression data.

(3) Calculated from pH depression or potentiometric titration data using gradual two-sided limitation of the constants for a model including all possible species (i.e., both anionic and neutral species).

(4) Calculated from pH depression data.

(5) Graphical method.

(6) Calculated from linear integration of peak areas for each species in Equation 2-2.

(7) Relative peak areas for each species adjusted for nonlinearity based on calibration with sorbitol.

(8) Calculated by using plate theory of ion exchange chromatography.

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strength.) This suggests that Paál's (1975, 1976) model using a two-sided limitation of the constants, which allows for formation of neutral as well as anionic complexes, and the model of Roy, Laferriere, and Edwards (1957) are equivalent for the 1,2-diols. The latter model uses the same assumptions as Antikainen's model. Conner and Bulgrin's data (1967), on the other hand, follow the same trends but differ significantly because of a correction incorporated for "medium effects;" this "medium" effect has since been refuted by Paál (1980b). Paál described the Lewis acid:base adducts that can be formed with polar solvents and thereby give the appearance of a "medium" effect. In some cases, the strength of the adducts approaches that of the weakest cyclic borate complexes with *cis*-diols (e.g., β_n =0.89 for dioxane).

The pH depression methods described above are not suitable for determining stabilities of 1,3-diol-borate complexes because they do not account for formation of both neutral and anionic complexes (Paál, 1980a). Spectroscopic techniques and polarimetric techniques at constant pH enable direct measurement of the complexing species and can therefore be used to measure both types of complexes. Paál (1980a) has also used potentiometry, with the equilibrium for the boric acid complex included, and extraction to measure the strength of complexes with 1,3-diols. The stability constant measured potentiometrically by Paál (1980a) for the anionic borate-1,3-butanediol complex is shown in Table 2-1c.

Stability constants for anionic borate complexes determined spectroscopically are also shown in Table 2-1. Values obtained by different researchers using ^{11}B-NMR agree fairly well with each other, but not with the values obtained by pH methods. The primary exception to this is the Dawber et al. (1988) data which adjusted the relative peak areas for nonlinearity based on a calibration with sorbitol. The corrected data are very different from other results in Table 2-1, except for glycerol. This suggests that the correction factor based on sorbitol may not be suitable for the low molecular weight diols that form very weak complexes with borate.

Despite the many discrepancies among the data in Table 2-1, the table does illustrate

some of the general trends for complex strength. In summary, as chain length of the diol increases, complexation becomes stronger, with inner CHOH groups favored over terminal CH$_2$OH groups. This phenomenon has been postulated to be related to the reduced freedom of rotation of the inner hydroxyl groups (Conner and Bulgrin, 1967; Dawber et al., 1988). Large differences in strength are also apparent for isomers of the same compound. For 2,3-butanediol, for example, the stability constant is much smaller for the *meso* form than the *levo*; Conner and Bulgrin attribute this to steric effects.

2.2.3 Separations using borate-diol complexes

These variations in the strengths of the stability constants for the complexes of different diols enable selective separation among diols including some isomers and stereoisomers. Strong anion exchangers in the borate form have been used to separate mixtures of glycols (Sargent and Rieman, 1956) and of mono-, di-, and trisaccharides (Khym and Zill, 1952; Zill, Khym, and Cheniae, 1953; Walborg and Lantz, 1968; Walborg, Ray and Öhrberg, 1969). Mixtures of ribo-, deoxyribo-, and aribonucleosides, on the other hand, have been separated on strong cation exchangers by elution with ammonium borate (Moran and Werkheiser, 1978; Pal, 1978). Anionic borate complexes of the saccharides and glycols were separated by anion exchange; the nucleosides, however, were separated by anion exclusion chromatography, wherein the anionic complexes are excluded from the column and the strongest complexes elute first.

Derivatives of boric acid have also been incorporated into affinity chromatography packings. Supports for the boronic acid ligands include agarose and sepharose adsorbents (Akparov and Stepanov, 1978; Bouriotis, Galpin, and Dean, 1981; Myöhänen, Bouriotis, and Dean, 1981), polyacrylamide beads (Maestas et al., 1980), porous polystyrene beads (Elliger, Chan, and Stanley, 1975), cellulose derivatives (Weith, Wiebers, and Gilham, 1970), and silica (Glad et al., 1980). Currently available commercial products include:

-Biorad "Affi-Gel® 601, Boronic Acid Gel for Cis-Diol Affinity Chromatography" (polyacrylamide)

-Pierce "Selectispher-10™ Boronate HPLAC Columns" (silica)

-Pierce "GLYCO•GEL™ B," Boronate affinity gel (agarose)

-Pierce "Immobilized Boronic Acid" on polyacrylamide

These products contain immobilized boronic acid ligands such as aminophenyl boronic acid. The substrates separated on these packings include ribonucleotides, ribonucleosides, sugars, catecholamines, enzymes, and glycoproteins. Regeneration is typically accomplished by adjusting the pH, i.e., creating acid conditions (Bio-Rad, 1986; Pierce, 1986, 1988).

Chromatographic techniques are most commonly used in chemical analyses or preparation of small quantities of high value products. To separate larger volume, commodity chemicals like propylene glycol, however, a process more suited to large scale industrial separations is desired.

Liquid-liquid extraction represents one possibility. Previous work has used this complexation phenomenon to extract boric acid from aqueous solutions using high molecular weight diols (e.g., 2-ethyl-1,3-hexanediol in chloroform) (Dyrssen, Uppström, and Zangen, 1969). 1,3-Diols extracted boric acid as the neutral complex from acid solution, while 1,2 - diols extracted borate in an ion-pair from alkaline solution. In Paál's study (1980a), a low molecular weight diol (1,3-butanediol) reduced the distribution of boric acid between n-butanol and water.

By using a boronic acid ligand with a high affinity for organic solvents, it should be possible to extract diol into the organic phase. Phenylboronic acid, 3-aminophenylboronic acid, 3-nitrophenylboronic acid and hexyl boronic acid, for example, are all slightly soluble in cold water, but soluble in polar organic solvents, such as ethers or alcohols (Weast, 1980). Several authors have studied complex formation in the organic phase between diols and substituted boronic acids, such as these (Babcock and Pizer, 1980; Barker et al., 1973; Lorand and Edwards, 1959). Substituting organic ligands on the boron eliminates the capacity for 1:2

complexes and polyborate formation, thereby making it easier to study the complexation reactions.

Another effect of changing the ligand on the boric acid is to change the pK_a of the acid, and, consequently, the pH at which the anionic complex begins to form. Alkylboronic acids, like methylboronic acid, are more basic than boric acid, whereas boronic acids with electron withdrawing groups, such as 3-nitrophenylboronic acid (NPBA), are more acidic (Babcock and Pizer, 1980; Bettman, Branch, and Yabroff, 1934; Branch, Yabroff, and Bettman, 1934; Yabroff, Branch, and Bettman, 1934; Torssell, 1964). In a study on monosaccharides, Barker et al. (1973) found that NPBA-diol complex formation began below pH 6 with 100% complexation observed near pH 7, which is close to the pK_a of the acid (7.3). Stability constants for anionic complexes of alkylboronic acids with diols are of the same order of magnitude as, and follow similar trends to, the stability constants for complex formation with borate. (For comparative studies of complexation of diols with alkyl boronic acids, see Lorand and Edwards, 1959 (phenylboronate and borate) and Babcock and Pizer, 1980 (borate, phenylboronate, 3-nitrophenylboronate, and methyl boronate).)

Shinbo et al. (1986) used phenylboronic acid in a liquid membrane to concentrate aqueous sugar (glucose, fructose, etc.) solutions. A schematic of that system is shown in Figure 2-4. Trioctylmethylammonium chloride was used to provide a counterion for the anionic boronic acid-diol complex in the dichloroethane membrane. After complexation extracted the sugar from alkaline solution, the complex diffused across the membrane to the acid layer where the sugar was released into acid solution, while the phenylboronic acid was regenerated. This study provides good evidence for complex formation in organic solution.

2.3 Selection of extracting system

For this study, 3-nitrophenylboronic acid (NPBA) was selected as the complexing agent. NPBA is only slightly soluble in cold water, but soluble in alcohols and ethers. It prefers water, however, to nonpolar solvents like benzene (D = 0.08, Leo, Hansch, and Elkins,

Aqueous, pH = 10
0.1M Na2CO3 - NaHCO3
5 x 10-4 M saccharide

Dichloroethane
0.001M PhB
0.001M TOMA+Cl-

Aqueous, pH=3
0.1M glycine - HCl buffer
5 x 10-4 M saccharide

saccharide

① PhB + OH- ⇌ PhB-   ③ PhB- + S ⇌ PhBS-
④   ②
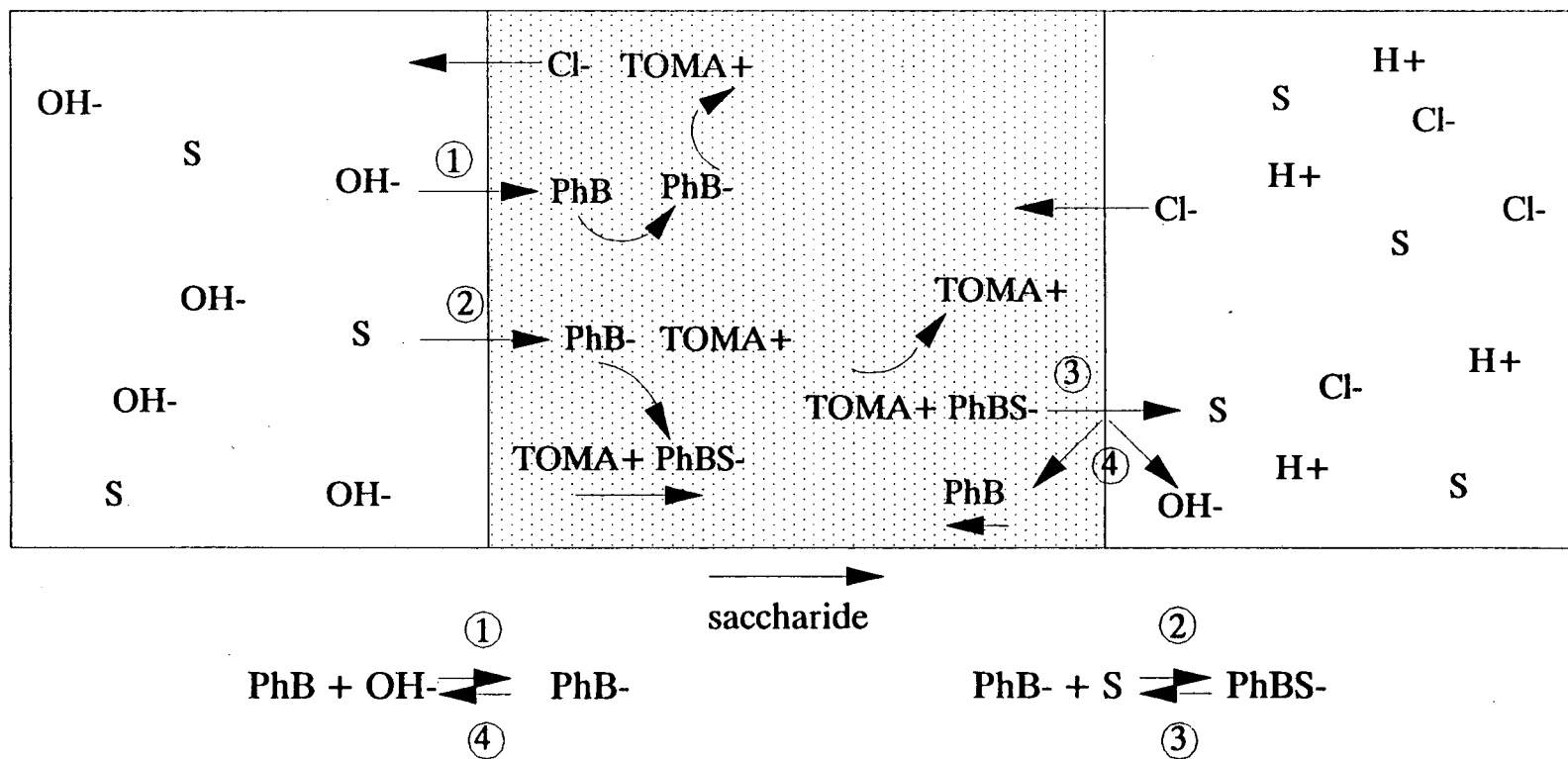
Figure 2-4. Transport of saccharides (S) against a concentration gradient by complexation with phenylboronic acid (PhB) in a bulk dichloroethane membrane also containing trioctylmethylammonium (TOMA+) chloride. Schematic of system employed by Shinbo et al., 1986.

1971). Since complex formation with NPBA occurs at pH close to neutral, regeneration by pH swing would be expected to use a minimum amount of chemicals (i.e., pH adjustment from 7 to 4). A quaternary ammonium ion, such as Aliquat 336 (Aldrich), can provide the counterion for the anionic complex formed with propylene glycol. Combining these in a diluent creates a mixed ionic extractant. Mixed ionic extractants have been used previously for extraction of inorganic acids and salts from aqueous solution. (Grinstead et al., 1969; Lynn and Charlesworth, 1972; Eyal and Baniel, 1982).

The diluent for this system must be able to solvate NPBA, Aliquat 336 and the complex. A low water solubility is also desirable. 2-Ethyl-1-hexanol, a common industrial solvent, meets these conditions.

Other considerations relate to the specific feed stream being processed. If fermentation broths are to be extracted *in situ*, toxicity may be a problem, because NPBA exhibits some bacteriostatic effects (Bean and Johnson, 1932). Specific effects of arylboronic acids on fermentation rates were investigated by Torssell (1957). Immobilization in a membrane or on a solid support is a potential method for addressing that issue.

Another possible problem is interference from other components of the solution. As mentioned earlier, byproducts and feed components in propylene glycol fermentation include acetate, lactate, ethanol and glucose. Acetate and ethanol do not have two hydroxyl groups available for complexing. Lactate is the salt form of an α-hydroxy carboxylic acid and forms a very strong complex with NPBA (Babcock and Pizer, 1980). Certain configurations of glucose also form strong complexes, but they represent a small percentage of most glucose solutions. Only the planar α-D-glucofuranose and the aldehydo-D-glucose have the coplanar *cis*-hydroxyl groups needed for borate complexation; together these make up less than ten percent of equilibrium solutions (Böeseken, 1949; Davis and Mott, 1980). Further, Davis and Mott found no evidence that the glucose equilibria shift in the presence of borate. Variations in the strength of complexes for each of the compounds in the fermentation broth could perhaps be used to develop a processing scheme that would enable a selective separation.

3 EXPERIMENTAL

3.1 Goals

The purpose of this research was to explore the viability of 3-nitrophenylboronic acid (NPBA) as a complexing agent for recovery of glycols from aqueous solution. Experiments were chosen that would provide data for evaluating such a separation:

- stability constant for complex formation

- effect of temperature on stability constant

- distribution of 1,2-propanediol, NPBA, and water between aqueous and organic phases,

- effect of pH on extractant ionization.

Aqueous measurements, including stability constants and their variation with temperature, are an analytically straightforward means of obtaining comparative data for different glycols. Since almost all previous work has been completed in aqueous systems, aqueous measurements facilitate comparison to literature values. Moreover, the stability constants can be used to calculate the free energy of formation of the NPBA-glycol complex, thereby providing a measure of complex reversibility. Variation in stability constant as a function of temperature can be used to estimate the enthalpy of bond formation. In systems with large bond enthalpies, the complex can often be regenerated by a change in temperature.

Data obtained by extracting the glycol into an organic phase provide direct measurements for evaluating process feasibility. Distribution ratios provide information on the selectivity and capacity of the extractant, as well as expected losses of extractant to the aqueous phase; losses are expected to be well below the aqueous solubilities. Extractant losses are also affected by pH of the contacting solution, since NPBA is more soluble in basic than in neutral aqueous solutions. pH also influences the ionization of NPBA; ionization is critical

to complex formation, since 1,2-diols complex with NPBA only in its anionic form. Finally, the pH dependence of ionization affords a means of estimating the expected amount of chemicals required to regenerate the process by pH swing.

If equilibrium data from extraction experiments can be correlated with aqueous stability constants, currently available data for aqueous systems can be used to extend the the results for a few glycols in a two-phase system to many.

3.2 Materials

The chemicals listed in Table 3-1 were used as received. Compressed gases (air, hydrogen, helium, and nitrogen) were obtained in cylinders from the University of California, Berkeley, (UCB) College of Chemistry. Aqueous solutions were prepared with 18-megohm distilled deionized water from a Millipore Milli-Q water purification system. Standardized solutions of 0.1 N HCl and 0.1 N NaOH were also obtained from the College. Sulfuric acid was diluted to the desired concentration and filtered with Millipore type-HA 0.45 micron filters; concentration was checked by titration with 0.1 N NaOH. Solids and viscous solutions were weighed on a Mettler balance, Model H51AR. Less viscid liquids were pipetted with calibrated glass pipettes or an Eppendorf automatic pipette (0.200 -1.000 ml).

3.3 Purity of materials

Additional tests were completed to verify formula weights of NPBA and Aliquat 336, since the supplier did not provide purity information.

3.3.1 Aliquat 336

Aliquat 336 is a quaternary amine in the chloride form with a mixture of C_8 and C_{10} chains. The manufacturer indicates that C_8 predominates and reports the formula weight as 404.17. Samples of the amine were analyzed for nitrogen and chloride, as described below, yielding calculated formula weights of 490 and 535, respectively. This discrepancy between

Table 3-1. Chemicals Used

Chemical	Purity	Supplier
1,2-propanediol (propylene glycol)	99%	Aldrich
1,3-propanediol (trimethylene glycol)	98%	Aldrich
2-ethyl-1-hexanol	99%	Aldrich
3-nitrophenylboronic acid	Lot 1: 01201TV Lot 2: 09005LW	Aldrich
Aliquat 336 (trioctylmethylammonium chloride)		Aldrich
Glycerol	Spectral grade	Mallinkrodt
Potassium Chloride	Reagent grade	Mallinkrodt
Potassium Phosphate Monobasic	Reagent grade	Mallinkrodt
Sulfuric Acid	Reagent grade	Mallinkrodt

the stated formula weight and that calculated from nitrogen and chloride analyses may be explained, in part, by a predominance of C_{10} chains, since for a mixture containing only C_{10} chains, the formula weight would equal 487. Other possibilities include faulty analyses (e.g., due to excessive water absorption), and/or the presence of impurities. A molecular weight of 500 was used in calculations.

3.3.2 NPBA

Two lots of NPBA were used in these experiments. The first lot was used for work determining aqueous stability constants, and the second was used for equilibrium measurements with an organic phase. The first lot contained fine white crystals, while the second contained amorphous mustard colored crystals, including several clumps (up to 1 or 2 mm in diameter). Although crystals in the second lot were visibly different in color and texture from the first, Aldrich verified the purity by running additional quality control tests, including thin layer chromatography and NMR spectroscopy. The second lot also took considerably longer to dissolve in water.

Aldrich reported the formula weight for NPBA as 166.93 and the melting point as 284-285°C (dec.). According to Seaman and Johnson (1931), however, this is the melting point of the anhydride, $NO_2C_6H_4B=O$, which has a formula weight of 148.91 (C, 48.37%; N, 9.41%). Elemental CHN analysis of the crystals corroborated that the NPBA was indeed supplied largely as the anhydride; molecular weights calculated from the carbon analysis were 150.5 (C, 47.88%; N, 9.19%) and 152.4 (C, 47.29%; N, 8.70%), for the two lots respectively. Since the nitrogen concentration found in the lot 2 crystals was lower than expected, with a corresponding molecular weight calculated at 161.3, these crystals were also analyzed for boron. The boron concentration was almost 25% lower than expected. Titration and boron analysis of aqueous solutions of these crystals, however, gave NPBA concentrations agreeing within 5% of the molecular weight of the anhydride (149.7 by titration and 143.2 by AA). A molecular weight of 149.7 was used in calculations with the second lot of crystals.

Contaminants that might be expected include unconverted phenylboronic acid (FW anhydride = 103.92), and byproducts nitrobenzene (FW = 123.11) and boric acid (Seaman and Johnson, 1931). The presence of significant amounts of nitrobenzene could significantly alter the boron concentration without necessarily having a large effect on the overall molecular weight as determined by CHN. Phenylboronic acid and boric acid, on the other hand, would not significantly alter the boron concentration, but would reduce the nitrogen concentration and the molecular weight calculated.

Water soluble contaminants (boric acid and phenylboronic acid) were ruled out for the first lot only, by comparing solubility results for solutions prepared directly and those prepared from crystals washed in cold water and from a supersaturated solution that had been restored to equilibrium. These aqueous samples were analyzed for boron concentration by both titration and AA. Analysis of replicate samples by the two analytical methods gave values agreeing within a few percent and resulted in a calculated molecular weight of 145. No significant differences were observed before and after washing. Further, HPLC analyses, as described below, of aqueous NPBA solutions from both lots showed no verifiable contaminants detectable by RI or UV (254 nm). Although periodic unidentified peaks were noted during several HPLC runs, they were very small and not present in every sample. Further, since the retention times of these peaks varied considerably, they can most likely be attributed to column contamination or guard column saturation.

In summary, it was concluded that the purity of NPBA for both lots was about 99% or possibly higher. The variation observed among analytical methods most likely resulted from experimental errors, including instrument calibration and solution preparation, as well as water absorption by the crystals after the bottle had been opened.

