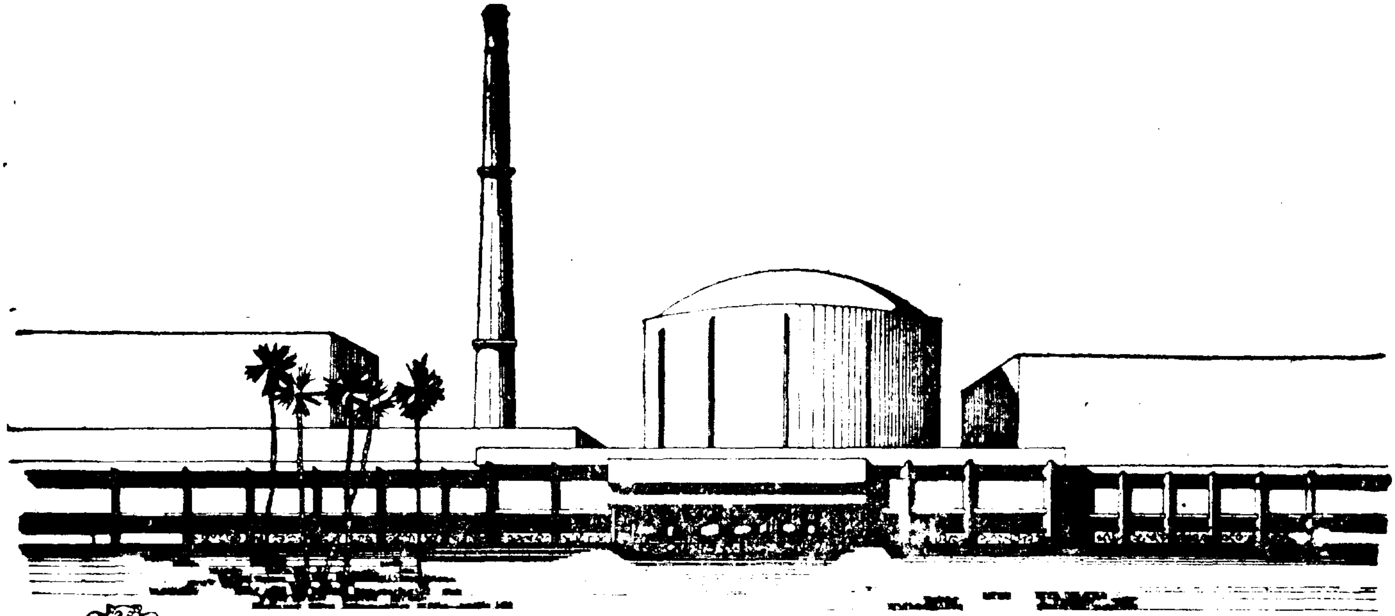
IGC-161
1994

IGC-161
1994

Separation of Boron Isotopes by Ion Exchange Chromatography: Studies with Duolite-162, A Type-II Resin

B.K. Sharma, R. Subramanian, R. Balasubramanian & P.K. Mathur



GOVERNMENT OF INDIA, DEPARTMENT OF ATOMIC ENERGY
INDIRA GANDHI CENTRE FOR ATOMIC RESEARCH KALPAKKAM

29 - 35

IGC-161
1994

GOVERNMENT OF INDIA

DEPARTMENT OF ATOMIC ENERGY

SEPARATION OF BORON ISOTOPES BY ION EXCHANGE CHROMATOGRAPHY: STUDIES WITH DUOLITE-162, A TYPE-II RESIN.

B.K.Sharma, R.Subramanian, R.Balasubramanian and P.K.Mathur

Indira Gandhi Centre for Atomic Research

Kalpakkam 603 102

Tamilnadu, India.

ABSTRACT:

The selection of resin plays an important role in the process of separation of boron isotopes by ion exchange chromatography. The determination of (i) ion exchange capacity of Duolite-162 resin for hydroxyl - chloride exchange, (ii) hydroxyl - borate exchange, (iii) isotopic exchange separation factor by batch method and (iv) effect of concentration of boric acid on isotopic exchange separation factor to test the suitability of the above resin for this process are discussed in this report.

