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Effect of complexing reagents on the ionization constant of boric acid and its relation to isotopic exchange separation factor

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The effect of change in concentration of complexing reagents having two or more hydroxyl groups, viz., ethylene glycol, propylene glycol, dextrose and mannitol on the ionization constant of boric acid has been studied by *p*H-metric titration method. The effect of increase in ionization constant of boric acid on isotopic exchange separation factor for the separation of isotopes of boron by ion exchange chromatography has been studied by the batch method.

Because of the higher cross-section of ^{10}B for the reaction ^{10}B (n, α)^{7}Li, boron compounds enriched in ^{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 enrich boron in ^{10}B isotope. Studies have been carried out to enrich ^{10}B isotope by ion exchange chromatography in which a strong-base anion exchange resin in hydroxyl form is equilibrated with boric acid solution containing a complexing reagent[3,4]. The increase in the isotopic exchange separation factor has been attributed to the increased ionization of boric acid[3].

The present study was undertaken to investigate the effect of a few commercially available diols and polyols (complexing reagents for boric acid) on the ionization of boric acid and its relation to isotopic exchange separation factor.

Experimental

AR grade chemicals were used and demineralized water, collected from a deionization CA-20 unit, was used throughout this study. NaOH solution was prepared in CO_2-free demineralized water and was standardized against standard potassium hydrogen phthalate solution *p*H-metrically. A 0.1 *M* soloution of boric acid containing the required amount of complexing reagents was prepared by appropriate dilution of stock solutions of boric acid and the complexing reagent. At least 3 aliquots from this sample solution were taken and titrated *p*H-metrically against standard NaOH solution. Another solution with varying concentration of complexing reagent was also prepared in 0.1 *M* boric acid and the entire procedure was repeated.

A Metrohm titroprocessor was used for *p*H-metric titrations. The electrode was calibrated with potassium hydrogen phthalate (*p*H 4.02), phosphate (*p*H 6.18) and borax (*p*H 9.12) buffers.

A macroporous strong base anion exchange indigenous resin (Tulsion A-27 MP) having quaternary amine type functional groups was used in the study. The characteristic properties of the resin have been described elsewhere[4].

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

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 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 converted to sodium metaborate by the addition of Na_2CO_3. The isotopic analyses of bor-

ic acid were carried out by using a VG Micromass 30BK mass spectrometer, having a thermal ionization chamber 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 ions containing ^{10}B and ^{11}B atoms respectively, produced by thermal ionization of Na_2BO_2.

Results and discussion

Out of various commercially available polyhydroxy compounds, four complexing reagents, viz., ethylene glycol, propylene glycol, dextrose and mannitol were selected for the present study with a view to selecting a suitable reagent that could be employed for an economical separation of isotopes of boron by using ion exchange chromatography. It was observed that there was no significant change in the *p*H-metric titration profiles of 0.1 *M* boric acid in the presence of 0.2 *M*-1.0 *M* ethylene glycol and propylene glycol. A significant change was, however, observed with dextrose and mannitol under similar conditions, which indicated that boric acid becomes a stronger acid in presence of these complexing reagents. This effect was much more pronounced in the case of mannitol than with dextrose. In fact, sufficiently large effect could be observed with mannitol even at relatively low concentrations (varied in the range 0.1-0.5 *M*). The sharp change in *p*H observed near the end point during the titrations was more in the presence of dextrose as compared to that with ethylene glycol and propylene glycol. This change was still sharper in the presence of mannitol indicating thereby that mannitol was more effective in increasing the ionization of boric acid.