3.4 Chemical Analyses

3.4.1 Elemental analyses

<u>C,H,N</u>--Elemental analysis for carbon, hydrogen, and nitrogen (CHN) was performed by the

University of California, Berkeley, College of Chemistry Microanalytical Laboratory (UCB Microlab) using a combustion analyzer with a thermal conductivity detector.

Chloride--Nonaqueous samples were analyzed for chloride by *Desert Analytics* using the Schoniger Flask Method. After subjecting the samples to combustion, the gases were absorbed into base (e.g., NaOH) and then titrated with 10^{-3} M silver nitrate, using an Orion chloride electrode. Aqueous samples were analyzed in this laboratory with an Orion model 720A ionalyzer and model 96-17B combination chloride electrode.

Boron--The UCB Microlab analyzed samples for boron using flame atomic absorption spectrometry (AA); solid samples were digested in concentrated sulfuric acid prior to boron analysis.

3.4.2 Water

Water concentrations in organic solutions were determined with a Quintel Computrac MS-1 Karl Fisher Titrator.

3.4.3 1,2-propanediol

Aqueous 1,2-propanediol concentrations were determined by HPLC, with a refractive index detector (Waters model 401). Samples were analyzed on a Bio-Rad Fast Acid column at 60°C with a mobile phase of 0.01N H_2SO_4 at 0.85 ml/min. A Perkin Elmer Series 10 Liquid Chromatograph pump with a 20 µl Rheodyne injection loop was used. Samples were diluted in the mobile phase, or slightly more concentrated sulfuric acid, and filtered with 0.22 µm Millipore GV filters.

Selected organic phase samples were analyzed for 1,2-propanediol by gas chromatography on a 4-foot column filled with Waters Porapak PS packing. A 4-foot reference column containing Porapak Q packing was in place. Samples (0.6 µl) were analyzed at 180°C on a Perkin Elmer model 3920 GC equipped with two Flame Ionization Detectors.

Temperature programming to 240°C was used to minimize tailing of the solvent (2-ethyl-1-hexanol). Even with temperature programming, tailing was excessive and column equilibrium was difficult to maintain; so, the organic phase was not analyzed for most samples.

3.4.4 NPBA

Unless otherwise specified, NPBA concentrations of aqueous stock solutions were determined by titration in a constant temperature bath set at 25°C. Solutions were sparged with nitrogen for several hours prior to titration to remove any dissolved carbon dioxide. Magnetically stirred solutions were titrated under nitrogen atmosphere in the presence of excess glycerol to the inflection point with 0.1 N NaOH. pH was measured with an Orion model 720A ionalyzer and a Ross™ model 8103 combination electrode. Base was dispensed from a Metrohm model 655 Dosimat automatic buret; minimum drop size was 0.001 ml.

Aqueous samples were also analyzed for NPBA by HPLC under the conditions described in Section 3.3.2. A Waters Model 440 Fixed Wavelength (254 nm) UV detector was used for NPBA quantitation.

3.5 Aqueous solubility of 3-nitrophenylboronic acid

Since no quantitative solubility data for NPBA could be located in the literature, solubility was measured in this laboratory. Three sets of NPBA crystals (lot 1) were placed in a flask with water and allowed to dissolve in a 25°C shaker bath (Fisher Scientific Versa-Bath® S) for a period of 5 to 12 days. The first set was not pretreated. The second set was first ground to a fine powder and washed with cold water before being placed in the shaker bath to equilibrate. Finally, to ensure that the equilibrium solubility had been reached, the third set was heated to about 70°C to dissolve all the crystals, and then allowed to cool and recrystallize before being placed in the water bath. The recrystallized sample was centrifuged before decanting the liquid. As a further check, samples from the supernatant of both the

washed and the recrystallized NPBA were taken after they had equilibrated several months at 25°C. These samples were analyzed by HPLC, as described above.

The supernatant from each sample was analyzed for boron concentration by AA (see above) or titration or both. Titrations were performed with an Orion model 601A or 701A Ionalyzer and a Ross model 8103 combination pH electrode. Titrant solutions of 0.01N and 0.001 N NaOH were prepared by dilution of standardized 0.1 N NaOH. All samples but one were titrated under nitrogen atmosphere to minimize carbon dioxide absorption. According to the Henderson equation (Mattock and Taylor, 1961), pH approximates the pK_a at half-neutralization. The pH measured at half neutralization was 7.30, which agrees with the value reported by Torssell (1964); Juillard and Gueguen (1967) reported a pK_a of 7.23.

3.6 Aqueous stability constant determinations

Stability constants were calculated using Antikainen's model, as described in Section 2.2.2. This technique uses the variation of observed pK_a with changing diol concentration to determine the stability constant graphically. The critical measurement is therefore the determination of the apparent pK_a of the boronic acid. References by Albert and Serjeant (1984) and Kortrum, Vogel and Andrussow (1961) describe a variety of procedures for this purpose. At least two potentiometric methods have been used in conjunction with the Antikainen model--the half-neutralization method (Davis and Mott, 1980; Dawber and Matusin, 1982) and the buffer capacity method (Antikainen, 1954; Huttunen, 1984).

The buffer capacity method eliminates many inconsistencies of other pH depression methods (Weser, 1967). It measures only potential differences, thereby eliminating errors in determining absolute potentials for pH measurement that depend on instrument calibration with buffers. Also, since only small amounts of base are required for titration, dilution error is minimized. Finally, unlike the half-neutralization method, in which the titration extends well into the basic region, the buffer capacity method is conducted entirely in the acidic region where carbon dioxide absorption will be minimal.

3.6.1 Buffer capacity method

This work uses the buffer capacity method developed by Kilpi (1952). The procedures and calculations closely parallel those of Huttunen (1984).

The buffer capacity, P, of a solution is the pH change when an acid or base is added. It was originally defined for a monobasic acid by Van Slyke (1922) as:

$$P - \frac{d[B]}{dpH} - 2.303 \left(\frac{K_a [H^+] c_a}{(K_a + [H^+])^2} + [H^+] + [OH^-] \right) \tag{3-1}$$

where d[B] is the change in concentration of base, c_a is the total concentration of acid in all forms, and K_a its ionization constant. Antikainen (1954) developed an expression implicitly relating the ionization constant to $[H^+]_m$, the hydrogen ion concentration at the minimum buffer capacity:

$$K_a c_a - \frac{\left([H^+]_m + K_a \right)^3}{[H^+]_m - K_a} \tag{3-2}$$

When K_a is much less than $[H^+]_m$, the following simplifications can be made:

$$K_a c_a - [H^+]_m^2 \tag{3-3}$$

$$P_m - 4.606 [H^+]_m \tag{3-4}$$

where P_m is the minimum buffer capacity.

For the NPBA-1,2-propanediol system, the pH of the solution never exceeds 5; therefore, the [OH$^-$] term will be much less than the other two terms on the right-hand side of Equation 3-1 and can be neglected, even when the other assumptions do not hold:

$$P - 2.303 \left(\frac{K_a [H^+] c_a}{(K_a + [H^+])^2} + [H^+] \right) \tag{3-5}$$

The minimum buffer capacity can be determined experimentally by measuring the maximum potential jump during back-titration of a strong acid that has been added to the solution of the weak acid. The maximum potential jump, $\Delta\xi_m$, can be calculated from the highest measured EMF change, $\Delta\xi_m^*$, using equation 3-6:

$$\Delta\xi_m = \Delta\xi_m^* + \frac{1}{8}\left((\Delta\xi_m^* - \Delta\xi_1) + (\Delta\xi_m^* - \Delta\xi_2) \right) -$$

$$\frac{(\Delta\xi_m^* - \Delta\xi_1) \times (\Delta\xi_m^* - \Delta\xi_2)}{2\left((\Delta\xi_m^* - \Delta\xi_1) + (\Delta\xi_m^* - \Delta\xi_2) \right)} \qquad (3-6)$$

where $\Delta\xi_1$ and $\Delta\xi_2$ are the values immediately before and after the maximum observed change. $\Delta\xi_m$ can then be substituted into the following equation to provide the minimum buffer capacity:

$$P_m = \frac{k(N_b)(V_b)}{V_m(\Delta\xi_m)} \qquad (3-7)$$

where

$k = 2.303\ RT/Fn = 59.16$ mv @ 25°C

N_b = Normality of base

V_b = Volume in ml of each increment of base added

V_m = Volume in ml of test solution at inflection point

$\Delta\xi_m$ = Maximum potential jump in mv

When $\Delta\xi_m$ is less than 10 mv, no additional correction terms are needed.

The calculated buffer capacity and the known acid concentration are substituted into Equations 3-2 and 3-5 and solved iteratively for K_a and $[H^+]$. A Fortran program was written to solve these equations, using Equations 3-3 and 3-4 as initial approximations. The program is provided in Appendix B.

3.6.2 Measurement of minimum buffer capacity

Stock solutions of NPBA (0.001M to 0.01M) and 1,2-propanediol (1M and 5M) were prepared in 0.1M KCl to maintain constant ionic strength. Solutions were prepared with distilled deionized water that had been boiled to remove carbon dioxide. Heating was sometimes used to speed dissolution of NPBA crystals. Concentration of the NPBA stock solutions was checked by titration with glycerol.

Additional solutions were prepared by pipetting the required amount of each stock solution into a volumetric flask and diluting with 0.1 M KCl. Diol concentration was varied from 0 to 1.0 M.

Initial determinations of pK_a with no diol present were made at NPBA concentrations of 0.005M and 0.01M, since initial measurements conducted at 0.001M NPBA yielded barely discernible end points. Further, Albert and Serjeant (1984) have shown that potentiometric titrations in more dilute solutions (<0.005M) can give erratic results. When diol was present, the inflection point was more clearly defined, even in dilute solutions. Most titrations were in solutions of 0.004M NPBA, although a few were at concentrations of 0.001M and 0.005M.

To ensure that carbon dioxide was removed, nitrogen, saturated with 0.1M KCl solution, was bubbled through the solutions for at least 12 hours before titrating. Sparging rate was kept low to minimize losses from spray. All titrations were done in a constant temperature water bath (25°C, 35°C, or 44.8°C) with magnetic stirring and nitrogen blanket. An Orion model SA720 pH meter with a Ross model 8103 combination pH electrode was used in the millivolt mode. Readout was precise to 0.1 mv with a relative accuracy of 0.2 mv. Two tenths of a milliliter of 0.1N HCl were added to 50 ml of solution and back titrated with constant increments of 0.1N NaOH. Drop size was selected to give a maximum EMF change between 7 and 10 mv. NaOH was dispensed using a Metrohm 655 dosimat, with a minimum drop size of 0.001 ml. Near the endpoint, equal drop increments were used and measurements were taken after 1 minute of mixing.

3.7 Measurement of two-phase equilibria

3.7.1 Partition coefficients

Partition coefficients for 1,2-propanediol distribution between water and 2-ethyl-1-hexanol were measured at 25 °C. The 2-ethyl-1-hexanol used in equilibrium experiments was first saturated with water by contacting in a separatory funnel. Equal volumes (5 or 10 ml) of aqueous and organic phases were pipetted into a 20 ml vial and equilibrated in a 25°C water bath (New Brunswick Scientific, Gyrotory Water Bath Shaker - Model G76). Agitation methods and duration were varied to verify that equilibrium had been achieved. Agitation techniques included:

1) Agitation by shaker bath only -- setting 4 -- for minimum of 48 hours;

2) Agitation by shaker bath supplemented with shaking vigorously by hand for about 30 seconds several times during equilibration time;

3) Agitation by shaker bath supplemented by several intervals (~15 minutes each) of magnetic stirring during equilibration time.

When entrainment was observed, samples were centrifuged (IEC-HN-SII Centrifuge) at 2000 rpm for five to ten minutes. After the two phases had been separated, the aqueous phase was analyzed for 1,2-propanediol by HPLC. For selected samples, the organic phase was analyzed for water and 1,2-propanediol and the aqueous phase for pH.

3.7.2 Conversion of NPBA to anionic form

Since 1,2-propanediol will complex with NPBA only in the anionic form, several methods of extractant pretreatment were tried to determine the minimum treatment necessary to convert the NPBA to ionic form. The percentage ionized cannot be measured directly, but can be estimated from the amounts of OH^- and Cl^- extracted from the organic extractant into an aqueous wash solution. Aliquat 336 and NPBA were weighed out in approximately equal molar amounts and diluted with water-saturated 2-ethyl-1-hexanol to about 0.2 M. Fifteen milliliter samples of extractant prepared in this way were then washed with five consecutive

aliquots of 5 ml of water or of 5 ml of 0.001N NaOH. The water-washed extractant was then washed with two 5 ml aliquots of pH 7.9 phosphate buffer ($\sim$0.046M $KNaHPO_4$-0.004M KH_2PO_4). Each wash was analyzed for chloride and pH. The extractant was also washed according to the procedure described by Grinstead et al. (1969) for preparation of a similar mixed ionic extractant--the extractant was washed with excess 0.1N NaOH to ionize the acid, followed by water to remove any NaCl that had been retained in the organic phase. This procedure was repeated to determine whether additional ionization could be achieved. These washes were also analyzed for pH and chloride.

3.7.3 Distribution between water and a mixed ionic extractant

The distribution of 1,2-propanediol between water and the mixed ionic extractant (NPBA-Aliquat 336 in 2-ethyl-1-hexanol) was determined by a procedure similar to that described in Section 3.7.1. In addition to the three agitation methods described in Section 3.7.1, a fourth method was used in an effort to prevent emulsion formation. In this method, the vigorous shaking of agitation technique 2 above was replaced with repeatedly inverting the vial. The extractant was prepared in one of two ways:

1) no pretreatment

2) washed once with excess 0.1N NaOH and water as described above.

Only the aqueous phase was analyzed for 1,2-propanediol and NPBA. Selected samples were also analyzed for aqueous pH and for water concentration of the organic phase.

4 RESULTS

4.1 Solubility of NPBA

The solubility of 3-nitrophenylboronic acid in water at 25°C was measured by titration, AA, and HPLC. The results are presented in Table 4-1.

Six days was sufficient time to reach the solubility limit and no significant differences were observed among crystals dissolved directly, crystals washed with water and dried before dissolution, and solutions that were first supersaturated and then allowed to recrystallize and equilibrate at 25 °C. Using the formula weight for the monohydrate (166.93), solubility data were converted from measured values in mol/l to weight percent. The 95% confidence interval for the solubility was calculated to be 0.45 +/-0.02 weight percent.

4.2 Stability constants in aqueous solution

The first ionization constant of the 3-nitrophenylboronic acid in 0.1M KCl was determined from buffer capacity data at three temperatures:

Temperature (°C)	pK_a
25	7.09
35	7.08
44.8	7.09

These values were used in the calculation of the stability constants for NPBA-diol complexes at the respective temperatures. For each temperature, an Antikainen plot was used to determine the stoichiometry, n, and the stability constant, β_n, where β_n is calculated using the intercept, pK_n, as defined in Equation 2-3:

$$\beta_n = \frac{K_n}{K_a}$$

Table 4-1. Aqueous solubility of 3-nitrophenylboronic acid at 25°C.

Dissolution Method	Analytical Method	Solubility [a] (g/100 g H_2O)	Equilibration Time
Unassisted dissolution	Titration [b,c]	0.46	7 days
	Titration [b]	0.49	8 days
Heated to supersaturation, cooled, reequilibrated	Boron by AA	0.44	8 days
	Titration [b,c]	0.44	6 days
	HPLC	0.46	18 mos.
Washed crystals, unassisted dissolution	Titration [b]	0.40	5 days
	Titration [b,c]	0.45	12 days
	Boron by AA	0.48	12 days
	HPLC	0.44	18 mos.

Notes:

[a] Crystals obtained as anhydride form Aldrich; solubility reported for monohydrate (MW =166.93).

[b] All titrations done at ionic strength = 0 and room temperature. All except first titration completed under nitrogen blanket.

[c] Estimated from titration to half-neutralization (pK_a = 7.3).

(See Appendix A for tabulation of the buffer capacity data used to determine K_a's and apparent K_a's.)

4.2.1 1,2-propanediol

For 1,2-propanediol (propylene glycol), the slopes, n, calculated from a linear least squares regression for each data set are very close to one. Since the expected stoichiometry is 1:1, each line was replotted in Figure 4-1 using a regression with n forced equal to 1. The stability constants measured for the 1,2-propanediol systems studied are presented in Table 4-2 for both the measured stoichiometries and the 1:1 stoichiometry.

Table 4-2. Stability constants measured for borate-1,2-propanediol complexes

Temperature, °C	Stoichiometry, n	Stability Constant, β_n measured stoichiometry	$\beta_{1,1}$ 1:1 stoichiometry
25	0.93 +/- 0.06	2.94 +/- 0.21	3.17 +/- 0.08
35	1.02 +/- 0.05	2.34 +/- 0.11	2.30 +/- 0.07
44.8	0.91 +/- 0.05	1.82 +/- 0.09	1.95 +/- 0.07

Ranges reported represent the standard error of the mean as determined from linear least squares regression analysis.

Plotting $\ln \beta_n$ vs. reciprocal temperature (See Figure 4-2) enables calculation of the bond enthalpy, $\Delta H°$, for the complex according to the following equation, derived from the Gibbs-Helmholtz equation:

$$\ln K = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (4-1)$$

From the slope of Figure 4-2, an enthalpy of complexation equal to -19 +/- 3 kJ/mol was calculated for the NPBA-1,2-propanediol complex. Similarly, the intercept can be used to
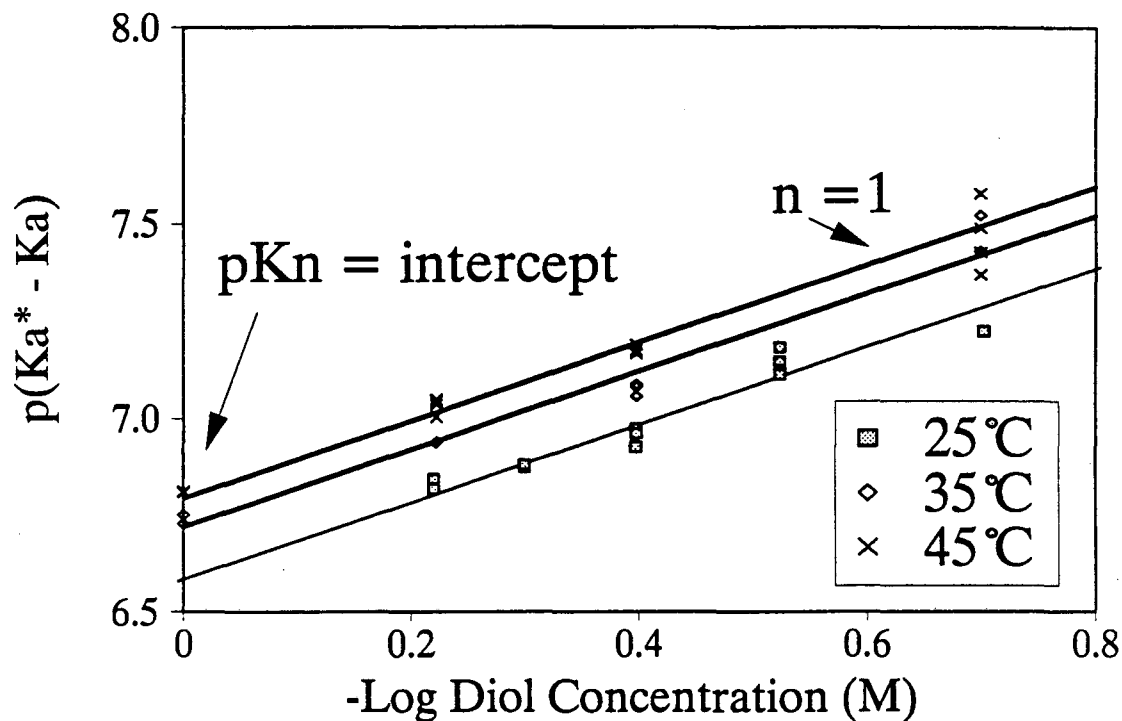
Figure 4-1. Antikainen plot for 1,2-propanediol complexation with NPBA in 0.1M KCl at 25, 35, and 45 C. Lines are forced through unit slope.

$$\text{Ln } B_n = \frac{-\triangle H}{R}\left(\frac{1}{T}\right) + \frac{\triangle S}{R}$$
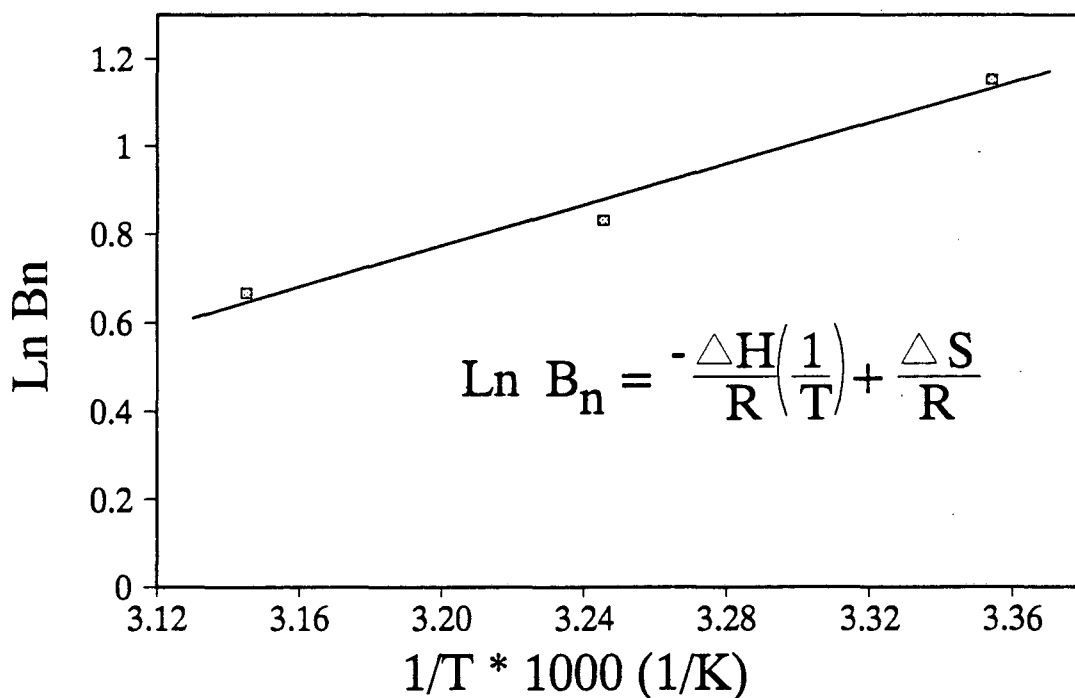
Figure 4-2. Temperature dependence of stability constant for NPBA-1,2-propanediol complex in 0.1M KCl.

approximate ΔS. The calculated value is -0.05 kJ/mol. The free energy, ΔG, of the complex, a measure of its reversibility, can be calculated according to :

$$\Delta G^\circ = -RT \ln K \qquad (4-2)$$

At 25°C, 35°C, and 44.8°C respectively, the values calculated were -2.8, -2.1, and -1.8 kJ/mol. Unlike K in Equations 4-1 and 4-2, which is based entirely on activities, β_n is a mixed constant including both activities (i.e., H^+) and concentrations. Therefore, the thermodynamic properties calculated from β_n are only approximations to the true values.