CONTENTS

SEPARATION OF BORON ISOTOPES BY ION EXCHANGE CHROMATOGRAPHY: STUDIES WITH DUOLITE-162, A TYPE-II RESIN.

B.K.Sharma[*], R.Subramanian[*],
R.Balasubramanian[1] and P.K.Mathur[2]

I INTRODUCTION:

Because of the higher cross-section of ^{10}B for the reaction $^{10}B(n,\alpha)^{7}Li$, boron compounds enriched in the ^{10}B isotope are generally used for control rods of Fast Breeder Reactors (FBRs), neutron counters, neutron capture therapy of malignant tissues and treatment of melanotic cancers and brain tumours[1,2]. Natural boron has 18.8 at.% of ^{10}B and 81.2 at.% of ^{11}B. For efficient control of fast reactors, it is required to use highly enriched boron in ^{10}B isotope. Ion exchange chromatography is one of processes that is used for the separation of natural isotopes of boron. In this process, a strong base anion exchange resin in hydroxyl form is exchanged with boric acid solution containing a complexing reagent. After loading boric acid to the required band length, it is displaced with an acid to achieve the desired enrichment.

Studies have been carried out earlier to enrich ^{10}B isotope by ion exchange chromatography where a strong-base anion exchange resin of Type-I in hydroxyl form and glycerol[3] or mannitol[4-6] was used as a complexing reagent for boric acid.

---

[*] Chemical Technology Section,
[1] Materials Chemistry Division,
[2] Water and Steam Chemistry Laboratory,
Applied Chemistry Division, B A R C,
Indira Gandhi Centre for Atomic Research,Kalpakkam.

The increase in the isotopic exchange separation factor due to the addition of a complexing reagent has been attributed to the increased ionization of boric acid[3,5]. The major cost factor for the operation of the plant based on this process depends upon the cost of NaOH, used as regenerant due to the higher amounts required for the regeneration of the Type-I resin from chloride form to hydroxyl form. However, a Type-II resin is known to have much better regeneration characteristics as compared to those of the Type-I resin. Hence, to access the suitability of a Type-II resin for the operation of the plant based on this process, batch experiments were carried out to determine (i) $OH^- - Cl^-$ exchange capacity, (ii) OH^- - borate exchange capacity, (iii) the effect of concentration of boric acid on the exchange capacity of the resin for boric acid and (iv) isotopic exchange separation factor for $^{10}B-^{11}B$ exchange at different concentrations of boric acid. In addition , isotopic exchange separation factor for $^{10}B- ^{11}B$ exchange at 0.1 M boric acid in presence of mannitol (a complexing reagent for boric acid) by using Duolite-162, a Type-II resin was also determined. Results of these experiments are discussed in the present report.

II EXPERIMENTAL METHODS:

Analar grade chemicals were used in this study. Demineralized water collected from CA-20 unit with conductivity of 1.5 microSiemens/cm was used throughout these experiments.

II a Preparation of boric acid solutions:

Approximate 0.05M, 0.10M and 0.15M solutions of boric acid were prepared and standardized alkalimetrically to phenolphthalein end point with the addition of mannitol. A solution of 0.1 M boric acid containing 0.1 M mannitol was prepared and standardized in a similar manner.

II b Pretreatment:

The Duolite-162 resin obtained from M/s Henkel Ltd., Bombay was washed with demineralized water and was pretreated prior to use by passing 1.0 N NaOH and 2.0 N HCl thrice in a cyclic manner after washing of the resin in each operation. This pretreated resin was used for subsequent experiments. The characteristic properties of the resin (given in Table-1) were determined using standard procedures[7].

II c Regeneration of the resin:

The required slurry of the pretreated resin in chloride form was taken in a pyrex glass column with int. dia. of 18.1 mm and height of about 50 cms. Regenerant 1.25 N NaOH was passed through this column at a constant flow rate (4.0 ml/min). The regeneration level was 300%. After the passage of the required volume of NaOH, the resin column was washed with demineralized water to remove the interstitial NaOH. The resin thus obtained in hydroxyl form was stored in a reagent bottle and was used for the batch experiments.