The ionization of boric acid or the polyol-boric acid complex (HA) may be represented as:

$$HA \rightleftharpoons H^+ + A^-$$

where A^- is the corresponding anion. The ionization constant for the above reaction is given by,

$$K_a = \frac{(H^+)(A^-)}{(HA)}$$

Solving for pK_a, we get

$$pK_a = pH + \log\frac{(HA)}{(A^-)}$$

or

$$pK_a = pH + \log\frac{[HA]\cdot y_{HA}}{[A^-]\cdot y_{A^-}}$$

where [HA] and $[A^-]$ are the concentrations of unionized acid and the corresponding anion[5] respectively and y_{HA} and y_{A^-} are the corresponding activity coefficients. For the dilute solutions the activity coefficients of the ionic species may be taken as unity. Thus,

$$pK_a = pH + \log\frac{[HA]}{[A^-]}$$

When the solution is half-neutralized, $[HA] = [A^-]$. Under such conditions $pK_a = pH$. Thus, *p*H of the half-neutralized solution represents the pK_a of the acid.

From the data obtained during the titrations, the volume of NaOH required to neutralize the acid was determined by plotting $\Delta pH/\Delta V$ versus the volume of the NaOH, and the value of *p*H at half-neutralization and, hence, pK_a was noted. The relevant data pertaining to dextrose and mannitol are presented in Table 1. As in the presence of ethylene glycol or propylene glycol the change in pK_a of 0.1 *M* boric acid was found to be quite insignificant (0.09 and 0.13 pK_a units for ethylene glycol and propylene glycol respectively), the data obtained in these cases are not included in Table

Table 1 – Ionization constant of 0.1 *M* boric acid in presence of dextrose and mannitol

Polyol	Conc. of polyol (*M*)	Ionization constant pK_a
–	–	9.12*
Dextrose	0.2	8.98
	0.4	8.71
	0.6	8.56
	0.8	8.43
	1.0	8.29
Mannitol	0.05	8.55
	0.10	7.88
	0.15	7.31
	0.20	6.93
	0.25	6.62
	0.30	6.42
	0.50	5.89

*pK_a of 0.1 *M* boric acid alone

1. It can be seen from Table 1 that pK_a of boric acid gets reduced from 9.12 to 7.93 when the concentration of dextrose is varied from 0 to 1.0 *M*. In the case of mannitol, however, the change in pK_a is from 9.12 to 5.89, i.e., by more than 3 pK_a units when its concentration changes from 0 to 0.5*M*. This confirms that among the reagents studied, mannitol is the best complexing reagent for increasing the ionization constant of boric acid and, hence, for the separation of isotopes of boron by ion exchange chromatography. From Fig. 1, it can be observed that there is an abrupt decrease in values of pK_a when concentration of mannitol increases from 0 to 0.2 *M* for 0.1 *M* boric acid. Beyond this concentration, the change in pK_a is relatively small indicating thereby that addition of 0.2 *M* mannitol to 0.1 *M* boric acid must be sufficient for its use as feed solution in the separation of the isotopes of boron by ion exchange chromatography.

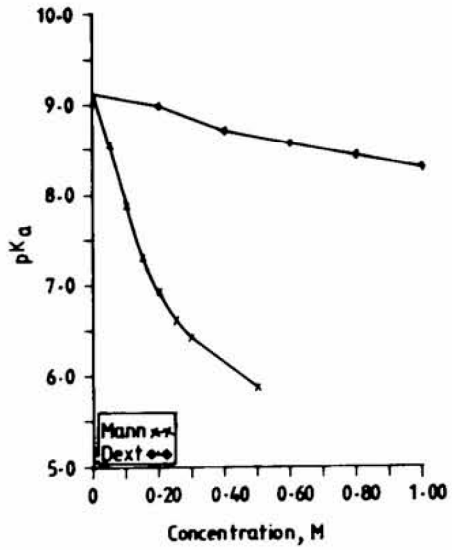

Fig. 1 – Variation of pK_a of 0.1 *M* boric acid with concentrations of dextrose and mannitol.

The order of four complexing reagents in increasing the ionization of boric acid (ethylene glycol ≃ propylene glycol < dextrose < mannitol) is analogous to the order of formation constants of the complexes of these polyols with hydrated borate ion[6-8].