4.2.2 1,3-propanediol

Antikainen plots for 1,3-propanediol (trimethylene glycol) at 25, 35 and 45°C are shown in Figure 4-3. The data exhibit considerably more scatter than the data for 1,2-propanediol, and the slopes are not constant over the temperature range. At 45°C, in particular, the slope is close to 0, suggesting that the anionic complex is not forming at this temperature. At all three temperatures, the deviation of the slope from the expected value of 1 for a 1:1 complex is most likely related to the formation of both anionic and neutral complexes with the 1,3-diol. The formation of anionic complexes reduces the activity of the NPBA anion and serves to increase the ionization constant, as shown in Equation 2-7:

$$K_a^* = \frac{[H^+]\left([AD_n^-] + [A^-]\right)}{[HA]} \qquad (2-7)$$

The formation of the neutral complex, on the other hand, reduces the activity of the neutral acid. When both complexes form, their effects partially cancel each other:

$$K_a^* = \frac{[H^+]\left([AD_n^-] + [A^-]\right)}{[HA] + [HAD_n]} \qquad (4-3)$$

These data seem to corroborate Paal's (1980) conclusion that the pH-depression method is not suitable for measuring stability constants when both neutral and anionic complexes can form. The neutral complexes cannot form for 1,2-propanediol.
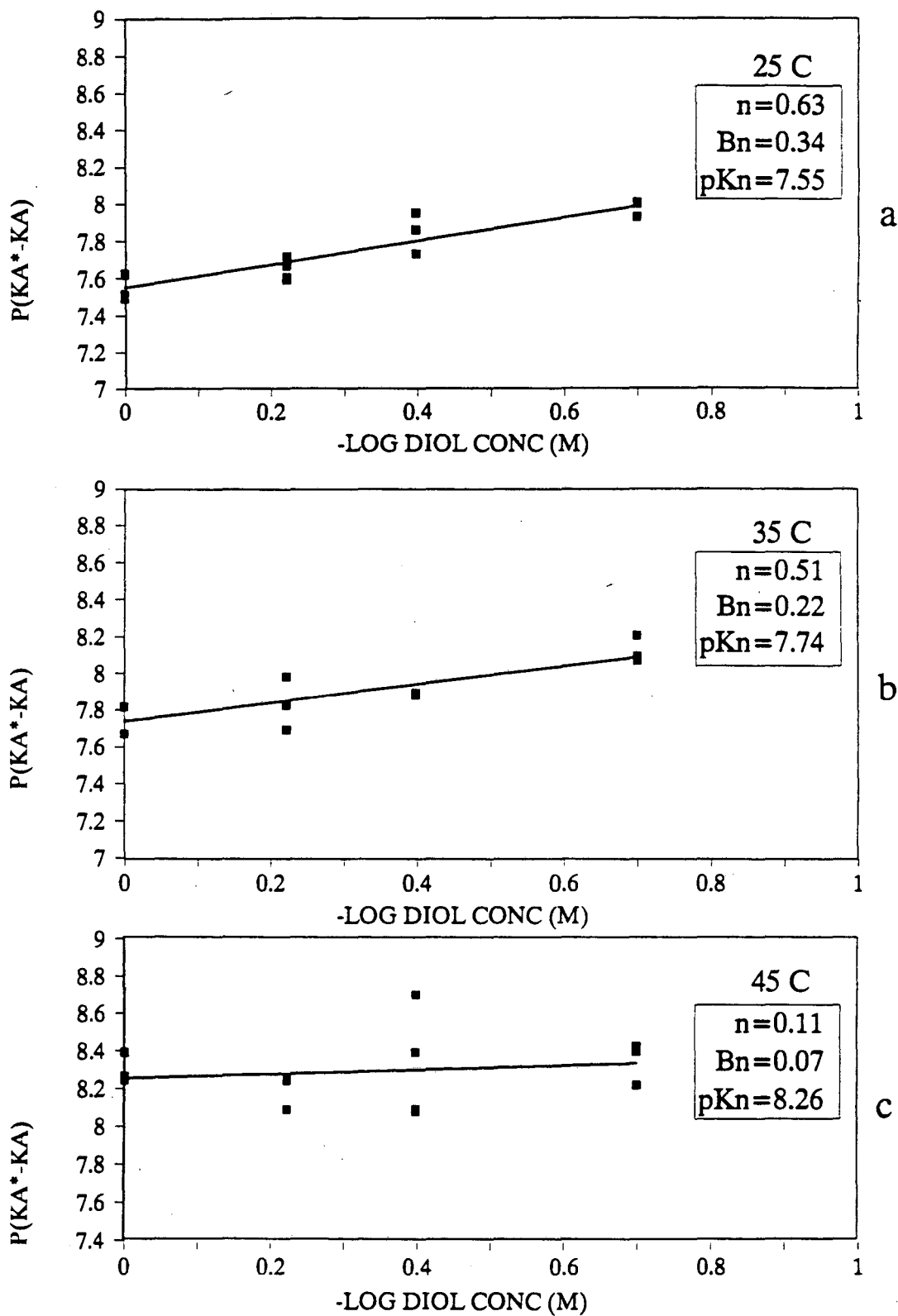
Figure 4-3. Antikainen plots for 1-3-propanediol complexation with NPBA in 0.1M KCl: (a) 25 C, (b) 35 C, (c) 45 C. NPBA concentration = 0.004M.

4.3 Measurement of two-phase equilibria

4.3.1 Partition coefficient of 1,2-propanediol between water and 2-ethyl-1-hexanol

Figure 4-4 presents the measured partition coefficient for 1,2-propanediol between water and 2-ethyl-1-hexanol at 25°C. For most samples, the aqueous phase was initially loaded with about 0.1M 1,2-propanediol. In addition, for two samples the aqueous phase was initially loaded at 0.05M glycol, and for two other samples the organic phase, not the aqueous phase, was preloaded with 0.1M glycol. The phase loaded and the initial concentration did not discernibly affect the measured partition coefficient.

Most of the data in Figure 4-4 were therefore obtained by forward extraction, i.e., extraction from the aqueous phase into the organic phase. Reliable measurements of the partition coefficient based on back-extraction from a loaded organic phase required analysis of both the organic and aqueous phases. The organic phase can be analyzed by gas chromatography, but the organic diol concentrations were very close to the detection limit. Therefore, calibration was difficult and very few samples were analyzed successfully. The results obtained, as shown in Table 4-3, indicate that with a preloaded organic phase the GC data for the equilibrium organic phase differed from that calculated using a mass balance and

Table 4-3. Comparison of GC and HPLC Data

Propylene Glycol Concentrations (mol/l)					Difference GC vs. HPLC
Aqueous		Organic			
Initial (HPLC)	Final (HPLC)	Initial	Final (GC)	Final (Calc.)	
0	0.0839	0.096	0.006	0.0121	102%
0	0.0850	0.102	0.0062	0.0170	174%
0.053	0.0494	0	0.004	0.0036	10%
0.106	0.0980	0	0.0074	0.0080	8%
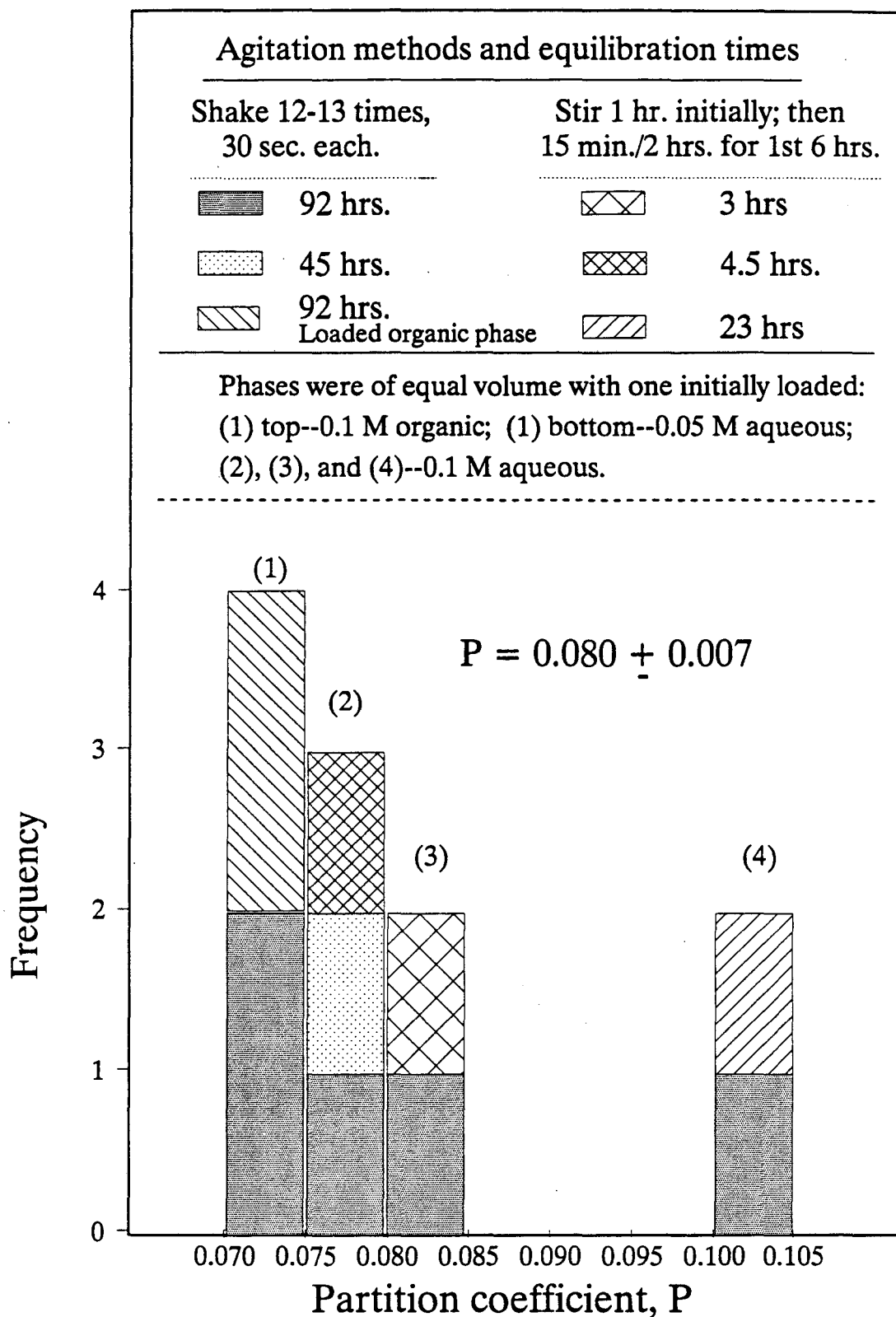
Figure 4-4. Distribution of 1,2-propanediol between water and 2-ethyl-1-hexanol at 25 C.

the measured aqueous concentration by 100% or more. This can most likely be attributed to an incorrect value for the initial organic glycol concentration, which was not verified by analysis. As shown in Table 4-3, when the aqueous phase was preloaded, the organic phase concentration calculated by mass balance agreed well with the GC data.

In addition to using both forward and back-extraction, several mixing techniques and equilibration times were employed to verify that equilibrium had been achieved. The samples from which the data in Figure 4-4 were obtained were all mixed vigorously so that very fine droplets were formed. Because of the high surface tension between 2-ethyl-1-hexanol and water, the droplets coalesced rapidly, often not requiring centrifugation. In addition to the mixing methods shown in Figure 4-4, two other methods--equilibration in a shaker bath and on a rotary agitator--were used; they are not included in Figure 4-4 because of poor temperature controls. One sample equilibrated 43 hours in a shaker bath at 28°C. The measured partition coefficient was 0.097. The other sample was rotated for 45 hours at ambient temperature (-20°C), and the measured partition coefficient equaled 0.068. These data fall toward the edges of the distribution at 25°C shown in Figure 4-4. Since the difference from the mean of 0.08 could easily be accounted for by temperature difference or simply random error, either of these methods may be sufficient to reach equilibrium. No data are available to evaluate whether mixing by rotary agitator or shaker bath is sufficient to achieve equilibrium at short times; however, the data in Figure 4-4 indicate that, when initial contacting is good, equilibration can be achieved in a few hours.

4.3.2 Conversion of NPBA to anionic form

A mixed ionic extractant was prepared by mixing approximately equimolar amounts of NPBA (an organic acid) and Aliquat 336 (chloride salt of an organic base--$TOMA^+Cl^-$) and diluting with 2-ethyl-1-hexanol to the desired concentration. In preparing a similar extractant, Grinstead et al. (1969), washed the mixed extractant with an excess of dilute NaOH to convert the acid to the corresponding anion. In that work, however, they did not

quantitate the extent to which the conversion occurred; rather, they reported only that "reaction to from the salt is probably not complete." Because of the very specific nature of the interaction between the NPBA anion and 1,2-diols, a more detailed knowledge of the extent of ionization is needed in order to model this system chemically. Therefore, the extractant was washed in several ways, as described in Section 3.7.2, and pH and chloride measurements of the wash solution were used to estimate the conversion for each component.

The main reactions occurring during the washing are acid-base reactions with NPBA:

NPBA   NPBA$^-$

$$R-B(OH)_2 + OH^- \rightleftharpoons R-B^-(OH)_3$$

$$R-B(OH)_2 + H_2O \rightleftharpoons R-B^-(OH)_3 + H^+$$
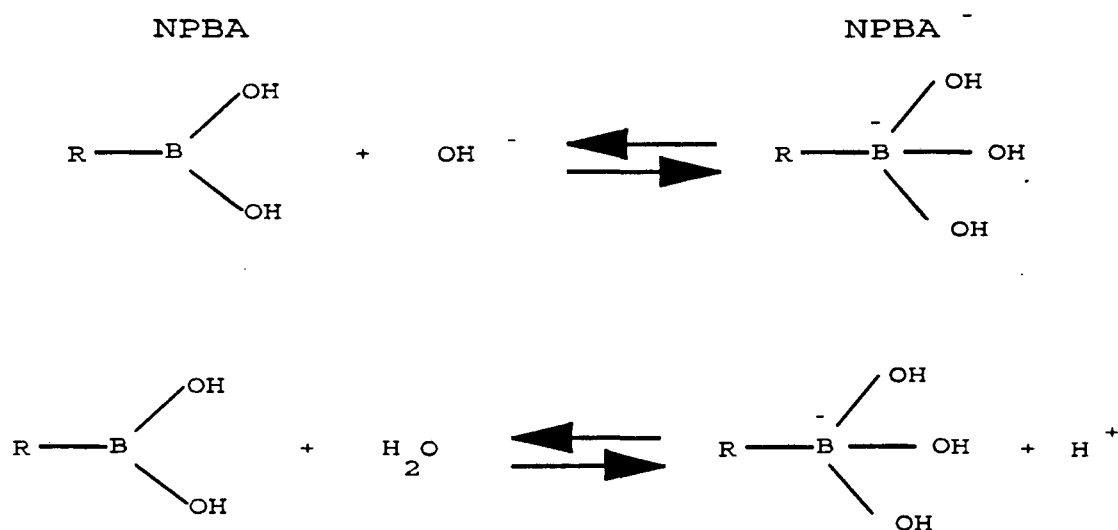
There is also a partitioning of the various ionic species between the two phases, constrained by the requirement for electroneutrality. The anions include OH⁻, NPBA⁻, and Cl⁻, while the cations include Na^+, H^+, and $TOMA^+$. $TOMA^+$ is not expected to partition significantly into water because of its hydrophobic nature and has not been included in subsequent calculations.

The concentrations of NPBA in anionic and neutral forms in the organic phase were determined using two calculation procedures, as described below.

Chloride removed (as fraction total chloride)

The amount of chloride removed is calculated according to Equation 4-4.

$$\frac{Cl^- \ removed}{total \ Cl^-} = \frac{[Cl^-]_{wash} \times v_{wash}}{[TOMA^+CL^-]_{org,i} \times v_{org}} \qquad (4\text{-}4)$$

where v equals volume in ml, wash denotes the aqueous phase, org denotes the extractant phase, and i denotes the starting concentration.

This calculation assumes that initially Aliquat 336 is composed of only $TOMA^+Cl^-$ and relies on the formula weight calculation for Aliquat 336. (See Section 3.3.1.) When the chloride is removed, the $TOMA^+$ can then be paired with either OH^- or $NPBA^-$. It is assumed that losses of $TOMA^+$ to the aqueous phase are negligible, and that in this basic environment the OH^- adds to NPBA to create $NPBA^-$. If these assumptions hold, then the number of equivalents of NPBA converted to anionic form and remaining in the organic phase equals the number of equivalents of chloride removed. The above analysis does not allow for retention of sodium chloride by the organic phase. If significant amounts of sodium chloride are retained, the conversion indicated by the above calculation would be lower than the true value. Water washing of the extractant after any treatment with base would, however, be expected to remove most of the NaCl.

OH⁻ Consumed (as fraction total NPBA)

The amount of NPBA converted to anionic form can also be determined by calculating the amount of OH^- removed from the aqueous wash solution either by neutralization or by exchange of the OH^- for the Cl^- as the counter-ion to $TOMA^+$. The calculation is based on the pH change of the wash solution :

$$\frac{OH^- \ consumed}{total \ NPBA} = \frac{\left(10^{(pH_i - 14)} - 10^{(pH_f - 14)} \times v_{wash} \right)}{[NPBA]_{tot,org,i} \times v_{org}} \qquad (4\text{-}5)$$

where pH_i and pH_f indicate initial and final pH, respectively, for the wash solution; the NPBA concentration is the total initial concentration in the organic phase; and v represents volume in ml.

Equation 4-5 is valid only at pH well above neutral. Otherwise there can be significant consumption of OH^- due to maintaining the equilibrium for the ionization constant of water ($H^+ + OH^- \rightleftharpoons H_2O$). If one again assumes that $TOMA^+$ is paired either with Cl^- or $NPBA^-$, and if there are no acidic or basic impurities in the mixed extractant, then the number of equivalents of OH^- consumed equals the number of equivalents of NPBA ionized. Since a fraction of the NPBA partitions into the aqueous phase, particularly into basic solutions, the amount of $NPBA^-$ in the organic phase must be corrected for aqueous losses of the anion. This calculation is fairly straightforward as long as the final aqueous pH is far removed from neutral (i.e., the NPBA is predominantly in one form--acid at low pH and anion at high pH). Further, since pH is a measure of activity, the calculation of OH^- consumed may not be entirely accurate. Nonetheless, if the assumptions are valid and the methods are reasonably precise, the Cl^- and OH^- methods should yield calculated values for the amount of NPBA converted agreeing to within a few percent and should provide a check against each other.

The results of the washing experiments are presented in Figure 4-5 and Table 4-4. In these experiments the initial concentrations were 0.207M NPBA and 0.18M $TOMA^+Cl^-$ in 2-ethyl-1-hexanol. Figure 4-5 shows the cumulative percentage of chloride removed from the extractant after each step of a series of washes with successive aliquots of water or a basic wash solution. Figure 4-5 clearly shows that a high pH wash, such as the 0.001N base, will not convert much of the NPBA to anionic form if the wash is not buffered or at a sufficiently high concentration. The pH 7.9 phosphate buffer, on the other hand, converted close to 20% of the acid to anionic form at less than a 1:1 wash:extractant volume ratio. Calculations based on pH change are not shown for these systems because the initial OH^- concentrations are low for water and 0.001N NaOH, and because the buffered solution is not amenable to the same calculation method. The decrease in pH for each system, however, illustrates that OH^- is being removed from the aqueous phase as chloride is removed from the organic phase.