II d Determination of $OH^- - Cl^-$ exchange capacity:

An aliquot of the resin in hydroxyl form, obtained as above, was measured by using a 10 ml measuring cylinder and transferred to an erlenmeyer flask. The supernate water was discarded. 10.0 ml aliquots of standard HCl solution (0.089 N) were equilibrated for 25 times and the supernate was collected in a reagent bottle. The excess of the acid was then washed with demineralized water and the washings were also collected in the same reagent bottle. The acid content of this solution was determined by alkalimetric titration of the solution to phenolphthalein end point. The volume of the effluent collected was measured.

II e Determination of OH^- - borate exchange capacity:

An aliquot of the resin in hydroxyl form was taken in an erlenmeyer flask. While maintaining 200% excess boric acid, the required volume of the boric acid solution was equilibrated in small lots and the supernate after each equilibration was collected in a reagent bottle. The resin was then washed with demineralized water and washings were collected in the same reagent bottle. The volume of the solution collected was measured and analysed for boric acid content after the addition of mannitol.

Boric acid was analysed by titrating it against standard NaOH solution after the addition of mannitol. In the mixture of boric acid with HCl, the analysis was carried out alkalimetrically[8] with standard NaOH by first titrating the sample to methyl red end point and then to phenolphthalein end point after the addition of mannitol.

II f Determination of isotopic exchange separation factor:

To determine the isotopic exchange separation factor by the batch method, a known quantity of the resin in hydroxyl form was taken in a stoppered bottle. To this, an aliquot of the boric acid solution containing the required amount of the complexing reagent was added. The solution was allowed to equilibrate for 10 min with intermittent stirring of the contents. The supernate was then discarded and a fresh aliquot of the solution was added. This procedure was repeated 20-25 times to ensure the completion of isotopic exchange reaction. The resin was thus converted to borate form. This resin was then transferred to a small pyrex glass column and the loaded boric acid was eluted with HCl. The effluent was isotopically analysed for $^{10}B/^{11}B$ ratios as described below:

To determine isotopic ratios, a sample of boric acid was treated with sodium carbonate to obtain 1:1 atom ratio of sodium to boron and was loaded on rhenium filament. Isotopic analyses of boric acid were carried out by using a VG Micromass 30BK mass spectrometer having a thermal ionization source and a Daly detector. $^{10}B/^{11}B$ ratios were determined by measuring the peak heights at mass numbers 88 and 89 for sodium metaborate ion, containing ^{10}B and ^{11}B atoms respectively, produced by thermal ionization of Na_2BO_2.

III RESULTS AND DISCUSSION:

The total exchange capacity of hydroxyl form of the resin for boric acid was calculated as follows:

Let the volume of the resin in hydroxyl form = V ml

Volume of boric acid solution equilibrated = V1 ml

Concentration of the acid solution = N1 eq/ltr

Volume of supernate and washings collected = V2 ml
Concentration of the effluent collected = N2 eq/ltr
mEqs of boric acid put (M1) = N1.V1
mEqs recovered (M2) = N2.V2
mEqs exchanged (Mex) = M1-M2
Capacity of the resin = Mex/V mEq/ml

The values of the capacity of the resin for boric acid obtained as above are listed in Table-2. The capacity of the resin for OH^- - Cl^- exchange was found to be 0.704 mEq/ml. For boric acid solution containing 0.1 M mannitol it was found to be 0.720 mEq/ml. This shows that there was no significant difference in resin capacity when boric acid solution containing mannitol was equilibrated as compared to that observed for OH^- - Cl^- exchange. In the absence of mannitol, however, the capacity of the resin for boric acid increased and reached a steady value as shown in Fig-1. This could be due to the exchange of polyborate ions with hydroxyl form of the resin. Thus, it could be inferrred that in presence of mannitol, the capacity of the resin remained same due the exchange of mononuclear mannitol-borate complex anion by reacting with polyborate ions[9] present in boric acid solutions at higher concentrations.