The effect of concentration of mannitol on the isotopic exchange separation factor was studied by batch method[9]. From the obtained values of isotopic ratios, isotopic exchange separation factor was calculated[4]. From these values of isotopic exchange separation factor (K), the values of pE were computed where E = K − 1. The data so obtained are presented in Fig. 2. From this figure, it is found that the value of isotopic exchange separation factor increases as the concentration of mannitol is increased from 0 to 0.2 *M*. Beyond this, there is no significant change in isotopic exchange separation factor. As a similar behaviour was observed for pK_a of boric acid, an attempt was made to derive a relation between pE and, hence, the isotopic exchange separation factor and pK_a of boric acid. It was found that there exists a linear relation between pK_a and pE as given below:

$$pE = 0.8554 + 0.12635\ pK_a$$

The close agreement between experimentally observed and computed values is depicted in Fig. 3.

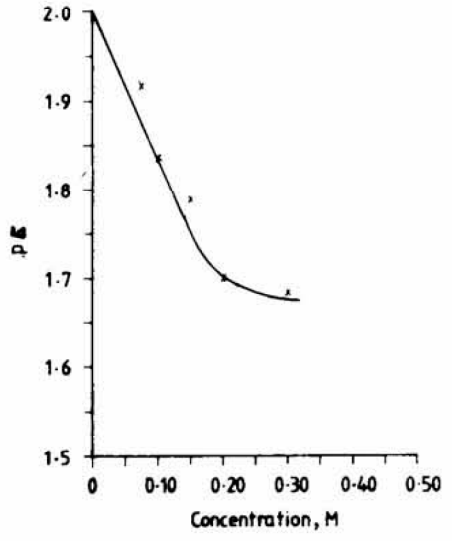

Fig. 2 – Variation of pE with concentration of mannitol in 0.1 *M* boric acid.

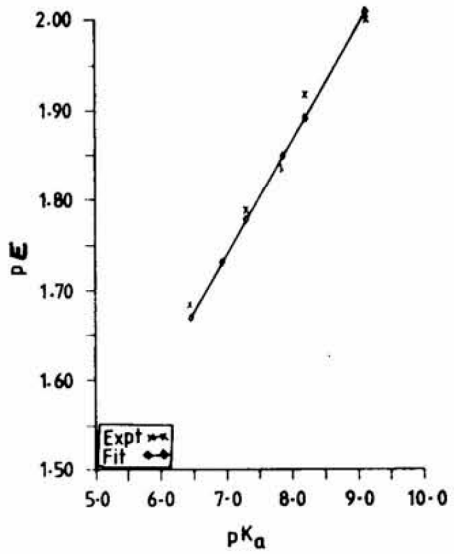

Fig. 3 – Variation of pE with pK_a of boric acid.

Conclusions

Isotopic exchange separation factor for isotopes of boron increases as a result of addition of complexing reagents to boric acid. This increase is due to the increased ionization of boric acid. Among the four complexing reagents under study, mannitol is the most suitable. Addition of 0.2 *M* of mannitol is sufficient for 0.1 *M* boric acid to be used as the feed material for the separation of isotopes of boron by ion exchange chromatography.

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References

1 Blue T E, Robert T C, Barth R F, Talnagi J W & Alam F, *Nucl Tech*, 77 (1987) 220.

2 Kakihana H, Kotaka M, Satoh S, Nomura M & Okamato M, *Bull chem Soc Jpn*, 50 (1977) 158.

3 Yoneda Y, Uchijima T & Makishima S, *J phys Chem*, 63 (1959) 2057.

4 Sharma B K, *Separation of boron isotopes by ion exchange chromatography*, M. Phil. Disser., Punjabi University, Patiala, 1986.

5 Bassett J, Denney R C, Jeffery G H & Mendham J, *Vogel's text book of quantitative inorganic analysis*, 4th Edn (The English Language Book Society, London), 1979, 19.

6 Paal T, *Acta chem hung*, 103 (1980) 181.

7 Roy G L, Laferriere A L & Edward J O, *J inorg nucl Chem*, 4 (1957) 106.

8 Mikan A & Bartusek M, *Coll Czech chem Commun*, 45 (1980) 2645.

9 Sharma B K & Subramanian R, *Symposium on radiochemistry & radiation chemistry*, IGCAR, Kalpakkam, 1989, paper ST-03.