Table 4-4 shows the results for a system washed with an excess of 0.1N NaOH. The final pH (Column 2) used in calculations was the pH of the aqueous phase after the base
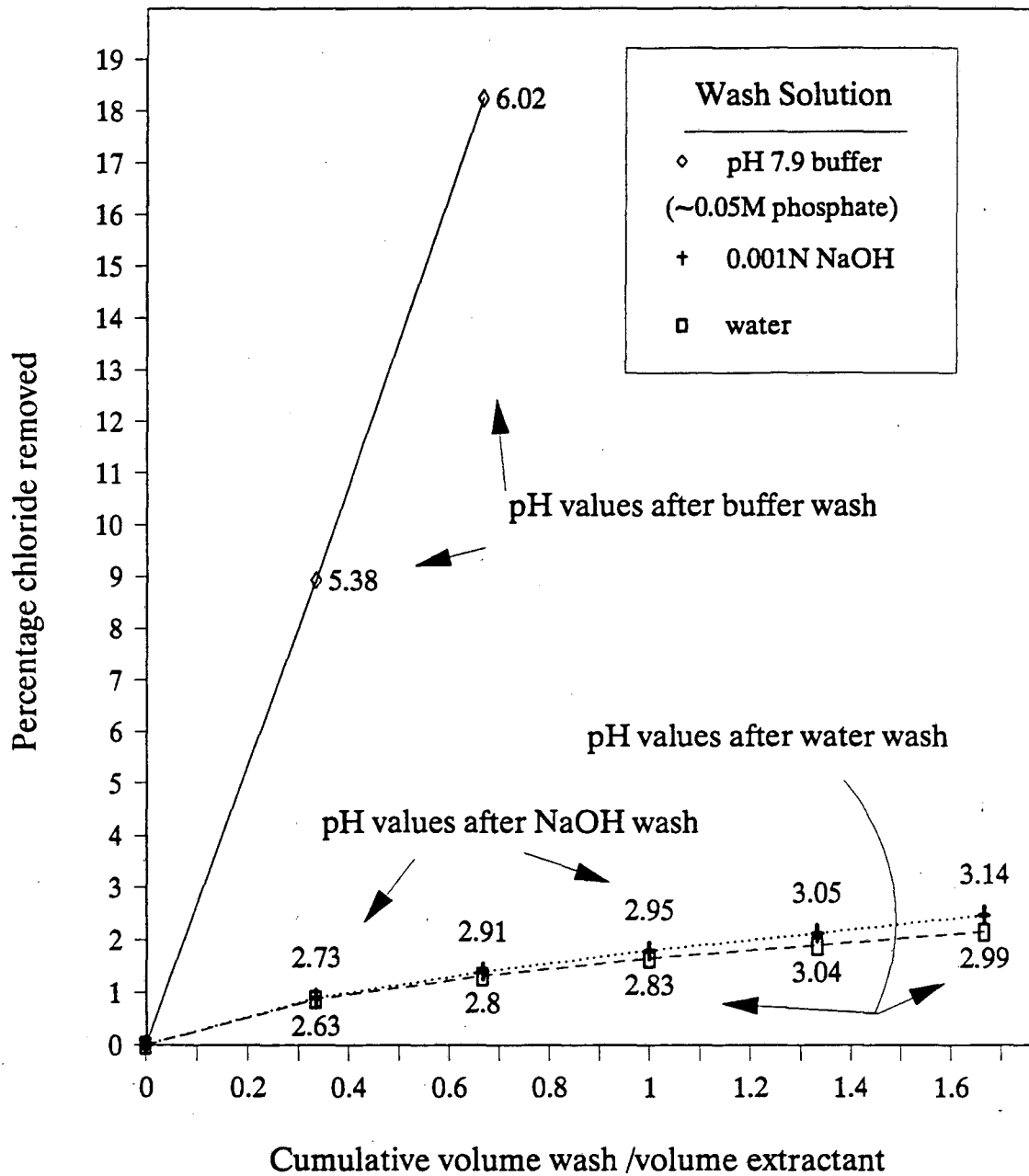
Figure 4-5. Conversion of NPBA to anionic form as measured by chloride removal from a mixed ionic extractant after aqueous washes.

Table 4-4. Conversion of NPBA to anionic form by base washing.

(1) Wash Step[a]	(2) final pH	(3) OH⁻ Consumed / OH⁻ added	(4) OH⁻ Consumed / total NPBA	(5) NPBA⁻ aq / total NPBA	(6) NPBA⁻ org[b] / total NPBA	(7) Cl⁻ removed / total Cl⁻
Ex-I		0.0	0.0	0.0	0.0	0.0
Ex-W1	12.66	0.54	0.66	0.13[c]	0.53 (0.61 final NPBA org)	0.52 (0.52 final NPBA org)
Ex-W2	12.68	0.53	1.16	na	na	0.90

a--Ex-I refers to initial extractant--0.207M NPBA, 0.18M Aliquat 336, in 2-ethyl-1-hexanol.

Ex-W1 refers to extractant and aqueous washings after washing with excess 0.1N NaOH followed by water.

Ex-W2 refers to extractant and aqueous washings after washing twice with excess 0.1N NaOH and water.

b--calculated from OH⁻ consumed.
c--estimated from analysis of similar washings.
na--not analyzed or insufficient data for calculation.

washing, while the initial pH was that of the original base wash solution. The chloride removed was calculated from the sum of values obtained from the concentration in the aqueous phase after the base washing and the concentration in the aqueous phase from the subsequent water wash. The additional chloride removed by the water wash was less than 5% of the total chloride in each case.

The third column in Table 4-4 shows that only about 50% of the base added was consumed for each step of the washing. It may be possible to increase the efficiency of the washing by increasing the contact time. For example, in another washing of the same initial extractant, where the contacting time was slightly longer but all other conditions were

identical, the final pH was 12.55.

The fourth column expresses the amount of OH^- consumed as a fraction of the total NPBA. Up to 66% of the NPBA was neutralized during the first wash and essentially all remaining NPBA was neutralized during the second wash. After the second wash, however, the fraction of NPBA converted exceeded one, suggesting that not all the assumptions involved in this calculation are valid. The presence of acidic impurities or of $TOMA^+$ at concentrations higher than calculated with the estimated formula weight of 500 may account for a significant portion of this discrepancy.

Column 5 shows the amount of NPBA lost to the aqueous phase during washing. The value shown for the first wash was estimated from analysis of another sample (corresponding to the 12.55 pH discussed above). Using this value, the fraction of NPBA in anionic form and still retained by the organic phase is about 53% of its initial concentration or 61% of the final concentration (column 6). No data are available for the amount of NPBA lost during the second wash, but from the OH^- calculation (column 4) one can conclude that close to 100% of the NPBA remaining in the organic phase is in anionic form.

The values calculated from the chloride measurement are somewhat lower. After the first wash with base and water, 52% of the chloride was removed, corresponding to an equal fraction of $NPBA^-$ remaining in the organic phase since the extractant was equimolar in NPBA and $TOMA^+$ after this step. About 90% of the chloride was removed after the second wash.

With the exception of one set of experiments completed without any washing of the extractant, the extractant used in subsequent extraction experiments corresponds to the extractant in Table 4-4 after wash 1, with some variation in initial concentrations of NPBA and $TOMA^+Cl^-$. Slight differences in the washing procedure for each set of experiments may have caused some variation in the amount of NPBA actually converted to anionic form. Since extractant preparation was almost identical for each set, a common value of 0.55 is used for the fraction of the NPBA in the organic phase that was in ionic form.

4.3.3 Distribution of 1,2-propanediol between water and NPBA loaded extractant

Distribution ratios, loadings (molar ratio of solute to extractant), and selectivities were calculated using data from extraction of 1,2-propanediol from dilute aqueous solution by an extractant containing approximately equimolar amounts of NPBA and Aliquat 336 dissolved in 2-ethyl-1-hexanol.

The distribution ratio, D, is used to describe the effectiveness of the extraction. D is defined in terms of the experimentally measured equilibrium concentrations of the solute (1,2-propanediol, unless otherwise specified) in each phase:

$$D = \frac{c_{org}}{c_{aq}} \qquad (4\text{-}6)$$

The distribution ratio is used instead of the thermodynamic partition coefficient, P, because the many chemical interactions taking place in this system make the activities required to calculate P for the different species difficult to evaluate.

The loading, z, is defined as the molar ratio of solute (diol) to total extractant in the extract phase:

$$z = \frac{[Diol]_{org}}{[NPBA^-]_{org}} \qquad (4\text{-}7)$$

The extractant for this system is defined as the anionic NPBA⁻, since it is accepted that this is the species that complexes with 1,2-diols. (See Section 2.2.1.) Since loading is often used to evaluate the stoichiometry of a complex, it is most meaningful when corrected for extraction by the diluent alone. The loading parameter is then defined as the amount of solute extracted in excess of that which would have been extracted by the diluent alone. In this case the numerator in Equation 4-7 becomes:

$$[Diol]_{org} = [Diol]_{org,tot} - P[Diol]_{aq} \times Vf \qquad (4\text{-}8)$$

Where Vf = volume fraction diluent in organic phase.
P = partition coefficient for diluent.

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The selectivity, α, for diol over water, is defined in Equation 4-9:

$$\alpha - \frac{D_{Diol}}{D_{H_2O}} \quad where \quad D_{Diol} - \frac{[Diol]_{org}}{[Diol]_{aq}} \quad and \quad D_{H_2O} - \frac{[H_2O]_{org}}{[H_2O]_{aq}} \qquad (4-9)$$

Only forward extraction results were used because data from back-extraction of diol from the mixed extractant, like the related experiments described in Section 4.3.1, were difficult to interpret. The GC method used for 1,2-propanediol in 2-ethyl-1-hexanol did not work satisfactorily for samples containing NPBA and Aliquat 336. In preliminary extraction experiments, an effort was made to verify attainment of equilibrium by varying both contact time and mixing method. In a timed experiment, where samples were equilibrated at 25°C in a shaker bath without additional agitation, excessive time was required to reach equilibrium. Even after 19 days, as shown in the data in Table 4-5, the final concentrations had not reached a constant value.

Table 4-5. Change in distribution ratio with time in shaker bath.
Extractant: 0.10M NPBA, 0.08M Aliquat 336 in 2-ethyl-1-hexanol--base washed.

| Time (days) | Propylene glycol concentrations (mol/l) | | Distribution Ratio | Temp. °C |
| | Aqueous (HPLC) | Organic (Calc.) | | |
	Initial	Final	Final		
2	0.102	0.0900	0.0120	0.133	28
14	0.102	0.0895	0.0125	0.140	25
19	0.102	0.0890	0.0130	0.146	25
19	0.102	0.0885	0.0135	0.153	25

Because of the apparent difficulty in reaching equilibrium with the gentle agitation of a shaker bath, more vigorous mixing methods were used for subsequent samples. Equilibration time was again investigated, as shown in Table 4-6. Although the scatter of the data in Table 4-6 (vigorous mixing) is greater than that in Table 4-5 (shaker bath), the latter decrease uniformly, while the former have a more random distribution. The unidirectional

Table 4-6. Change in distribution ratio with contact time for well agitated samples at 25°C.

| Time (hrs) | Propylene glycol concentrations (mol/l) | | Distribution Ratio | Extractant |
| | Aqueous (HPLC) | Organic (Calc.) | | |
	Initial	Final	Final		
3[a]	0.106	0.091	0.0151	0.17	(1)
4.5[b]	0.106	0.089	0.0174	0.20	(1)
29[c]	0.106	0.090	0.0156	0.17	(1)
3[a]	0.103	0.097	0.0068	0.070	(2)
4.5[b]	0.103	0.094	0.0095	0.10	(2)
29[c]	0.106	0.098	0.0084	0.086	(2)

(1) 0.09M NPBA, 0.09M Aliquat 336 in 2-ethyl-1-hexanol. Base washed.

(2) 0.10M NPBA, 0.09M Aliquat 336 in 2-ethyl-1-hexanol. Not washed.

a Mixed by magnetic stirring at ambient temperature for first hour, equilibrated in shaker bath.

b Mixed by magnetic stirring for first hour and again after 3 hours, equilibrated in shaker bath.

c Mixed by magnetic stirring for 1 hour. Placed in shaker bath next day and shaken vigorously by hand 3 times over 29 hours.

change suggests that equilibrium had not been attained. Random error, on the other hand, is expected from experimental variability. In both cases variabilities of order 1% for the aqueous analyses create variability of order 10% in the calculated distribution ratio. Therefore, without a reliable method for analyzing the organic phase, only minimal precision can be achieved for systems at these concentrations.

The formation of a third phase in the samples may be another cause of experimental variability. Observations related to third phase formation are summarized in Table 4-7.

Table 4-7. Observations during extraction runs

No.	Aliquat 336 (g/l)	NPBA (g/l)	Base Washed?	Aqueous Phase	Mixing Technique	Observations
(1)	40.1 (0.08M)	15.4 (0.10M)	yes	0.1M diol	(A)	emulsion coalesces precipitate
				0.1M diol	(A),(B)	emulsion coalesces
				0.1N NaOH	(B)	emulsion coalesces
(2)	45.4 (0.09M)	15.5 (0.10M)	no	water	(B)	stable emulsion
				0.1M diol	(A-C)	stable emulsion
(3)	45.4 (0.09M)	15.5 (0.09M)	yes	water	(B)	stable emulsion
				0.1M diol	(A-C)	coacervate
(4)	90.9 (0.18M)	31.0 (0.18M)	yes	0.1N NaOH	(B)	emulsion coalesces
				0.05-0.1M diol	(A),(D)	coacervate precipitate

The header "Extractant Solution *" spans the Aliquat 336, NPBA, and Base Washed columns.

*Weights are initial values before washing; molarities are calculated using inferred molecular weights and calculated losses of NPBA during washing.

(A) Shaker bath 25°C for minimum of 3 hours.
(B) Shake vigorously by hand for about 30 seconds.
(C) Magnetic stirring at high speed for at least 15 minutes.
(D) Shake gently by hand--repeatedly inverting vial over 30 seconds to 1 minute.

The stable emulsion reported in Table 4-7 consisted of a white, seemingly emulsified interface (in contrast to the rust colored organic phase). In samples where the extractant had not been washed with base, the emulsion comprised a volume close to ten percent of the main organic phase. When the extractant had been washed with base, however, the third phase was much smaller and did not cover the entire interface. A precipitate of fine black particles and

thin wisps of white emulsion or coacervate (identified as coacervate in Table 4-7) were also observed at the interfaces of several samples. Unless coalescence is reported, the third phase did not disappear after centrifuging.

From the data in Table 4-7 several patterns emerge with respect to the effect of extractant composition and mixing technique on third phase formation:

- Stable emulsions formed when samples containing the higher ratio of Aliquat 336 to NPBA in the extractant were vigorously agitated. This effect was most pronounced when the extractant had not been pretreated with base to ionize the acid.

- No stable emulsion or coacervate formed with the extractant (no. 1) containing the smaller ratio of Aliquat 336 to NPBA.

- A precipitate was observed in many, but not all, samples that contained an ionized extractant.

- No third phase was observed during base washing.

These data suggest that third phase formation can be avoided by appropriate selection of mixing technique and Aliquat 336 to NPBA ratio. The ratios in the extractants used were very close to 1:1; moreover, if the molecular weight of Aliquat 336 were closer to 450 than the 500 used in calculations, they would fall on either side of 1:1. This indicates that a stoichiometric ratio less than 1:1 (i.e., an excess of NPBA) is desirable to prevent emulsions. The presence of low molecular weight salts (i.e., NaOH and NaCl retained in organic phase after washing) also appears to inhibit emulsion formation.

Because of the variability in experimental results, including marked differences in the nature of the third phase formed, quantitative modeling of the data is difficult. Nonetheless, some definite trends were observed with respect to ratio of extractant to diol concentration. The data used in modeling include samples with the higher ratios of Aliquat 336 to NPBA (i.e., nos. 2-4 in Table 4-7). Calculations requiring the concentration of anionic NPBA$^-$ assumed 55% ionization for all NaOH-washed samples based on the results discussed in Section 4.3.2.

In Figure 4-6, the results of the extraction experiments are compared for systems containing different ratios of NPBA to diol. Results are averages of at least two identical samples. (Appendix C provides full tabulation of data.) Samples represented by columns 1 and 2 in Figure 4-6 were mixed by a gentle shaking by hand and those in columns 3 and 4 were mixed by high speed magnetic stirring (see Table 4-6). The extractants used in columns 1-3 were washed with NaOH, that used for column 4 was not. Column 5 is an average for the partition coefficient obtained from Figure 4-4.

As illustrated in Figure 4-6a, the distribution ratio for diol between the aqueous and organic phases does not differ substantially between the system containing no NPBA (column 5) and that with NPBA predominantly in the acid form (Column 4). The corresponding pH measurement, shown in Figure 4-6b, column 4, indicates that HCl is being extracted from the organic phase, but, as described in Section 4.3.2, the extraction of HCl by water corresponds to negligible ionization of NPBA. When a substantial fraction of the NPBA is in the ionic form, however, as shown by the three columns on the left of Figures 4-6a and 4-6c, the increases in distribution and loading are marked. These findings indicate that complex formation in 2-ethyl-1-hexanol is similar to that in water; in both cases, the complex will form only with anionic borate compounds.

Figure 4-6b shows the observed final pH for the aqueous phase in the extractions performed. The pH of the aqueous phase is related to the diol and NPBA concentrations as well as the amount of HCl extracted from the organic phase. In the aqueous phase some of the NPBA will ionize based on the pH in relation to its pK_a, and some will complex with the diol, thereby lowering the pH more than would be expected based on the pK_a alone. The pH near 3 observed when the extractant had not been washed with base can easily be explained by the extraction of HCl from the organic to the aqueous phase. The differences in pH for data in columns 1 to 3, on the other hand, are more likely related to extraction and ionization of NPBA by the aqueous phase.

As shown in Figure 4-7, the selectivity of the extractant for diol over water increases

(1)	(2)	(3)	(4)	(5)