The data obtained for isotopic ratios of samples are presented in Table-3. From these isotopic ratios, the mole fractions of ^{10}B in the samples were calculated from the equation $X = R/1+R$, where R is the abundance ratio i.e. $^{10}B/^{11}B$ for a particular sample. The values of isotopic exchange separation factor, K, were then determined from the following equation:

$$K = \frac{(X_r) \cdot (1-X_s)}{(1-X_r) \cdot (X_s)}$$

where X_r is the mole fraction of ^{10}B in the resin phase i.e. for solution obtained after elution of boric acid from the resin with HCl and X_s in the solution phase(natural boron 0.1997). The values of isotopic exchange separation factor obtained by equilibrating the Duolite-162 resin in the hydroxyl form at different concentrations of boric acid are plotted in Fig 2 and included in Table - 3. From this figure, it could be observed that as the concentration of boric acid was increased, the value of isotopic exchange separation factor decreased. This could be due to the exchange of polynuclear complexes of boric acid called polyborates with hydroxyl form of the resin. Thus, from the present study it could be concluded that with the increase in the concentration of boric acid , the exchange capacity increases and separation factor value decreases which could be due to the exchange of polyborate anions with hydroxyl form of the resin.

Acknowledgements:

The authors are grateful to Dr. Placid Rodriguez, Director, IGCAR and Shri S.B. Bhoje, Director, Reactor Group, for their keen interest in this work. Thanks are also due to Shri P.Rajamani, Chemical Technology Section for helpful discussions and Dr. C. K. Mathews, Director, Chemical Group, IGCAR for allowing us to use mass spectrometer for isotopic analyses.

References:

1. T.E. Blue, T.C. Robert, R.F. Barth , J.W. Talnagi and F.Alam, *Nucl. Tech.*,**77**(1987) 220.
2. H.Kakihana, M.Kotaka, S.Satoh, M.Nomura and M.Okamato, *Bull Chem Soc Jpn*, **50**(1977) 158.
3. Y.Yoneda, T.Uchijima and S.Makishima, *J. phys Chem*, **63**(1959) 2057.
4. B. K. Sharma, *Separation of boron isotopes by ion exchange chromatography*, M. Phil. Disser., Punjabi University, Patiala, 1986.
5. B.K. Sharma, R. Subramanian and P.K. Mathur, *Indian Journal of Chemistry*, **30 A**(1991) 66.
6. B.K. Sharma, R. Subramanian and P.K. Mathur, *Indian Journal of Chemistry*,**30 A** (1991) 531.
7. J. Incezdy, *"Analytical applications of ion exchangers"*, Pergamon press(1966) Ch.5
8. J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham, *Vogel's text book of quantative inorganic analysis*, 4th edn (The English Language Book Society, London),1979, 309.
9. T. Paal, *Acta chem Hung*, **103** (1980) 181.

Table – 1

Characteristic properties of Duolite –162 resin

Physical Form	Macroporous Beads
Total exchange capacity	0.974 mEq/ml
Water content	41.39 %
Degree of cross–linking	8.50 %
Swelling	17.03 %
Dry density	1.175 g/ml
Wet resin density	1.092 g/ml
Void Volume	36 %
Changes in volume:	
Cl^- to OH^-	+ 12.5 %
OH^- to borate	+ 5.0 %
Functional group	$R-CH_2N^+(CH_3)(C_2H_4OH)OH^-$

Table - 2

Exchange capacity of Duolite-162 resin for boric acid

Boric acid concn. /M	Mannitol concn. /M	Exchange capacity mEq/ ml
0.041	nil	1.04
0.083	- ,, -	1.162
0.154	- ,, -	1.175
0.083	0.10	0.720

Table - 3

Isotopic exchange separation factor for ^{10}B - ^{11}B exchange at different concentrations of boric acid

Boric Acid Concn. (M)	Mannitol Concn. (M)	Isotopic Ratio	Separation Factor
0.041	nil	0.2530	1.0136
0.083	- ,, -	0.2510	1.0055
0.083	- ,, -	0.2512	1.0064
0.154	- ,, -	0.2507	1.0045
0.083	0.1	0.2550	1.0216

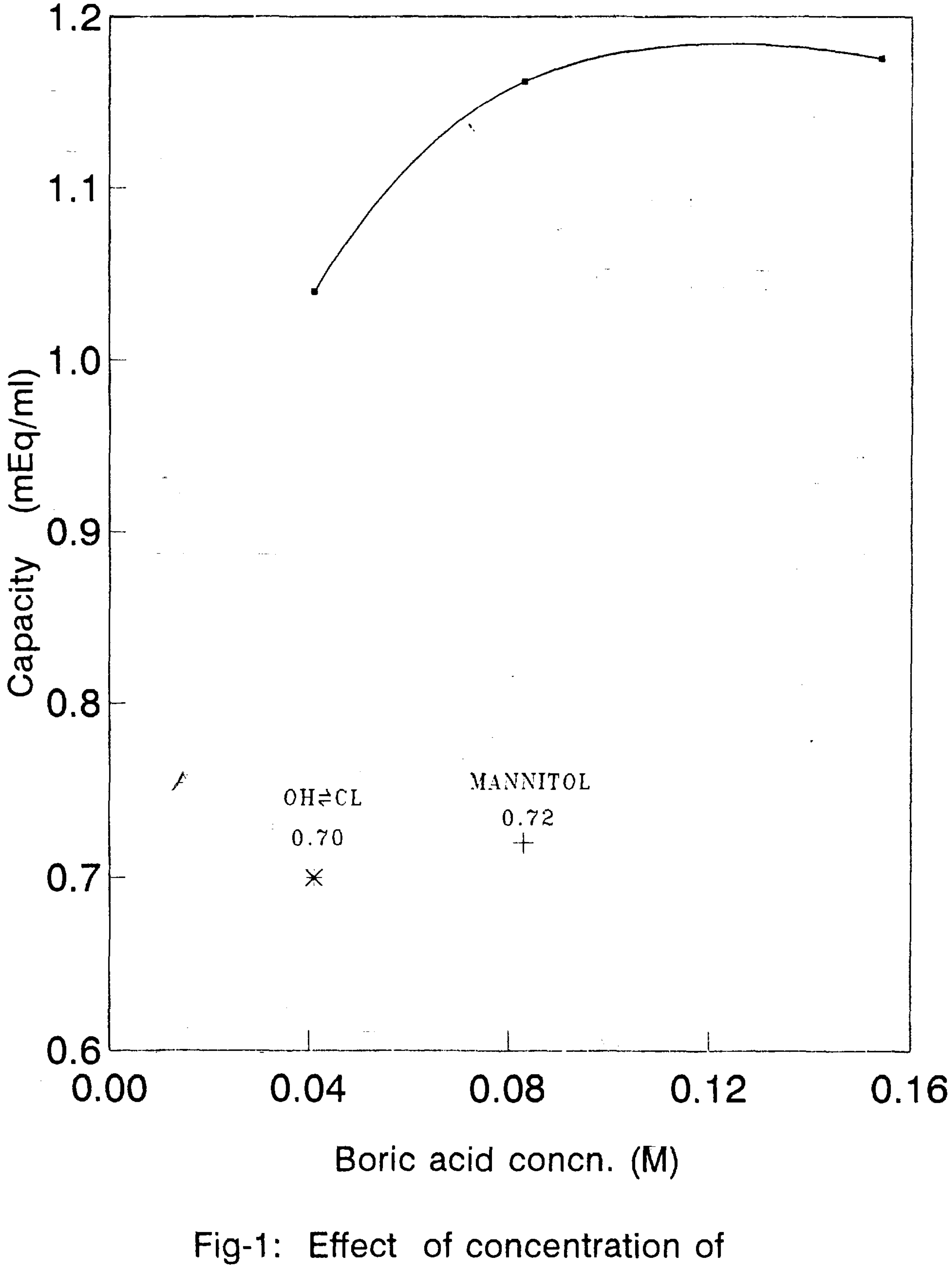


Fig-1: Effect of concentration of boric acid on the exchange capacity of Duolite-162 resin