Distribution ratio

0.51   0.32   0.18   0.09   P   0.08

a

pKa NPBA = 7.3   **Final Aqueous pH**

7.1   6.6   5.6   3.1   6.5

b

Loading: complexed diol/NPBA-

0.15   0.20   0.19   0/0   0/0

c

0.18M NPBA	0.18M NPBA	0.09M NPBA	0.10M NPBA	0 NPBA
(55% ionized)	(55% ionized)	(55% ionized)	(very little ionized)	
0.05M PG	0.10M PG	0.10M PG	0.10M PG	0.05-0.10M PG
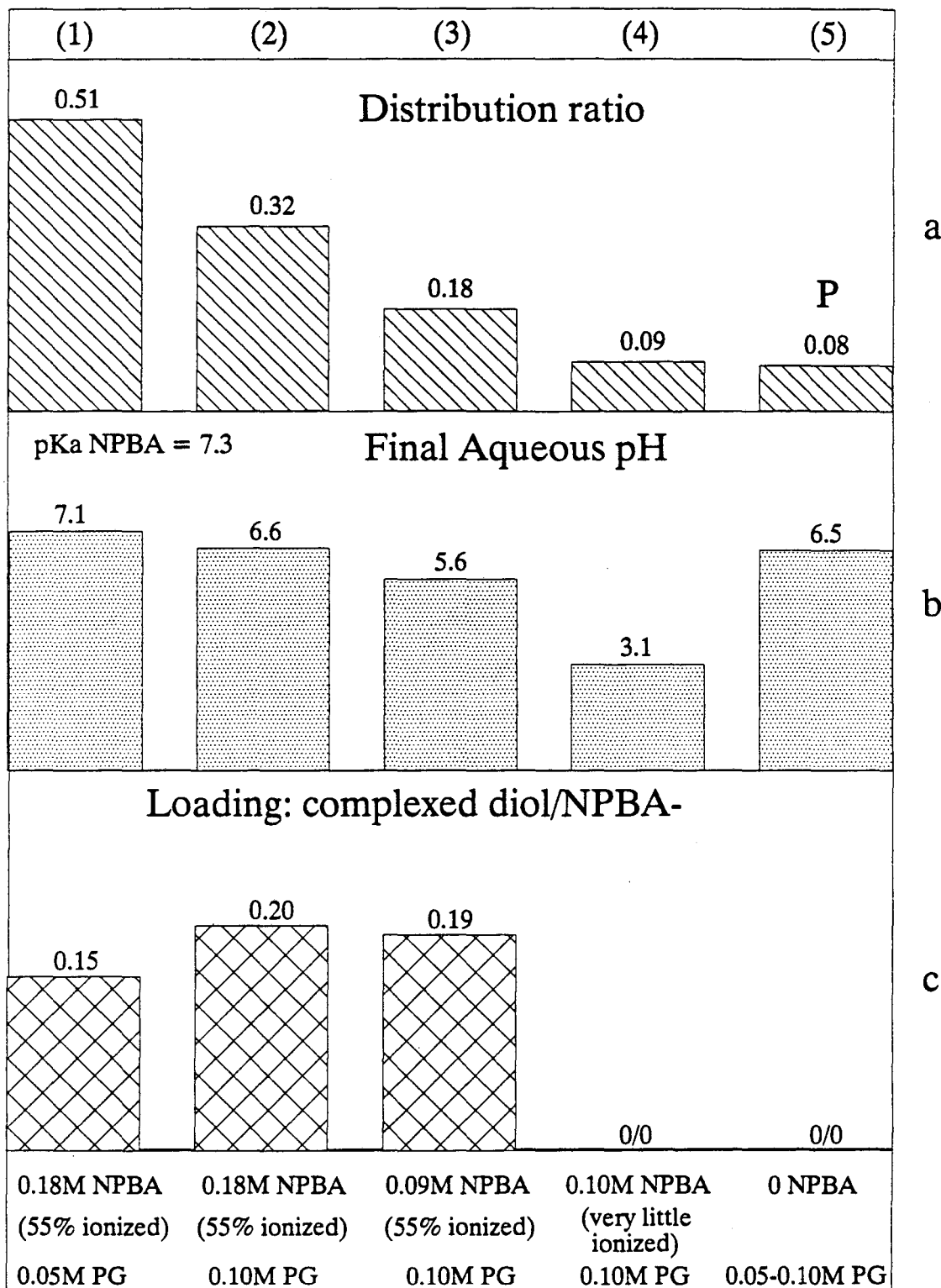
Figure 4-6. Equilibrium data (25 C) for 1,2-propanediol distributed between water and 2-ethyl-1-hexanol loaded with equimolar NPBA and Aliquat 336; volumetric phase ratio = 1:1.
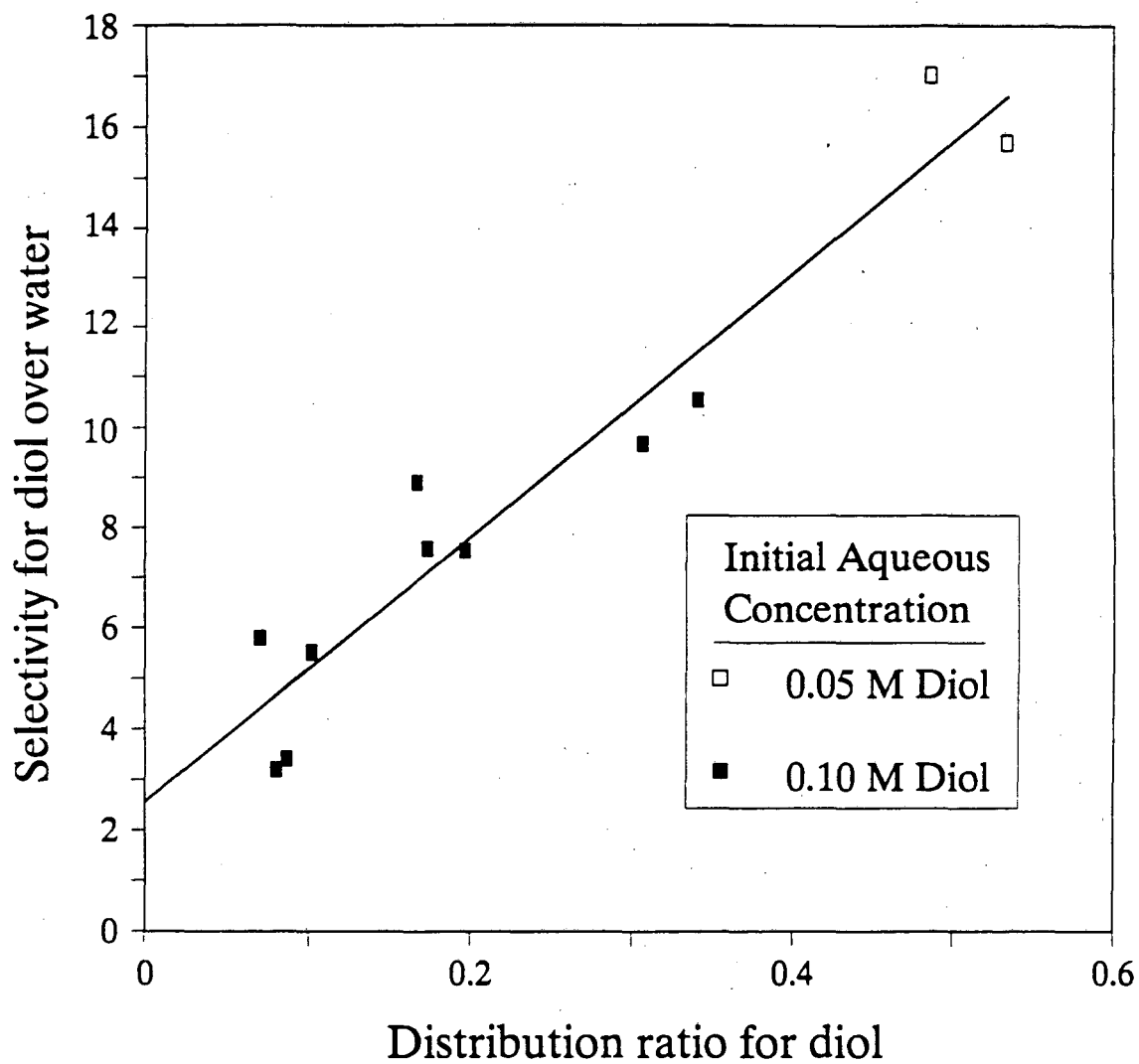
Figure 4-7. Selectivity vs. distribution ratio for 1,2-propanediol extracted from aqueous solution by 2-ethyl-1-hexanol loaded with equimolar NPBA and Aliquat 336 (0-0.18M).

proportionally to the distribution ratio over the limited concentration range studied. (Water extraction data are tabulated in Appendix C.) In essence, with increasing concentrations of NPBA in the organic phase, more diol is extracted but the amount of water coextracted remains relatively constant. The concentration of water in the mixed extractant, is, however, greater than that for 2-ethyl-1-hexanol alone. In the absence of NPBA, the 2-ethyl-1-hexanol remained saturated with water at a relatively constant concentration (approximately 3% by weight) both before and after extraction of diol. (The reported solubility of water in 2-ethyl-1-hexanol is 2.6% (Flick, 1985)). This is not surprising, since very small amounts of diol were extracted into the solvent under the conditions studied.

4.3.4 Chemical modeling of extraction data

The simplest relationship found to fit the extraction data is a linear dependence of the distribution ratio upon the ratio of NPBA⁻ to diol. As shown in Figure 4-8, this relationship holds for ratios of both equilibrium and initial concentrations.

A model can be constructed by assuming that the 1:1 anionic complex between NPBA⁻ and 1,2-propanediol forms in the organic phase. An equilibrium "constant" for complex formation, β_{org}, is defined incorporating the partition coefficient for the diol:

$$\beta_{org} = \frac{[NPBA \cdot Diol^-]_{org}}{[NPBA^-]_{org}[Diol]_{aq}} \qquad (4\text{-}10)$$

The model assumes that the ratio of activity coefficients for the three species in Equation 4-10 remains relatively constant with respect to concentration and can be incorporated into the equilibrium "constant". Equation 4-10 can be rearranged to get Equation 4-11.

$$\beta_{org}[NPBA^-]_{org} = \frac{[NPBA \cdot Diol^-]_{org}}{[Diol]_{aq}} \qquad (4\text{-}11)$$

Assuming that all the diol extracted in excess of that predicted by the partition coefficient for the diluent is complexed, then the left-hand-side of Equation 4-11 is equal to the distribution
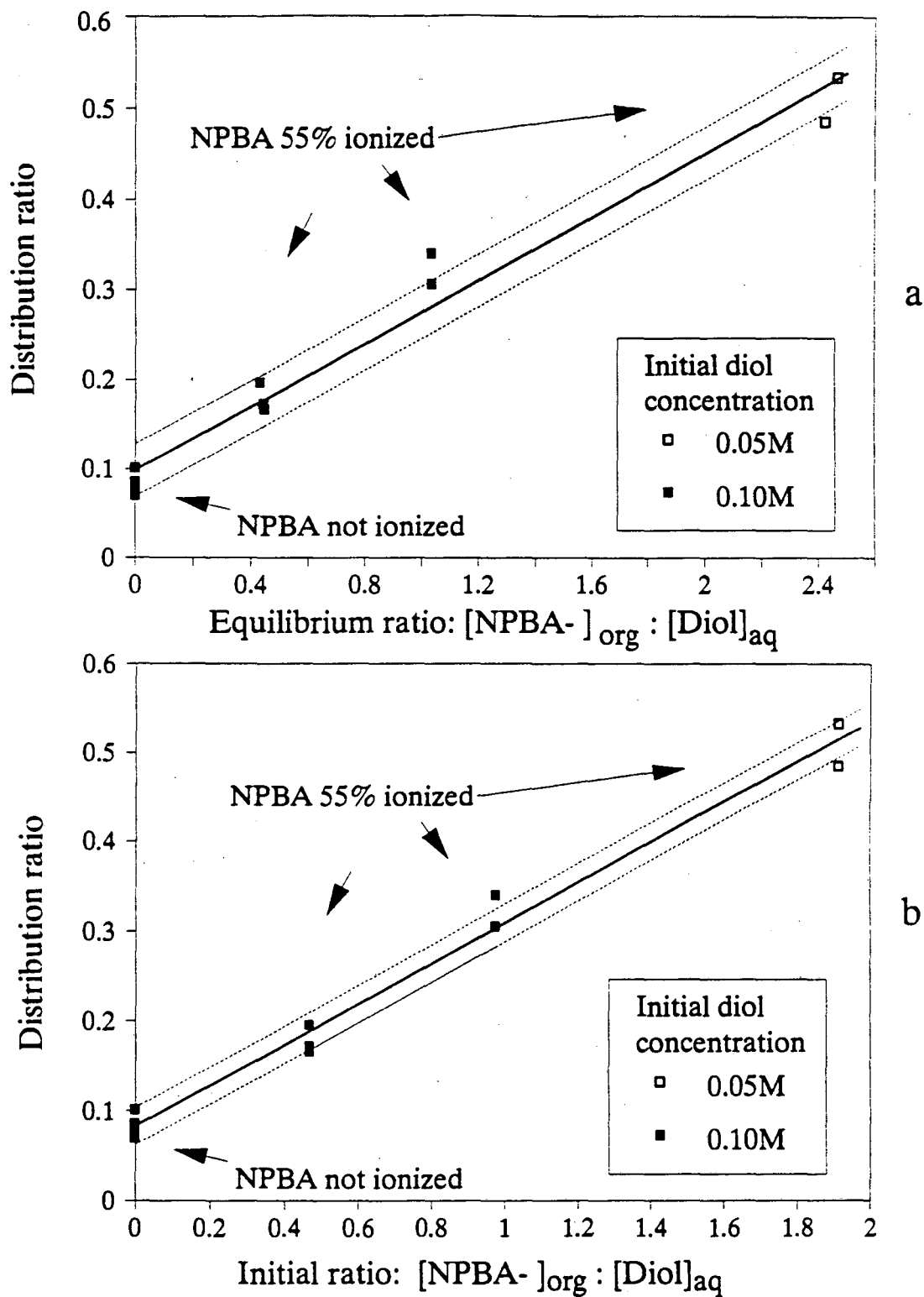
Figure 4-8. Change in distribution ratio for 1,2-propanediol with changing
(a) equilibrium ratio and (b) initial ratio of NPBA- to solute. Diluent is
2-ethyl-1-hexanol, counterion is TOMA+, T=25 C.

ratio after subtracting out the amount extracted by the diluent.

$$\frac{[NPBA \cdot Diol^-]_{org}}{[Diol]_{aq}} = D - P \times Vf \qquad (4\text{-}12)$$

When extractant concentrations are low, the volume fraction of diluent is close to one. By combining and rearranging Equations 4-11 and 4-12, a linear dependence of D on equilibrium anionic NPBA concentration at low extractant concentrations is obtained:

$$D = \beta_{org}[NPBA^-]_{org} + P \qquad (4\text{-}13)$$

D is plotted against $[NPBA^-]_{org}$ in Figure 4-9. The model appears to fit the data for a constant (0.1M) initial diol concentration. The distribution ratios for the pair of points at a lower (0.05M) diol concentration, however, are much higher than predicted by the model.

Figure 4-10 compares the data to the model for a 1:1 complex, plotted as loadings. As with Figure 4-9, samples with different total diol concentrations do not appear to fit the same loading curve.

4.3.5 Extractant losses

Table 4-8 presents data on the distribution of NPBA between the aqueous and extractant phases for the systems discussed in Section 4.3.4. In all cases, NPBA lost to aqueous solution was less than 1% of the total. Greatest losses were observed when the extractant had not been washed with base prior to extraction experiments. In these cases, the initial ratio of NPBA to Aliquat exceeded 1:1, whereas in the other cases, acid losses during pretreatment by base washing resulted in a ratio very close to 1:1. Small increases in losses were also observed with increasing equilibrium aqueous diol concentration. In Figure 4-11, the aqueous NPBA concentrations are shown as a function of pH. Using the pH, the pK_a, and the aqueous $\beta_{1,1}$ determined in Section 4.2.1, the aqueous concentrations are broken into the different species of NPBA. For the 1,2-propanediol concentrations in this system, it was concluded that about
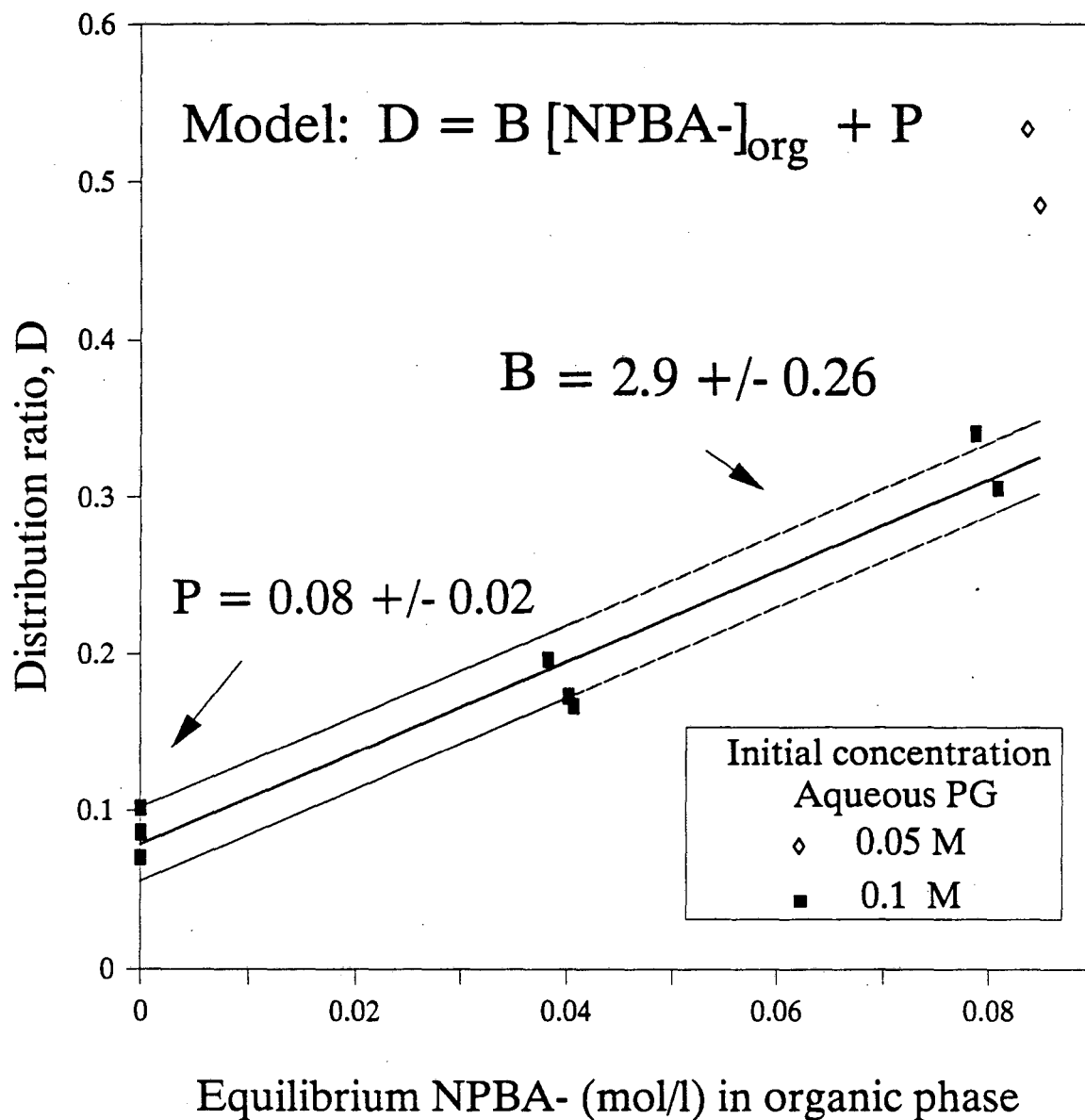
Figure 4-9. Dependence of distribution ratio for 1,2-propanediol on NPBA-concentration. Diluent is 2-ethyl-1-hexanol, counterion is TOMA+, T=25 C, NPBA is ca. 55% ionized.

Model for 1:1 Complex: $Z = \dfrac{B_{1,1}[\text{diol}]}{1 + B_{1,1}[\text{diol}]}$
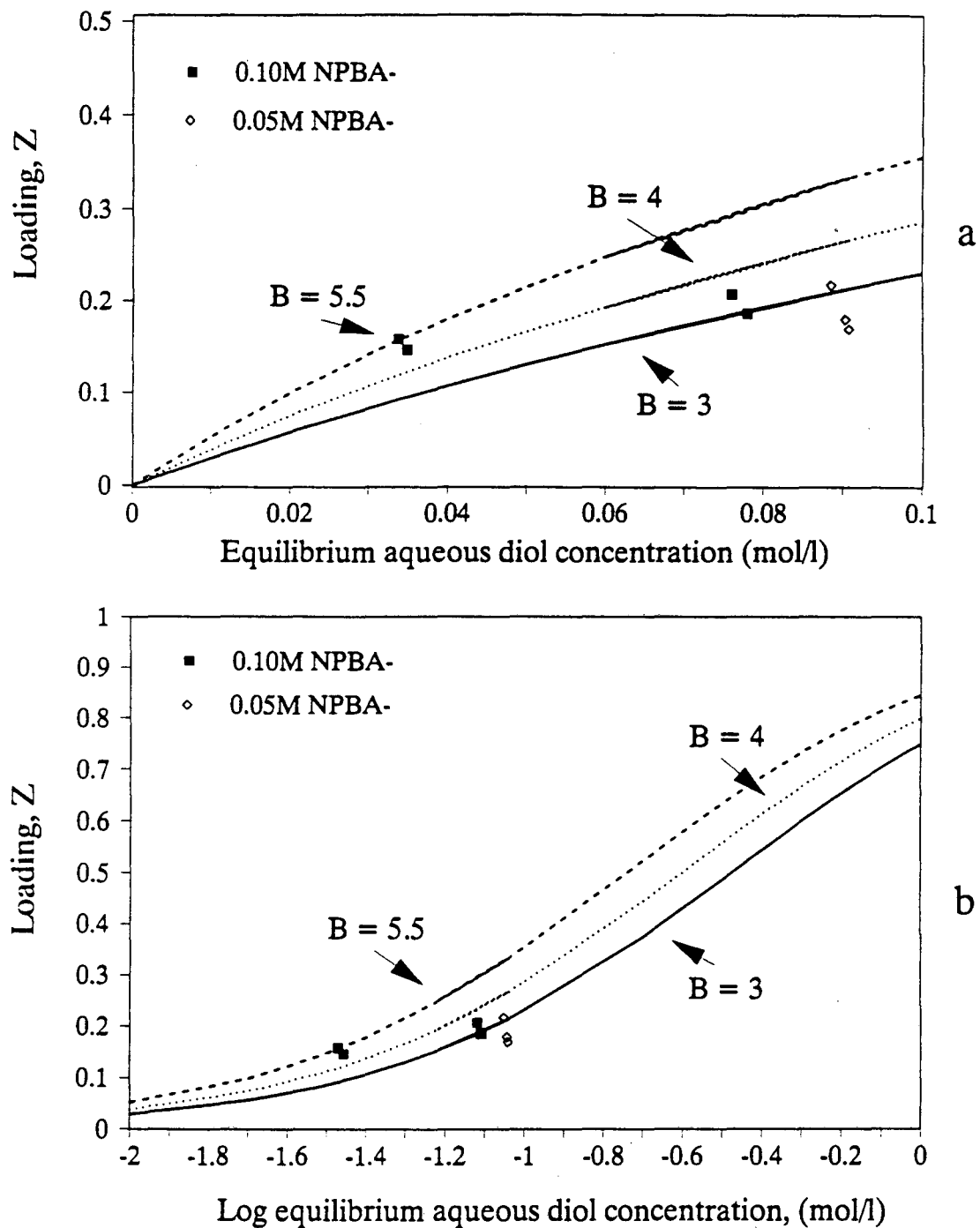
Figure 4-10. Loading of 1,2-propanediol on NPBA⁻ compared to models for 1:1 complexes. 25 C.

Table 4-8. Distribution of NPBA between aqueous and organic phases.

Aqueous Diol Concentration		Ratio: NPBA	NPBA Concentration		NPBA Losses	D
Initial	Final	Aliquat 336	Organic Initial	Aqueous Final	to Aqueous Solution	
0.05	0.034	1:1	0.18	2.0E-04	0.11%	920
0.10	0.077	1:1	0.18	2.2E-04	0.12%	830
0.10	0.090	1:1	0.09	3.1E-04	0.34%	290
0.10	0.096	1.2:1	0.10	8.0E-04	0.78%	130

Concentrations in mol/l.

Values represent averages of two or more identical samples.