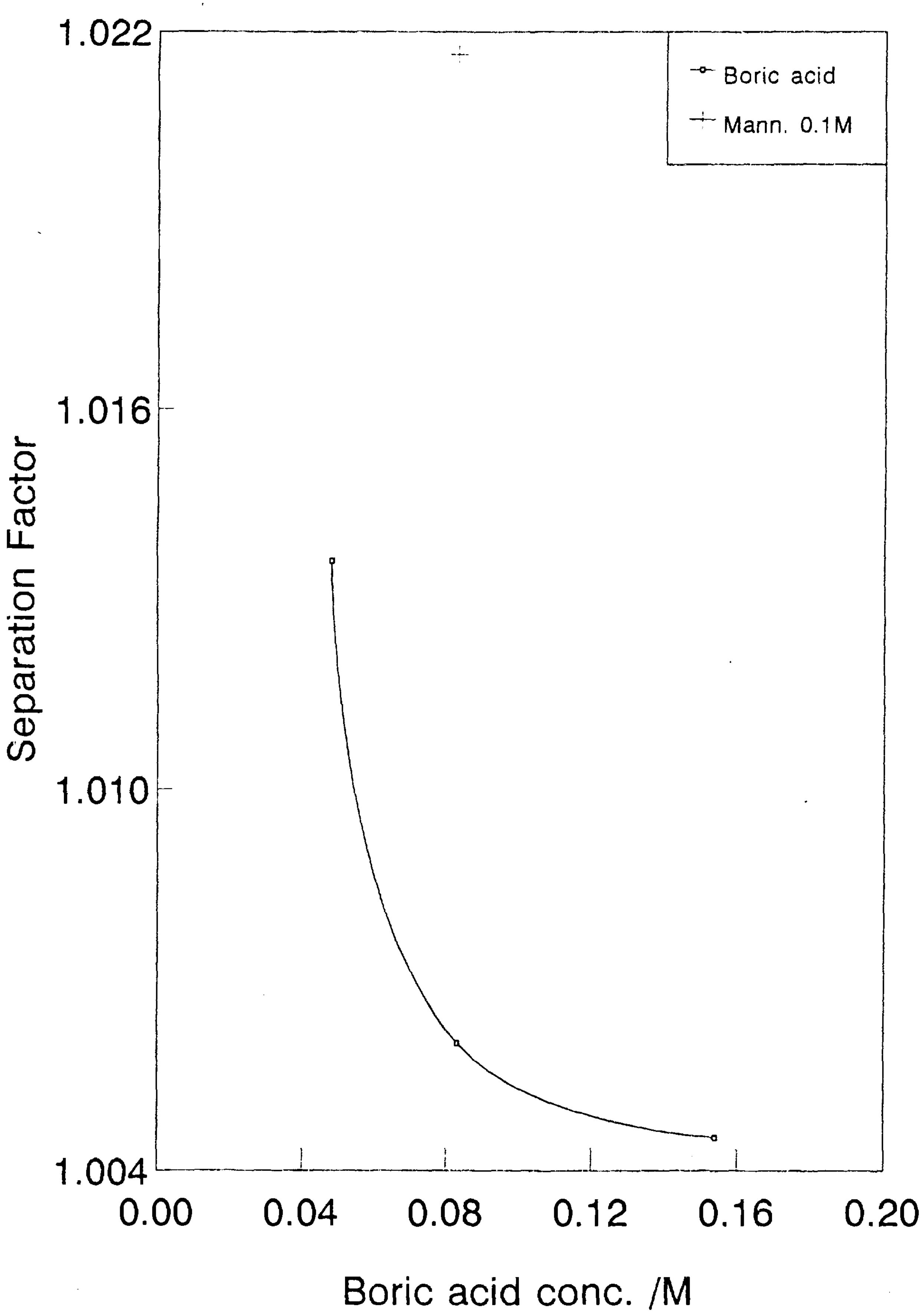


Fig-2: Effect of concentration of boric acid on separation factor