10% of the anionic species would be complexed. At the pH values observed in these experiments, that results in a very small fraction of NPBA complexed in the aqueous phase.
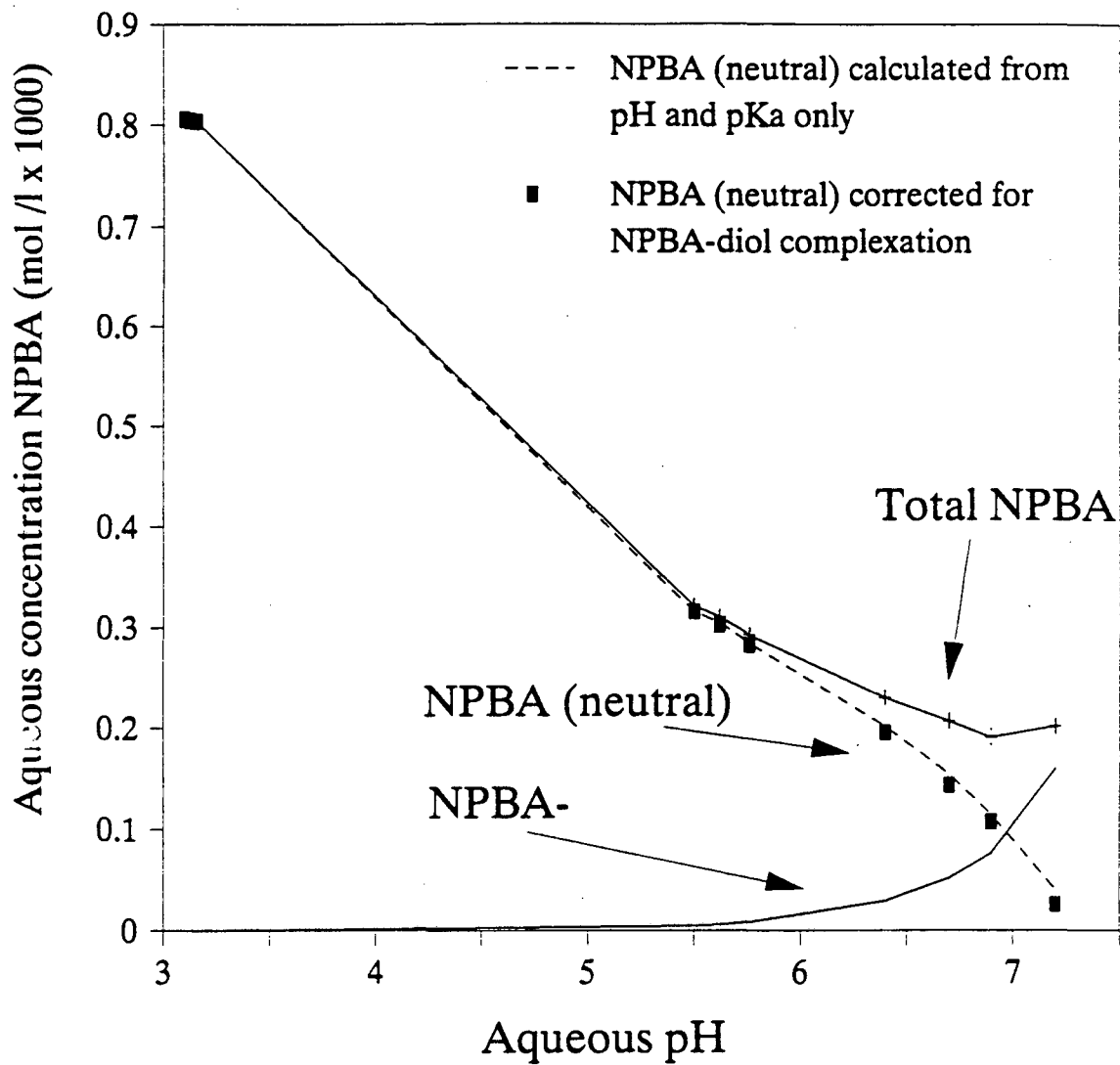
Figure 4-11. Effect of pH on concentration of NPBA in various forms in raffinate after 1,2-propanediol extraction by mixed ionic extractant containing NPBA and Aliquat 336. T = 25 C, Baq = 3.

5 DISCUSSION

5.1 Aqueous stability constants

The stability constants measured at 25°C for the 1,2-propanediol-NPBA complex are comparable to values for borate-1,2-propanediol complexes obtained by other researchers using pH-depression methods. (See Table 5-1.) The different value from Conner and

Table 5-1. Aqueous stability constants for 1:1 complexes of 1,2-propanediol with borate, phenylboronate (PBA⁻), and 3-nitrophenylboronate (NPBA⁻) at 25°C.

Anion	pK_a	Acid Solubility (g/100g H_2O)	$\beta_{1,1}$[a] $(mol/l)^{-1}$	Ionic Strength	Reference
Borate	8.98[b]	6.35[c]	4.05	0.05M[d]	Conner and Bulgrin, 1967.
			3.24	0.05M[e]	Paál, 1976.
			3.10	0.04M[d]	Roy, Laferriere, and Edwards, 1957.
PBA⁻	8.72[b]	2.5[f]	3.8		Lorand and Edwards, 1958.
NPBA⁻	7.1	0.45	3.17	0.1M[g]	Randel (this work).

[a] Stability constants determined by pH-depression and potentiometric methods.
[b] Babcock and Pizer, 1980. Measured in 0.1M KNO_3.
[c] Weast, 1980.
[d] $NaB(OH)_4^-$
[e] NaBr
[f] Windholz, 1983.
[g] KCl

Bulgrin's work (1967) can be attributed to their adjustment of the data for a "medium effect,"

which has since been refuted by Paál (1980b). The stability constant shown in Table 5-1 for the phenylboronate-1,2-propanediol complex is larger than the values for either borate or NPBA⁻. The aqueous solubility of NPBA, however, is less than one-tenth the solubility of boric acid and less than one-fifth that of phenylboronic acid, and the first ionization constant for NPBA is considerably larger (smaller pK_a) than both. Hence desirable properties of low solubility and low pK_a are achieved without significant decrease in strength of the complex formed.

The thermodynamic properties of the NPBA⁻-1,2-propanediol complex are compared in Table 5-2 to literature values for the 1:1 complex formed with borate. The values obtained

Table 5-2. Thermodynamic parameters for complexation reactions of 1,2-propanediol with borate and nitrophenylboronate ions to form a 1:1 complex in aqueous solution at 25°C.

log β	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol °K)	Method
Borate complexes				
0.46 +/- 0.01[a]	-2.64 +/- 0.08	- 9.3+/-0.6	-22 +/-2	Calorimetric[a]
0.50+/-0.01	-2.85	-21.4+/-2.1	-62.0+/-6.3	Temp. dep. of β[b]
0.61	-3.47+/-0.10	-12.6+/-1.3	-30.5+/-8	Temp. dep. of β[c]
NPBA⁻ complexes				
0.50+/-0.01	-2.86+/-0.06	-19 +/- 3	-56 +/- 10	Temp. dep. of β[d]

Error ranges represent the standard error of the mean.

[a] Aruga, 1985. Values for 1.0M $NaNO_3$. β (1.0M $NaClO_4$) obtained from Paál, 1976.

[b] Paál, 1977. Values for 0.004M and 0.008M $NaB(OH)_4^-$.

[c] Conner and Bulgrin, 1967. Values for 0.05M $NaB(OH)_4^-$. "Medium" correction applied.

[d] This work. Values for 0.1M KCl.

in this experiment for the NPBA complex are very close to the values determined by Paál

(1977) for the 1:1 borate complex; Paál also used temperature dependence of the equilibrium constant to calculate enthalpy and entropy. Conner and Bulgrin's data do not match as closely, but are of the same order of magnitude. Aruga's value for $\Delta H°$, measured calorimetrically for the borate complex, is less than half the value obtained by Paál for the same complex. Calorimetric values for complexation enthalpy are generally considered more reliable (Aruga, 1985).

When comparing thermodynamic data for borate-1,2-propanediol complexes with those for other diols, Aruga (1985) noted that both sign and relative magnitude of $\Delta G°$ are determined by $\Delta H°$. He postulated that this dependence on enthalpy indicated a stronger influence of solute-solute interaction, rather than medium interaction, on the complexation. By calculating the electrostatic and nonelectrostatic components of the enthalpy, Aruga confirmed that electrostatic contributions were minimal and that covalent borate-polyol interactions were dominant in determining $\Delta H°$ and $\Delta G°$.

Paál (1977) also discusses the covalent character of the C-O-B bond, making reference to Lewis acid-base concepts. Although boric acid is generally considered a hard Lewis acid, the thermodynamic data for borate:diol complex formation correspond to those predicted for soft-soft interactions. Aqueous complex formation between soft ions and weaker soft neutral ligands is exothermic, and the entropy change can be negative. Covalent interactions dominate these soft-soft interactions (Jensen, 1980, 286). Further, the electron donor properties of the methyl group on 1,2-propanediol increase the covalent character of the C-O-B bond. Conner and Bulgrin (1967) investigated the change in complexation strength along a series of methyl-substituted homologs of 1,2-ethanediol. They found that $\Delta H°$ increased monotonically with the degree of substitution of the hydroxyl carbons. Paál cites this as further evidence of the covalent character of the bond.

The predominance of solute-solute interactions over electrostatic and solvating effects indicates that complex strength in organic solvents capable of solvating all reacting species and products should be of a similar order of magnitude to that in aqueous solutions. This was

in fact observed in this study, as will be discussed below.

The magnitude of the free energy of bond formation ($\Delta G°$) for the 1,2-propanediol-NPBA$^-$ complex, 2.81 kJ/mol at 25°C, is less than the 10-50 kJ/mol range cited by King (1987) as most suited for chemically complexing separation processes. Because of this, very large ratios of extractant to diol should be required before there is a substantial concentrating effect observed in the organic phase.

5.2 Conversion of NPBA to anionic form

NPBA was converted to anionic form by washing with a strong base or a high pH (7.9) buffer. When 0.1N NaOH contacted the mixed extractant for a few minutes, slightly more than 50% of the base was consumed, primarily through ionization of NPBA. The amount of NPBA converted to anionic form was measured both by exchange of chloride (the initial counter-ion for TOMA$^+$) and base consumption (via pH change), with the calculated conversions differing by about 15 to 20 %. The chloride calculation may be superior because the chloride measurement is more precise and because the calculation does not require any assumptions regarding OH$^-$ and NPBA equilibria in the aqueous phase.

Losses of NPBA to a basic wash solution can be substantial. In one wash with 0.1N NaOH, for example, 13% of the total NPBA was lost during pretreatment. NPBA losses to buffered solutions were not measured, but losses to a water wash were less than 1%. These results suggest that extractant pretreatment can be optimized by comparing amounts of NPBA converted to anionic form with losses to the aqueous phase. It is possible that buffers at a lower pH than 0.1N NaOH may extract less NPBA from the organic phase, while still converting NPBA to anionic form at a reasonably high efficiency.

5.3 Extraction of 1,2-propanediol by a mixed ionic extractant

1,2-propanediol was extracted from aqueous solution by a mixed ionic extractant composed of NPBA and Aliquat 336 dissolved in 2-ethyl-1-hexanol. In extraction

experiments where the Aliquat 336 to NPBA (total) ratio was near 1:1 and possibly somewhat higher, coacervates, precipitates, or emulsions frequently formed. This phenomenon occurred primarily when the aqueous and organic phases were vigorously mixed.

Although mixed ionic extractants containing quaternary amines have been reported to form emulsions when shaken with dilute aqueous salt solutions (Lynn and Charlesworth, n.d.), it was hoped that the use of 2-ethyl-1-hexanol would suppress third phase formation. 2-Ethyl-1-hexanol is commonly used to inhibit third phase and emulsion formation in commercial solvent extraction processes (Ritcey and Ashbrook, 1988). In batch extraction experiments using a similar diluent, 1-octanol, Tamada (Tamada, 1989; Tamada, Kertes, and King, 1990) also noted coacervate formation. The "pseudo-third phase" formed when succinic acid was extracted from water using a tertiary amine, Alamine 336 (Henkel Corporation), in 1-octanol. A third phase did not form when 1-octanol was mixed with an approximately equal volume of chloroform or when other active diluents, including methylene chloride and methyl isobutyl ketone, were used.

Another similarity between the systems investigated in this work and Tamada's 1-octanol/Alamine 336/succinic acid system is the shape of the loading curve. As shown in Figure 4-10, the loading of NPBA⁻ was relatively constant (about 0.15-0.2) with respect to equilibrium diol concentration and did not appear to fit the model for a 1:1 complex. In Tamada's system, the loading curve was flat at low loadings and the obvious plateau at unity expected for 1:1 complexes did not occur. She interpreted that data as a complex with two amines per acid. Since loading did not increase as a function of NPBA⁻ concentration in this work, Tamada's explanation does not appear applicable. Additional data over a broader concentration range are needed before firm conclusions can be drawn.

The data clearly showed, however, that the presence of NPBA, in anionic form and paired with Aliquat 336, significantly enhanced extraction of the diol by the organic phase. Distribution ratios increased as ratio of NPBA⁻ to diol increased. The distribution ratio without pretreating the extractant to convert NPBA to anionic form was about 0.09, compared

to a partition coefficient of 0.08 for the diluent, 2-ethyl-1-hexanol. Using an extractant pretreated with base yielded distribution ratios from 0.18, for an NPBA⁻ to diol ratio of 1:2, to 0.51, for a ratio of 2.5:1. While still quite low, these distribution ratios approach the highest reported distribution ratio for 1,2-propanediol--D = 0.7 for m-cresol diluted both in m-xylene and in chloroform at a molar ratio of about 20:1, m-cresol:diol (Arenson, 1989). At higher extractant concentrations, one can reasonably expect that extraction by NPBA⁻-TOMA⁺ ion-pairs will yield higher distribution ratios for 1,2-propanediol than for previously studied extractants.

Further, for a given total diol concentration (0.1M aqueous), the distribution ratio varied approximately linearly with equilibrium NPBA⁻ concentration. From this, the stability constant for complex formation in the organic phase was calculated. This value, 2.9, was nearly equal to the value calculated in the aqueous phase, 3.17. At a total diol concentration of 0.05M, the distribution was considerably higher than would be predicted from the 0.1M data and the aqueous stability constant. Additional data are needed to determine whether these deviations represent a true dependence of the complex stability on total diol concentration or whether the effect is true only for low loadings of extractant (i.e., low NPBA⁻ to diol ratios). In order to model this system fully, however, both additional data and a review of the assumptions and simplifications, particularly with respect to activity coefficients, are needed.

Nonetheless, these data support the hypothesis that complex formation in the organic phase occurs with anionic NPBA and that the strength of the complex is of the same order of magnitude as that in the aqueous phase. These results are entirely consistent with the thermodynamic data discussed above, which indicate that complex strength is more dependent on the solutes interacting than on the solvating medium. The data obtained for 1,2-propanediol provide information on some of the characteristics of NPBA⁻-diol complexation in organic solvents that can be applied to studies of diols which form stronger

complexes with NPBA and other borate compounds. The similarity between the values for the stability constant obtained in the aqueous and the organic phases suggests that the aqueous stability constants, for which there is a wide literature, and which are easier to determine experimentally, can be used as predictors of which diols are likely to be effectively extracted from aqueous solution by means of complexation with boronic acids.

5.4 Implementation

The data gathered in this work indicate several phenomena that may hamper implementation of the NPBA-diol complexation reaction in an industrial separation process. First, a commercial solvent extraction process is very difficult to operate without rapid coalescence of the two phases. Future tests with several other diluents may reveal that emulsion formation is particular to 2-ethyl-1-hexanol and related solvents. Or, control of Aliquat 336 to NPBA ratio and agitation rates may be sufficient to suppress emulsion formation. In the event that emulsion formation cannot be controlled, incorporation of this system into a liquid emulsion membrane, like that used by Shinbo et al. (1986), may be feasible. Alternatively, NPBA can be incorporated into a solid support, such as an adsorbent. An adsorbent would be expected to function best when the aqueous feed solution was at a pH higher than 7. There is also some evidence that surface buffering effects can occur, for example, by incorporating amines into the support near the NPBA functionalities (Lochmüller and Hill, 1986). Such a technique can be used as an alternative to buffering the aqueous feed at a high pH.

Another critical concern is the economics of the process. Important factors include irrecoverable losses of the extractant to the aqueous phase. Losses to the initial wash solution are likely to be more easily recovered than losses, during extraction, to the raffinate or losses during regeneration. Further, regeneration methods need to be explored to determine if any concentrating effects from the extraction process can be maintained through the regeneration step. Costs of regeneration chemicals, if needed are also a significant factor.

REFERENCES

Akparov, V. and V. Stepanov. 1978. Phenylboronic acid as a ligand for biospecific chromatography of serine proteinases. *J. Chrom.* **155**, 329-336.

Albert, A. and E.P. Serjeant. 1984. *The determination of ionization constants--A laboratory manual.* New York: Chapman and Hall.

Aldrich Chemical Company, Inc. 1988. *Catalog handbook of fine chemicals.* Milwaukee, WI: Aldrich Chemical Company, Inc.

Antikainen, P.J. 1954. The influence of the concentrations of boric acid and mannitol on the ionization of boric acid in aqueous solutions of some alkali salts. *Ann. Acad. Sci. Fennicae Ser. A II.* **56**, 1-61.

Arenson, D.R. 1989. Separation of low molecular weight alcohols from dilute aqueous solutions by reversible chemical complexation. Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley.

_____, A.S. Kertes, and C.J. King. 1988. Extraction of butanol isomers by m-cresol. *J. Solution Chem.* 17(12): 1119-1132.

Aruga, R. 1985. Borate-polyol complexes in aqueous solution: Determination of enthalpies by thermometric titrimetry. *Talanta.* **32(6)**, 517-519.

Babcock, L. and R. Pizer. 1980. Dynamics of boron acid complexation reactions. Formation of 1:1 boron acid-ligand complexes. *Inorg. Chem.* **19**, 56-61.

Barker, S.A. et al. 1973. The interaction of areneboronic acids with monosaccharides. *Carbohyd. Res.* **26**, 33-40.

Bean, F.R. and J.R. Johnson. 1932. Derivatives of phenylboric acid, their preparation and action upon bacteria. II. Hydroxyphenylboric acids. *J. Am. Chem. Soc.* **54**, 4415-4425.

Bettman, B., G.E.K. Branch, and D.L. Yabroff. 1934. Dissociation constants of organic boric acids. *J. Am. Chem. Soc.* **56**, 1865-1870.

Bio-Rad. 1986. Affi-Gel® 601 boronate affinity gel to separate ribonucleotides, ribonucleosides, sugars, catecholamines, and coenzymes. Bulletin 1066.

Böeseken, J. 1949. The use of boric acid for the determination of the configuration of carbohydrates. *Adv. Carbohydr. Chem.* **4**, 189-210.

Bouriotis, V., I.J. Galpin, and P.D.G. Dean. 1981. Applications of immobilized phenylboronic acids as supports for group-specific ligands in the affinity chromatography of enzymes. *J. Chrom.* **210**, 267-278.

Branch, G.E.K., D.L. Yabroff, and B. Bettman. 1934. The dissociation constants of the chlorophenyl and phenetyl boric acids. *J. Am. Chem. Soc.* **56**, 937-941.

Brown, E.S., et al. 1980. Glycols (ethylene and propylene) in *Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed. vol 11*. New York: John Wiley & Sons. pp. 933-956.

Busche, R.M. 1984. Recovering chemical products from dilute fermentation broths. *Biotechnology and Bioengineering Symp*. No. 13, 597-615.

_____. 1985. The business of biomass. *Biotech. Progress*. 1(3), 165-180.

Cameron, D.C. and C.L. Cooney. 1986. A novel fermentation: The production of R(-)-1,2-propanediol and acetol by clostridium thermosaccharolyticum. *Biotechnology*. 4: 651-654.

_____, I-Teh Tong, and M. Cockrem. 1990. Microbial production of propanediols. *Proceedings, Corn Utilization Conference III*. St. Louis, MO: National Corn Growers Association.

Chemical Marketing Reporter. February 9, 1987.

Collander,R. 1951. The partition of organic compounds between higher alcohols and water. *Acta Chem. Scand*. 5, 774-780.

Conner, J.M. and V.C. Bulgrin. 1967. Equilibria between borate ion and polyols in aqueous solution. *J. Inorg. Nucl. Chem*. 29, 1953-1961.

Conway, J.B., and J.J. Norton. 1951. Ternary system furfural-ethylene glycol-water. *Ind. Eng. Chem*. 43(6), 1433-1435.

Davis, H.B. and C.J.B. Mott. 1980. Interaction of boric acid and borates with carbohydrates and related substances. *J. Chem Soc., Faraday Trans. I*. 76, 1991-2002.

Dawber, J.G. et al. 1988. A polarimetric and [11]B and ^{13}C nuclear magnetic resonance study of the reaction of the tetrahydroxyborate ion with polyols and carbohydrates. *J. Chem Soc., Faraday Trans. I*. 84, 41-56.

_____ and D.H. Matusin. 1982. Potentiometric and polarimetric studies of the reaction of boric acid and tetrahydroxyborate ion with polyhydroxy compounds. *J. Chem. Soc., Faraday Trans. I*. 78, 2521-2528.

_____ and S.I.E. Green. 1986. An [11]B nuclear magnetic resonance study of the reaction of the tetrahydroxyborate ion with poyhydroxy compounds. *J. Chem. Soc., Faraday Trans. I*. 82, 3407-3413.

Dyrssen, D., L. Uppström, and M. Zangen. 1969. A study of the extraction of boric acid with 2,2-diethylpropanediol-1,3 and 2-ethylhexanediol-1,3 in chloroform. *Anal. Chim. Acta*. 46, 55-61.

Elliger, C.A., B.G. Chan, and W.L. Stanley. 1975. p-Vinylbenzeneboronic acid polymers for separation of vicinal diols. *J. Chrom*. 104(1), 57-61.

Eyal, A., and A. Baniel. 1982. Extraction of strong mineral acids by organic acid-base couples. *Ind. Eng. Chem. Proc. Des. Develop*. 21, 334-337.

Flick, E.W. Ed. 1985. *Industrial solvents handbook*, 3rd ed. Park Ridge, NJ: Noyes Data Corp.

Glad, M. et al. 1980. High-performance liquid affinity chromatography of nucleosides, nucleotides and carbohydrates with boronic acid-substituted microparticulate silica. *J. Chrom.*, **200**, 254-260.

Grinstead, R.R., et al. 1969. Extraction by phase separation with mixed ionic solvents. *Ind. Eng. Chem. Prod. Res. Develop.* **8**, 218-227.

Hansch, C. and A. Leo. 1979. *Substituent constants for correlation analysis in chemistry and biology*. New York: Wiley.

Henderson, W.G., et al. 1973. The interconversion of aqueous boron species and the interaction of borate with diols: A ^{11}B N.M.R. study. *Carbohyd. Res.* **28**, 1-12.

Huttunen, E. 1984. Chelation of pentoses and pentitols with boric, phenylboronic, germanic, arsenious and telluric acids in aqueous solutions. *Ann. Acad. Sci. Fennicae Ser A II.* **201**, 1-45.

Jain, M.K., R. Datta, and J.G. Zeikus. 1989. High-value organic acids fermentation--emerging processes and products. *Bioprocess engineering--the first generation*. Chapter 25. ed., T.K. Ghose. Chichester: Ellis Horwood Ltd.

Jenson, W.B. 1980. *The Lewis acid-base concepts--An overview*. New York: John Wiley and Sons.

Juillard, J. and N. Gueguen. 1967. Sur la dissociation de quelques acides arylboriques en solvants mixtes eau-méthanol. *C. R. Hebd. Séances Acad. Sci., Ser. C.* **264**, 259-261.

Kertes, A.S., and C.J. King. 1987. Extraction chemistry of low molecular weight aliphatic alcohols. *Chem. Rev.* **87**, 687-710.

Khym, J.P. and L.P. Zill. 1952. The separation of sugars by ion exchange. *J. Am. Chem. Soc.* **74**, 2090-2094.

Kilpi, S. 1952. A differential potentiometric method of measuring acid and base dissociation constants. *J. Am. Chem. Soc.* **74**, 5296-5298.

King, C.J. 1987. Separation processes based on reversible chemical complexation. *Handbook of Separation Process Technology*. Chapter 15. R.W. Rousseau, ed. NY: Wiley.

Korenman, Y.I. 1972. The salting-in and salting-out of napthols. *Russ. J. Phys. Chem.* **46**(10), 1496-99.

_____. 1973a. Molecular complexes of napthols in non-aqueous solutions. *Russ. J. Phys. Chem.* **47**(3), 313-314.

_____. 1973b. Formation of molecular complexes of *p*-halogenophenols in aqueous solution. *Russ. J. Phys. Chem.* **47**(3), 348-350.

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_____. 1974a. Salting-in and salting-out of *o*-halogenophenols. *Russ. J. Phys. Chem.* **48**(2), 385-387.

_____. 1974b. Extraction of xylenols in the presence of hydrotropic compounds. *Russ. J. Phys. Chem.* **48**(3), 653-655.

Kortrüm, G., W. Vogel, and A. Andrussow. 1961. *Dissociation constants of organic acids in aqueous solution.* London: Butterworths.

Laddha, G.S., and J.M. Smith. 1948. The systems glycol-amyl alcohol-water and glycol-hexyl alcohol-water. *Ind. Eng. Chem.* **40**, 494-496.

Leo, A., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. *Chemical Reviews.* **71**(6), 525-616.

Levina, K.S. and A.S. Zheleznyak. 1975. Distribution of monohydric and dihydric alcohols in the ethyl-acetate-water and butyl-acetate-water systems. *Russ. J. Phys. Chem.* **49**(4), 499-501.

Lochmüller, C.H. and W.B. Hill. 1986. Manipulation of stationary-phase acid-base properties by a surface-buffering effect: Boronic acid-saccharide complexation, in *Chromatography and Separation Chemistry, ACS Symposium Series 297.* Washington, D.C.: American Chemical Society, pp. 210-225.

Lorand, J.P. and J.O. Edwards. 1959. Polyol complexes and structure of the benzeneboronate ion. *J. Org. Chem.* **24**, 769-774.

Lynn, S. and R.K. Charlesworth. n.d. Mixed ionic solvents for extraction of inorganic salts from aqueous solution (unpublished).

_____. March 14, 1972. Extraction of alkali, alkaline earth and lead halides and chlorates using an acid-amine mixed-extractant. U.S. Patent No. 3,649,219.

Maestas, R.R., et al. 1980. Polyacrylamide-boronate beads saturated with biomolecules: A new general support for affinity chromatography of enzymes. *J. Chrom.* **189**, 225-231.

Matsumoto, K., and S. Sone. 1956. Mutual solubility of monoethyleneglycol-water-butanol system. *J. Pharm. Soc. Japan.* **76**(5), 475-478.

Mattock, G. and G.R. Taylor. 1961. *pH measurement and titration.* London: Heywood and Company, Ltd.

Moran, R.G., and W. C. Werkheiser. 1978. A borate column for the separation of ribo- and deoxyribonucleosides. *Analytical Biochemistry.* **88**, 668-674.

Myöhänen, T.A., V. Bouriotis, and P.D.G. Dean. 1981. Affinity chromatography of yeast α-glucosides using ligand mediated chromatography on immobilized phenylboronic acids. *Biochem. J.* **197**, 683-688.

National Research Council. 1987. *Separation and Purification: Critical Needs and Opportunities.* National Academy Press: Washington, D.C.

Nikurashina, N.I., A.I. Gei, and G.I. Kharitonova. 1976. Investigation of the miscibility of acrylonitrile, ethylene glycol, and water by the method of sections. *Russ. J. Phys.Chem.* 50(1), 74-75.

Oertel, R.P. 1972. Raman study of aqueous monoborate-polyol complexes. Equilibria in the monoborate-1,2-ethanediol system. *Inorg. Chem.* 11(3), 544-549.

Onak, T.P., et al. 1959. The B^{11} nuclear magnetic resonance chemical shifts and spin coupling values for various compounds. *J. Phys. Chem.* 63, 1533-1535.

Othmer, D.F., et al. 1945. Liquid-liquid extraction data: systems used in butadiene manufacture from butylene glycol. *Ind. Eng. Chem.* 37(9), 890-894.

Paál, T.L. 1976. On the formation of glycol-borate complexes in aqueous medium, III. *Acta Chim. (Budapest).* 91(4), 393-402.

_____. 1977. Formation of glycol-borate complexes in aqueous medium, IV. *Acta. Chim. (Budapest).* 95(1), 31-40.

_____. 1980a. Study of the glycol-boric acid complex formation equilibria in aqueous solution. *Acta Chim. Acad. Sci. Hung.* 103(2), 181-191.

_____. 1980b. Study of the weak interactions operating between boric acid and polar organic compounds in aqueous solutions. *Acta Chim. Acad. Sci. Hung.* 103(2), 193-198.

_____ and L. Barcza. 1975. The formation of glycol-borates in aqueous medium, I. *Acta Chim. (Budapest).* 85(2), 139-146.

Pal, B.C. 1978. Novel application of sugar-borate complexation for separation of ribo-, 2'-deoxribo-, and aribonucleosides on cation-exchange resin. *J. Chrom.* 148, 545-548.

Perry, R.H. and D. W. Green, Eds. 1984. *Perry's Chemical Engineers' Handbook*, 6th ed. New York: McGraw-Hill, Inc.

Pierce. 1986. GLYCO• GEL™. Technical bulletin.

Pierce. 1988. SelectiSpher-10™ boronate HPLAC columns. HPLAC Bulletin No.1.

Raja Rao, M., and C. Venkata Rao. 1957. Ternary liquid equilibria. IV. Various systems. *J. Appl. Chem.* 7, 659-666.

Reiche, C.R. and J.A. Heckman. July 20, 1976. Method of producing glycols. U.S. Patent No. 3,970,711.

Ritcey, G.M. and A.W. Ashbrook. 1988. Hydrometallurgical Extraction. *Handbook of separation techniques for chemical engineers, 2nd ed.* Section 2.2. ed. P.A. Schweitzer. New York: McGraw-Hill. pp. 2-105 to 2-130.

Roy, G.L., A. L. Laferriere, and J.O. Edwards. 1957. A comparative study of polyol complexes of arsenite, borate, and tellurate ions. *J. Inorg. Nucl. Chem.* 4, 106-114.

Sánchez-Riera, F., D.C. Cameron, and C.L. Cooney. 1987. Influence of environmental factors in the production of R(-)-1,2-propanediol by clostridium thermosaccharolyticum. *Biotechnology Letters.* 9(7), 449-454.

Sargent, R. and W. Rieman III. 1956. Application of the plate theory to the anion-exchange chromatography of glycols. *J. Phys. Chem.* 60, 1370-1372.

Seaman, W. and J.R. Johnson. 1931. Derivatives of phenylboric acid, their preparation and action upon bacteria. *J. Am. Chem. Soc.* 53, 711-723.

Shinbo, T., et al. 1986. Uphill transport of monosaccharides across an organic liquid membrane. *J. Chem. Soc., Chem. Commun.* No. 4, 349-351.

Sienkiewicz, P.A., and D.C. Roberts. 1980. Chemical Affinity systems-I: pH dependence of boronic acid-diol affinity in aqueous solution. *J. Inorg. Nucl. Chem.* 42, 1559-1575.

Simon, E.S., et al. 1987. A combined microbial/chemical synthesis of (+)-(R)-methyloxirane having high enantiomeric excess. *J. Org. Chem.* 52, 4042-4044.

Tamada, J.A. 1989. Extraction of carboxylic acids by amine extractants. Ph.D. Dissertation, Department of Chemical Engineering, University of California, Berkeley.

_____, A.S. Kertes, and C.J. King. 1990. Extraction of carboxylic acids with amine extractants: 1. Equilibria and law of mass action modeling. *Ind. Eng. Chem. Res.* 29: 1319-1326.

_____, and C. J. King. 1990a. Extraction of carboxylic acids with amine extractants: 2. Chemical interactions and interpretations. *Ind. Eng. Chem. Res.* 29: 1327-1333.

_____. 1990b. Extraction of carboxylic acids with amine extractants: 3. Temperature, water coextraction , and process considerations. *Ind. Eng. Chem. Res.* 29: 1333-1338.

Torssell, K. 1957. The chemistry of arylboric acids: V. Effects of arylboric acids on micro-organisms and enzymes. *Arkiv för Kemi.* 10(39): 529-540.

_____. 1964. Chemistry of boronic and borinic acids in *Progress in Boron Chemistry.* vol 1. Eds. H. Steinberg and A.L. McCloskey. New York: Pergamon Press, pp. 369-415.

Van Slyke, D.D. 1922. On the measurement of buffer values and on the relationship of buffer value to the dissociation constant of the bufffer and the concentration of the buffer solution. *J. Biol. Chem.* 52, 525-570.

Van Duin, M., et al. 1984. Studies on borate esters, I: The pH dependence of the stability of esters of boric acid and borate in aqueous medium as studied by ^{11}B NMR. *Tetrahedron.* 40(15), 2901-2911.

_____. 1985. Studies on borate esters, II: Structure and stability of borate esters of polyhyroxycarboxylates and related polyols in aqueous alkaline media as studied by ^{11}B NMR. *Tetrahedron.* 41(16), 3411-3421.

Walborg, E.F. Jr., and R.S. Lantz. 1968. Separation and quantitation of saccharides by ion-exchange chromatography utilizing boric acid/glycerol buffers. *Analytical Biochemistry*. 22, 123-133.

_____, D.B. Ray, and L.E. Öhrberg. 1969. Ion-exchange chromatography of saccharides: An improved system utilizing boric acid/ 2,3-butanediol buffers. *Analytical Biochemistry*. 29, 433-440.

Weast, R.C., ed. 1980. *CRC Handbook of Chemistry and Physics*. 61st ed. Boca Raton, FL: CRC Press.

Weith, H.L., J.L. Wiebers, and P.T. Gilham. 1970. Synthesis of cellulose derivatives containing the dihyroxyboryl group and a study of their capacity to form specific complexes with sugars and nucleic acid components. *Biochemistry*. 9(22), 4396-4401.

Weser, U. 1967. Chemistry and structure of some borate polyol compounds of biochemical interest. *Struct. Bond*. 2, 160-180.

Windholz, M., ed. 1983. *The Merck Index*, 10th ed. Rahway, NJ: Merck and Co., Inc.

Yabroff, D.L., G.E.K. Branch, and B. Bettman. 1934. The relative strengths of some hydrocarbon derivatives of boric acid. *J. Am. Chem. Soc.* 56, 1850-1857.

Zill, L.P., J.P. Khym, and G.M. Cheniae. 1953. Studies on the separation of the borate complexes of sugars and related compounds by ion-exchange chromatography. *J. Am. Chem. Soc.* 75, 1339-1342.

Zittle, C.A. 1951. Reaction of borate with substances of biological interest in *Advances in Enzymology and Related Subjects of Biochemistry, vol XII*. ed. F.F. Nord. New York: Interscience. 493-527.

APPENDIX A. CALCULATION OF AQUEOUS STABILITY CONSTANTS FROM BUFFER CAPACITY DATA

Calculation of K_a and K_a^*

Ionization constants, K_a, and apparent ionization constants, K_a^*, for solutions of 3-nitrophenylboronic acid (NPBA) with varying concentrations of diols were calculated using the minimum buffer capacity, P_m, of the solution. Minimum buffer capacity was determined by potentiometric titration. The minimum buffer capacity and the NPBA concentration, c_a, were then used to determine the K_a by an iterative solution to the following equations:

$$K_a c_a = \frac{\left([H^+]_m + K_a\right)^3}{[H^+]_m - K_a} \qquad (3-2)$$

$$P = 2.303 \left(\frac{K_a [H^+] c_a}{(K_a + [H^+])^2} + [H^+] \right) \qquad (3-5)$$

The Fortran code used for this calculation is provided in Appendix B. Tables A-1 to A-7 present the output from that program.

Calculation of β_n and corresponding confidence interval

The mean K_a for each temperature (calculated from Table A-1) was used in a modified version of Equation 2-9 for the graphical determination of n and pK_n:

$$p\left(K_a^* - K_a\right) = pK_n - nLog\, C_D \qquad (2-9^*)$$

In addition, for 1,2-propanediol, $pK_{1,1}$ was calculated for each data point by setting n=1 in

Equation 2-9[*]. The stability constants were calculated according to Equation 2-3:

$$\beta_n = \frac{K_n}{K_a} \qquad (2-3)$$

The confidence intervals for β_n and $\beta_{1,1}$ were calculated using the general formula for calculation of the standard error, α, of a function:

$$\alpha^2 = \sqrt{\left(\frac{\delta f}{\delta m_1}\right)^2 \alpha_1^2 + \left(\frac{\delta f}{\delta m_2}\right)^2 \alpha_2^2}$$

where

$$f = \beta = \frac{10^{(-pK_n)}}{K_a}$$

and m_1 is the mean pK_n, m_2 is the mean K_a and α_1 and α_2 are the respective standard errors of the means (Hall, 1977). Standard errors were calculated from the sample standard deviations for K_a and $pK_{1,1}$. n and pK_n were calculated from linear regression analysis on Lotus 1-2-3 (Release 2). The standard error of the slope, n, and the standard error of the y-estimate, s_y, were computed by the software. The standard error of the intercept, pK_n, was calculated as follows:

$$\alpha_{pK_n} = s_y \sqrt{\frac{1}{k} + \frac{\overline{x}^2}{\Sigma (x - \overline{x})}}$$

where k = the number of independent measurements, x is the abscissa ($\log C_D$ in this case) and $\overline{x}$ is the mean value of the abscissa.

Symbols used in Tables A-1 through A-7

CA = molar concentration of 3-nitrophenylboronic acid
CD = molar concentration of diol
Pm = minimum buffer capacity
Chi = initial value for H+ conc. at min. buffer capacity
Ch+ = final value for H+ conc. at min. buffer capacity
Kai = initial value for apparent ionization constant
Ka = final value for apparent ionization constant

Table A-1. Calculation of ionization constant for NPBA in 0.1M KCl

Temperature: 25 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
08-MAY-90E	0.0010	0.0	4.20E-05	9.20E-06	9.10E-06	8.60E-08	8.7290E-08
08-MAY-90F	0.0010	0.0	4.50E-05	9.80E-06	9.70E-06	9.60E-08	9.8330E-08
08-MAY-90G	0.0010	0.0	4.40E-05	9.60E-06	9.60E-06	9.40E-08	9.5920E-08
08-MAY-90H	0.0010	0.0	4.70E-05	1.00E-05	1.00E-05	1.00E-07	1.0580E-07
08-MAY-90B	0.0050	0.0	9.20E-05	2.00E-05	2.00E-05	8.10E-08	8.1600E-08
08-MAY-90C	0.0050	0.0	9.60E-05	2.10E-05	2.10E-05	8.80E-08	8.8670E-08
08-MAY-90D	0.0050	0.0	9.10E-05	2.00E-05	2.00E-05	7.90E-08	7.9500E-08
08-MAY-90A	0.0099	0.0	1.30E-04	2.80E-05	2.80E-05	8.00E-08	8.0170E-08
10-may-90A	0.0099	0.0	1.30E-04	2.80E-05	2.80E-05	7.80E-08	7.8870E-08
10-may-90B	0.0099	0.0	1.30E-04	2.80E-05	2.80E-05	8.00E-08	8.0700E-08
10-may-90C	0.0099	0.0	1.30E-04	2.80E-05	2.80E-05	8.00E-08	8.0120E-08

Table A-1.   Calculation of ionization   constant for NPBA in 0.1M KCl (Continued)

Temperature: 35 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
20-JUN-90B	0.0111	0.0	1.40E-04	3.10E-05	3.10E-05	8.50E-08	8.5860E-08
21-JUN-90D	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	8.10E-08	8.1150E-08
25-jul-90C	0.0112	0.0	1.40E-04	3.00E-05	3.00E-05	7.90E-08	7.9200E-08
21-JUN-90C	0.0111	0.0	1.40E-04	3.10E-05	3.10E-05	8.70E-08	8.7770E-08
21-JUN-90A*	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	8.40E-08	8.4360E-08
25-jul-90B	0.0112	0.0	1.40E-04	3.00E-05	3.00E-05	8.10E-08	8.0970E-08
25-jul-90A	0.0112	0.0	1.40E-04	3.00E-05	3.00E-05	7.90E-08	7.9050E-08
20-JUN-90A*	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	7.90E-08	7.9370E-08
21-JUN-90B	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	8.30E-08	8.3620E-08

Temperature: 44.8 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
24-JUN-90A	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	7.90E-08	7.9810E-08
24-JUN-90D	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	8.20E-08	8.2570E-08
24-JUN-90C	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	8.10E-08	8.1870E-08
24-JUN-90E	0.0111	0.0	1.40E-04	3.00E-05	3.00E-05	8.00E-08	8.0460E-08
24-JUN-90B	0.0111	0.0	1.40E-04	3.10E-05	3.10E-05	8.50E-08	8.5130E-08

Table A-2. Calculation of the apparent ionization constant for NPBA when complexed with 1,2-propanediol at 25 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
12-jun-90A	0.0039	0.2	1.10E-04	2.30E-05	2.30E-05	1.40E-07	1.4110E-07
12-jun-90B	0.0039	0.2	1.10E-04	2.30E-05	2.30E-05	1.40E-07	1.4090E-07
10-may-90D	0.0010	0.3	5.50E-05	1.20E-05	1.20E-05	1.40E-07	1.4670E-07
10-may-90F	0.0010	0.3	5.60E-05	1.20E-05	1.20E-05	1.50E-07	1.5500E-07
10-may-90E	0.0010	0.3	5.60E-05	1.20E-05	1.20E-05	1.50E-07	1.5230E-07
11-may-90A	0.0050	0.3	1.30E-04	2.80E-05	2.80E-05	1.50E-07	1.5590E-07
11-may-90C	0.0050	0.3	1.30E-04	2.80E-05	2.80E-05	1.60E-07	1.5720E-07
11-may-90B	0.0050	0.3	1.30E-04	2.80E-05	2.80E-05	1.60E-07	1.5780E-07
26-may-90C	0.0010	0.4	6.40E-05	1.40E-05	1.40E-05	1.90E-07	1.9820E-07
26-may-90A	0.0010	0.4	6.20E-05	1.30E-05	1.30E-05	1.80E-07	1.8660E-07
26-may-90B	0.0010	0.4	6.20E-05	1.40E-05	1.30E-05	1.80E-07	1.8910E-07
29-may-90A	0.0010	0.5	6.60E-05	1.40E-05	1.40E-05	2.10E-07	2.1180E-07
29-may-90B	0.0010	0.5	6.60E-05	1.40E-05	1.40E-05	2.10E-07	2.1330E-07
29-may-90C	0.0010	0.5	6.60E-05	1.40E-05	1.40E-05	2.10E-07	2.1140E-07
12-jul-90C	0.0039	0.6	1.30E-04	2.90E-05	2.90E-05	2.20E-07	2.2280E-07
12-jul-90B	0.0039	0.6	1.40E-04	3.00E-05	2.90E-05	2.30E-07	2.3100E-07

Table A-3. Calculation of the apparent ionization constant for NPBA when complexed with 1,2-propanediol at 35 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
20-Jul-90B	0.0039	0.2	9.60E-05	2.10E-05	2.10E-05	1.10E-07	1.1240E-07
20-Jul-90A	0.0039	0.2	9.90E-05	2.10E-05	2.10E-05	1.20E-07	1.1940E-07
20-Jul-90C	0.0039	0.2	9.90E-05	2.10E-05	2.10E-05	1.20E-07	1.1960E-07
4-Jul-90B	0.0039	0.4	1.20E-04	2.50E-05	2.50E-05	1.70E-07	1.6980E-07
4-Jul-90D	0.0039	0.4	1.20E-04	2.50E-05	2.50E-05	1.60E-07	1.6490E-07
4-Jul-90C	0.0039	0.4	1.20E-04	2.50E-05	2.50E-05	1.60E-07	1.6400E-07
4-Jul-90A	0.0039	0.4	1.20E-04	2.50E-05	2.50E-05	1.60E-07	1.6490E-07
6-Jul-90A	0.0039	0.6	1.30E-04	2.80E-05	2.70E-05	1.90E-07	1.9720E-07
6-Jul-90B	0.0039	0.6	1.30E-04	2.70E-05	2.70E-05	1.90E-07	1.9670E-07
6-Jul-90C	0.0039	0.6	1.30E-04	2.80E-05	2.70E-05	1.90E-07	1.9720E-07
28-Jun-90B	0.0039	1	1.50E-04	3.20E-05	3.20E-05	2.60E-07	2.6440E-07
26-Jun-90D	0.0039	1	1.40E-04	3.20E-05	3.10E-05	2.50E-07	2.5910E-07
28-Jun-90A	0.0039	1	1.50E-04	3.20E-05	3.20E-05	2.60E-07	2.6870E-07

Table A-4. Calculation of the apparent ionization constant for NPBA when complexed
with 1,2-propanediol at 44.8 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
12-JUN-90C	0.0039	0.2	9.90E-05	2.10E-05	2.10E-05	1.20E-07	1.1930E-07
12-JUN-90D	0.0039	0.2	1.00E-04	2.20E-05	2.20E-05	1.20E-07	1.2460E-07
20-JUL-90D	0.0039	0.2	9.40E-05	2.00E-05	2.00E-05	1.10E-07	1.0840E-07
20-JUL-90E	0.0039	0.2	9.60E-05	2.10E-05	2.10E-05	1.10E-07	1.1430E-07
13-JUN-90C	0.0039	0.4	1.10E-04	2.40E-05	2.40E-05	1.50E-07	1.4650E-07
13-JUN-90B	0.0039	0.4	1.10E-04	2.40E-05	2.40E-05	1.50E-07	1.5000E-07
13-JUN-90A	0.0039	0.4	1.10E-04	2.40E-05	2.40E-05	1.50E-07	1.4870E-07
06-JUL-90E	0.0039	0.6	1.20E-04	2.60E-05	2.60E-05	1.70E-07	1.7360E-07
12-JUL-90E	0.0039	0.6	1.20E-04	2.60E-05	2.60E-05	1.80E-07	1.8070E-07
12-JUL-90D	0.0039	0.6	1.20E-04	2.60E-05	2.50E-05	1.70E-07	1.7090E-07
06-JUL-90D	0.0039	0.6	1.20E-04	2.60E-05	2.60E-05	1.70E-07	1.7210E-07
26-JUN-90A	0.0039	1.0	1.40E-04	3.00E-05	3.00E-05	2.30E-07	2.3550E-07
26-JUN-90B	0.0039	1.0	1.40E-04	3.00E-05	3.00E-05	2.30E-07	2.3620E-07
26-JUN-90C	0.0039	1.0	1.30E-04	2.90E-05	2.90E-05	2.20E-07	2.2390E-07

Table A-5. Calculation of apparent ionization constant for NPBA when complexed
           with 1,3-propanediol at 25 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
27-jul-90A	0.0039	1.0	9.20E-05	2.00E-05	2.00E-05	1.00E-07	1.0480E-07
27-jul-90D	0.0039	1.0	9.60E-05	2.10E-05	2.10E-05	1.10E-07	1.1350E-07
27-jul-90B	0.0039	1.0	9.50E-05	2.10E-05	2.10E-05	1.10E-07	1.1170E-07
27-jul-90C	0.0039	1.0	9.30E-05	2.00E-05	2.00E-05	1.00E-07	1.0530E-07
7-aug-90A	0.0039	0.6	9.20E-05	2.00E-05	2.00E-05	1.00E-07	1.0270E-07
7-aug-90B	0.0039	0.6	9.30E-05	2.00E-05	2.00E-05	1.00E-07	1.0590E-07
7-aug-90D	0.0039	0.6	9.30E-05	2.00E-05	2.00E-05	1.10E-07	1.0680E-07
7-aug-90C	0.0039	0.6	9.00E-05	2.00E-05	2.00E-05	9.90E-08	1.0040E-07
31-jul-90A	0.0039	0.4	9.00E-05	2.00E-05	1.90E-05	9.90E-08	9.9850E-08
31-jul-90B	0.0039	0.4	8.80E-05	1.90E-05	1.90E-05	9.40E-08	9.5120E-08
31-jul-90C	0.0039	0.4	8.70E-05	1.90E-05	1.90E-05	9.10E-08	9.2480E-08
3-aug-90A	0.0039	0.2	8.60E-05	1.90E-05	1.90E-05	9.00E-08	9.1320E-08
3-aug-90B	0.0039	0.2	8.60E-05	1.90E-05	1.90E-05	9.00E-08	9.1150E-08
3-aug-90C	0.0039	0.2	8.70E-05	1.90E-05	1.90E-05	9.20E-08	9.3100E-08

Table A-6. Calculation of apparent ionization constant for NPBA when complexed
with 1,3-propanediol at 35 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
26-jul-90C	0.0039	1.0	8.90E-05	1.90E-05	1.90E-05	9.60E-08	9.7550E-08
26-jul-90B	0.0039	1.0	9.20E-05	2.00E-05	2.00E-05	1.00E-07	1.0370E-07
26-jul-90A	0.0039	1.0	8.90E-05	1.90E-05	1.90E-05	9.60E-08	9.7550E-08
1-aug-90B	0.0039	0.6	8.70E-05	1.90E-05	1.90E-05	9.20E-08	9.2710E-08
1-aug-90C	0.0039	0.6	9.10E-05	2.00E-05	2.00E-05	1.00E-07	1.0250E-07
1-aug-90A	0.0039	0.6	8.90E-05	1.90E-05	1.90E-05	9.60E-08	9.7200E-08
31-jul-90D	0.0039	0.4	8.80E-05	1.90E-05	1.90E-05	9.40E-08	9.5440E-08
31-jul-90E	0.0039	0.4	8.80E-05	1.90E-05	1.90E-05	9.40E-08	9.5040E-08
31-jul-90F	0.0039	0.4	8.80E-05	1.90E-05	1.90E-05	9.40E-08	9.5040E-08
3-aug-90F	0.0039	0.2	8.60E-05	1.90E-05	1.90E-05	9.00E-08	9.0400E-08
3-aug-90D	0.0039	0.2	8.60E-05	1.90E-05	1.90E-05	9.00E-08	9.0850E-08
3-aug-90E	0.0039	0.2	8.50E-05	1.90E-05	1.80E-05	8.80E-08	8.8590E-08

Table A-7. Calculation of apparent ionization constant for NPBA when complexed with 1,3-propanediol at 44.8 C

Sample ID	CA	CD	Pm	Chi	Ch+	Kai	Ka
26-jul-90E	0.0039	1.0	8.50E-05	1.80E-05	1.80E-05	8.70E-08	8.7630E-08
26-jul-90D	0.0039	1.0	8.40E-05	1.80E-05	1.80E-05	8.60E-08	8.7350E-08
26-jul-90F	0.0039	1.0	8.40E-05	1.80E-05	1.80E-05	8.50E-08	8.5980E-08
1-aug-90F	0.0039	0.6	8.50E-05	1.80E-05	1.80E-05	8.70E-08	8.7610E-08
1-aug-90D	0.0039	0.6	8.50E-05	1.80E-05	1.80E-05	8.70E-08	8.7500E-08
1-aug-90E	0.0039	0.6	8.60E-05	1.90E-05	1.90E-05	8.90E-08	8.9990E-08
2-aug-90C	0.0039	0.4	8.30E-05	1.80E-05	1.80E-05	8.30E-08	8.3940E-08
2-aug-90D	0.0039	0.4	8.60E-05	1.90E-05	1.80E-05	8.90E-08	8.9990E-08
2-aug-90A	0.0039	0.4	8.60E-05	1.90E-05	1.90E-05	8.90E-08	9.0170E-08
2-aug-90B	0.0039	0.4	8.40E-05	1.80E-05	1.80E-05	8.50E-08	8.5970E-08
8-aug-90C	0.0039	0.2	8.40E-05	1.80E-05	1.80E-05	8.50E-08	8.5930E-08
8-aug-90D	0.0039	0.2	8.50E-05	1.80E-05	1.80E-05	8.70E-08	8.7950E-08
8-aug-90B	0.0039	0.2	8.40E-05	1.80E-05	1.80E-05	8.50E-08	8.5710E-08
8-aug-90A	0.0039	0.2	8.10E-05	1.80E-05	1.80E-05	8.00E-08	8.0660E-08

REFERENCES

Hall, C.W. 1977. *Errors in experimentation.* Champaign, IL: Matrix Publishers, Inc.

APPENDIX B. FORTRAN CODE TO ITERATIVELY CALCULATE K_a

```
c    FILE PKA.F

c    This file uses an iterative procedure to calculate the ionization

c    constant using Antikainen's equation.  An approximation was used to

c    calculate an initial value from the experimental data in Lotus 1,2,3.


     IMPLICIT DOUBLE PRECISION (A-H, O-Z)

     INTEGER N, NSIG, ITMAX, IER, k

c    VARIABLE KEY:

c    n = number of variables in iteration

c    nsig = number of significant figures for iteration

c    itmax = maximum number of iterations

c    diol= diol read from input file

c    id =sample id,  and is keyed to titration data

c    k = number of samples in given input file; counter for do loop

c    temp = temperature of samples from given input file

c    ca = molar concentration of NPBA

c    cd = molar diol concentration

c    pm = minimum buffer capacity

c    kai = initial approximation for apparent $K_a$

c    chi = initial approximation for hydrogen ion concentration

c        at minimum buffer capacity
```

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```
c       par and x are variables for imsl subroutine

c       fname = name of file containing data imported from Lotus 123

c

c       VARIABLE INITIALIZATION

        external fcn

        integer n, nsig, itmax, k, j, ier

        character diol*16, id*16, temp*6, fname*20, outfname*20


        DOUBLE PRECISION PAR(2), X(2), FNORM, WK(42), kai, chi, pm


        print *, 'list input file name:'

c       name of input file is input from terminal

        read(5, 260)fname

        print *, 'list output file name:'

        read(5, 260)outfname

        rewind 9

        open (unit = 9, file = outfname, status = 'new')


        rewind 8

        open (unit = 8, file = fname, status = 'old')

        read(8, 260) diol

        read (8, 270) temp

        read (8, 280) k

        write(9, 290)'Calculation of Apparent Ionization Constant for NPBA'

        write (9, 300) 'when complexed with ', diol, 'at ', temp

        write(9, 310)'Sample ID      ', 'CA   ', 'CD ', 'Pm      ', 'Chi    ',

     &              'Ch+     ', 'Kai    ', 'Ka        '
```

```
          n = 2

          NSIG = 6

          ITMAX = 200

c


c       Do loop iteratively calculates Ka and Ch +  using IMSL subroutine


        do 50 j = 1, k

        read(8, 250) id, ca, cd, pm, chi, kai

        write(6, 250) id, ca, cd, pm, chi, kai

        X(1) = kai

        X(2) = chi

        par(1) = ca

        par(2) = pm

        CALL ZSCNT (FCN, NSIG, N, ITMAX, PAR, X, FNORM, WK, IER)

        write(9, 320) id, ca, cd, pm, chi, x(2), kai, x(1)


50      continue


        write(9, 330)'KEY'

        write(9, 290)'CA  = molar concentration of 3-nitrophenylboronic acid'

        write(9, 290)'CD  = molar concentration of diol                     '

        write(9, 290)'Pm  = minimum buffer capacity                         '

        write(9, 290)'Chi = initial value for H+  conc. at min. buffer capacity'

        write(9, 290)'Ch+ = final value for H+  conc. at min. buffer capacity'

        write(9, 290)'Kai = initial value for apparent ionization constant  '

        write(9, 290)'Ka  = final value for apparent ionization constant    '
```

```
250   format (a16, f8.6, 4x, f3.1, 3x, d11.5, 3x, d8.2, 3x, d8.2)

260   format (a16)

270   format (a6)

280   format (i2)

290   format (a60)

300   format (15x, a20, a16, a3, a6//)

310   format (a15, a8, a5, a10, a10, a10, a10, a12/)

320   format (a15, f8.4, f5.1, d10.2, d10.2, d10.2, d10.2, d12.4)

330   format (a3/)


      close (unit = 8, status = 'keep')

      close (unit = 9, status = 'keep')


      STOP

      END

      SUBROUTINE FCN(X, F, N, PAR)

      IMPLICIT DOUBLE PRECISION (A-H, O-Z)

      DOUBLE PRECISION X(2), F(2), PAR(2)

      F(1) = X(1) - (X(2) + X(1))**3/PAR(1)/(X(2) - X(1))

      F(2) = X(2) - PAR(2)/2.303 + X(1)*X(2)*PAR(1)/(X(1) + X(2))**2

      RETURN

      END
```

APPENDIX C. TABULATION OF EXTRACTION DATA

Results of the batch extraction experiments are presented in Tables C-1 to C-4. The experimentally measured quantities are:

H$_2$O

Ci-org = initial organic phase concentration, weight percent

Cf-org = final organic phase concentration, weight percent

1,2-propanediol

Ci-org = initial organic phase concentration, mol/l

Ci-aq = initial aqueous phase concentration, mol/l

Cf-aq = final aqueous phase concentration, mol/l

Cf-org = final organic phase concentration, mol/l, where annotated by GC for gas

　　　chromatographic analysis

NPBA (total concentrations)

Ci-org = initial organic phase concentration, mol/l

Cf-aq = final aqueous phase concentration, mol/l

Aliquat 336

Ci-org = initial organic phase concentration, mol/l

pH   = -log activity {H$^+$}

Values calculated from these data are:

NPBA: Cf-org = final organic phase concentration, mol/l

NPBA-: Ci-org = initial organic phase concentration, mol/l

> = fraction ionized x Ci-org (total NPBA)

[NPBA-]org = unreacted equilibrium concentration in organic phase

$$= (Ci\text{-}org_{NPBA-} - (Cf\text{-}org_{diol} - Cf\text{-}aq_{diol} \times P \times \text{volume fraction diluent})$$

H_2O: Cf-aq = final aqueous phase concentration, mol/l

D   = distribution ratio = Cf-org/Cf-aq

α = selectivity = D_{diol}/D_{H2O}

z   = loading = $(Cf\text{-}org_{diol} - Cf\text{-}aq_{diol} \times P \times \text{volume fraction diluent})/(Ci\text{-}org_{NPBA-})$

Table C-1. Partition coefficient for 1,2-propanediol between water and 2-ethyl-1-hexanol at 25 C

ID	Final pH	[H2O] (wt.%)		1,2-propanediol concentrations (mol/l)					D (diol): Cf-org/Cf-aq
		Ci-org	Cf-org	Ci-org	Ci-aq (HPLC)	Cf-org (calc.)	Cf-aq (HPLC)	Cf-org (GC)	
PG11 (20 C)				0	0.102	0.0065	0.096		0.068
PG01 (28 C)				0	0.102	0.0090	0.093		0.097
PG15	6.51			0	0.103	0.0076	0.096		0.080
PG16				0	0.103	0.0073	0.096		0.076
PG17	6.46			0	0.103	0.0094	0.094		0.100
PG27				0	0.103	0.0072	0.095		0.076
PG31		2.93	2.90	0	0.106	0.0097	0.0963		0.101
PG32		2.93	2.70	0	0.106	0.0080	0.098	0.0074	0.082
PG33		2.93	2.84	0	0.106	0.0078	0.0982		0.079
PG34		2.93		0	0.053	0.0036	0.0494	0.004	0.073
PG35		2.93	2.87	0	0.053	0.0036	0.0494		0.073
PG38		2.93	3.00	0.096	0	0.0121	0.0839	0.006	0.072
PG39		2.93	3.07	0.102	0	0.0170	0.085	0.0062	0.073

Concentrations in mol/l.

Table C-2. Distribution ratios for 1,2-propanediol extracted by NPBA-Aliquat 336
in 2-ethyl-1-hexanol at 25 C.

ID	NPBA Ci-org	Aliquat 336 Ci-org	Diol Ci-aq	Final pH	NPBA Cf-aq (HPLC)	Diol Cf-org (Calc.)	Diol Cf-aq (HPLC)	D(diol): Cf-org ------ Cf-aq
Extractant not pretreated								
PG21	0.10	0.09	0.103	3.2	8.03E-04	0.0068	0.097	0.070
PG22	0.10	0.09	0.103	3.1	8.04E-04	0.0095	0.094	0.102
PG23	0.10	0.09	0.106	3.1	8.05E-04	0.0084	0.098	0.086
Extractant washed with base								
PG04-2*	0.1	0.08	0.102		5.02E-04	0.0120	0.090	0.133
PG05-14	0.1	0.08	0.102		3.52E-04	0.0125	0.090	0.140
PG05-19	0.1	0.08	0.102		5.28E-04	0.0130	0.089	0.146
PG06-19	0.1	0.08	0.102		5.28E-04	0.0135	0.089	0.153
PG24	0.09	0.09	0.106	5.8	2.93E-04	0.0151	0.091	0.167
PG25	0.09	0.09	0.106	5.6	3.11E-04	0.0174	0.089	0.196
PG26	0.09	0.09	0.106	5.5	3.22E-04	0.0156	0.090	0.173
PG43	0.18	0.18	0.102	6.7	2.08E-04	0.0259	0.076	0.340
PG44	0.18	0.18	0.102	6.4	2.31E-04	0.0239	0.078	0.306
PG45	0.18	0.18	0.052	7.2	2.02E-04	0.0181	0.034	0.534
PG46	0.18	0.18	0.052	6.9	1.92E-04	0.0170	0.035	0.486

* T=28 C
Concentrations in mol/l.

Table C-3. Coextraction of water during extraction of 1,2-propanediol by NPBA and Aliquat 336 in 2-ethyl-1-hexanol at 25 C

ID	NPBA Ci-org	Aliquat 336 Ci-org	Diol Ci-aq	H2O Cf-aq	H2O Cf-org (wt %)	H2O Cf-org (mol/l)	D(H2O) Cf-org / Cf-aq	D(diol) Cf-org / Cf-aq	Selectivity D(diol) / D(H2O)
Average for partition coefficient in 2-ethyl-hexanol									
P	0	0	0.0-0.1	55.6	3	1.39	0.025	0.08	3
Extractant not pretreated									
PG21	0.10	0.09	0.103	56.0	1.4	0.67	0.012	0.070	6
PG22	0.10	0.09	0.103	55.9	2.2	1.01	0.018	0.102	6
PG23	0.10	0.09	0.106	56.0	3.0	1.38	0.025	0.086	3
Extractant washed with base									
PG24	0.09	0.09	0.106	55.9	2.2	1.03	0.018	0.167	9
PG25	0.09	0.09	0.106	55.9	3.1	1.42	0.025	0.196	8
PG26	0.09	0.09	0.106	55.9	2.7	1.25	0.022	0.173	8
PG43	0.18	0.18	0.102	55.9	3.82	1.79	0.032	0.340	11
PG44	0.18	0.18	0.102	55.9	3.75	1.76	0.031	0.306	10
PG45	0.18	0.18	0.052	55.7	4.06	1.90	0.034	0.534	16
PG46	0.18	0.18	0.052	55.7	3.41	1.60	0.029	0.486	17

Concentrations in mol/l unless otherwise specified.
Organic phase densities (g/ml) used in calculations:
 P: d=0.833, PG21-PG26: d=0.830, PG43-PG46: d=0.844.

Table C-4. Loading of 1,2-propanediol relative to NPBA- achieved by extraction with
NPBA-Aliquat 336 in 2-ethyl-1-hexanol and distribution of total NPBA
between organic and aqueous phases at 25 C.

ID	NPBA Ci-org	NPBA- Ci-org	NPBA Cf-aq	Unreacted [NPBA-]org	D (NPBA) Cf-org / Cf-aq	diol Ci-aq	diol Cf-aq	Loading z
Extractant not pretreated								
PG21	0.10	minimal	8.0E-04		128	0.103	0.097	
PG22	0.10	minimal	8.0E-04		128	0.103	0.094	
PG23	0.10	minimal	8.1E-04		127	0.106	0.098	
Extractant washed with base (ca. 55% ionized)								
PG24	0.09	0.050	2.9E-04	0.041	307	0.106	0.091	0.18
PG25	0.09	0.050	3.1E-04	0.038	290	0.106	0.089	0.23
PG26	0.09	0.050	3.2E-04	0.040	280	0.106	0.090	0.19
PG43	0.18	0.099	2.1E-04	0.079	869	0.102	0.076	0.21
PG44	0.18	0.099	2.3E-04	0.081	782	0.102	0.078	0.19
PG45	0.18	0.099	2.0E-04	0.084	893	0.052	0.034	0.16
PG46	0.18	0.099	1.9E-04	0.085	943	0.052	0.035	0.15

Concentrations in mol/l.
Partition coefficient =0.08
Volume fraction diluent : PG21-23: vf=0.93, PG23-26: vf=0.92, PG43-46: vf=0.87.

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