Effect of Quaternary Ammonium Salts on the Extraction of 1,3-Propanediol with Phenylboronic Acid

Michiaki MATSUMOTO*, Kikuko SHIMIZU, Yuji HARADA and Kazuo KONDO

Department of Chemical Engineering and Materials Science

Doshisha University, Kyotanabe, Kyoto 610-0321 Japan

(Received December 30, 2015; Accepted January 26, 2016)

The microbial production of 1,3-propanediol from renewable resources is of great interest. However, its strong hydrophilic property makes the separation of 1,3-propanediol from the fermentation broth difficult. In this study, reactive extraction using boronate esterification, and anion exchange with a quaternary ammonium salt were utilized to extract 1,3-propanediol from an aqueous solution. For this process, the effects of the quaternary ammonium cation and the counter anion on the extraction were examined. Symmetrical quaternary cations were found to provide higher distribution ratios than their unsymmetrical counterparts. Following this, quaternary ammonium fluoride and hydroxide (which have smaller association constants than commercially available quaternary ammonium salts) were prepared. It was found that the distribution ratio of symmetrical quaternary ammonium hydroxide such as $[N_{8,8,8,8}][OH]$ increased by roughly double that for Aliquat 336.

1. Introduction

1,3-Propanediol is a promising bulk chemical, attracting attention due to its wide applications in polymers, solvents, etc [1]. Although 1,3-propanediol was produced by means of the chemical conversion of acrolein, in recent times microbial production from renewable resources has received more attention. Due to the high boiling point (214°C) and high hydrophilicity of 1,3-propanediol, its recovery from fermentation broths becomes an important factor in its industrial production. The development of an efficient and economic recovery technique is desired to improve the economics of the production process based on a biological route. Several separation methods involving reactive extraction, liquid–liquid extraction, evaporation, distillation, membrane filtration, pervaporation and ion exchange chromatography have been proposed [2]. Reactive extraction methods using a reversible reaction such as esterification with boronates [3] (shown in Scheme 1), and acetalization with aldehydes in the presence of an acid catalyst [4] were proposed to selectively separate 1,3-propanediol. In the latter process, there are concerns about the inactivation of the catalyst in the real fermentation medium and regeneration of 1,3-propanediol from its dioxolane derivative [1]. On the other hand, reactive extraction using esterification of 1,3-propanediol with boronates, and anion exchange of the boronate anion complex with a quaternary ammonium salt is problematical because of a relatively low partition coefficient [3].

In this study, in order to enhance the extractability of 1,3-propanediol, we examined the effects of the quaternary ammonium cations and counter-anions on the extraction of 1,3-propanediol.

2. Experimental

2.1 Chemicals

The quaternary ammonium salt extractants used are listed in Table 1, along with their abbreviations. For the conversion of these extractants into their fluoride and hydroxide forms, the quaternary ammonium salts were contacting with either concentrated sodium fluoride or sodium hydroxide solutions according to the procedure presented by Kyuchoukov *et al.* [5]. The conversion ratio was determined by means of analyzing chloride or bromide concentrations in the aqueous phase. Almost complete conversions were confirmed. 1-Octanol was used as the diluent. The other reagents including 1,3-propanediol and phenylboronic acid were used as received.

Scheme 1. Extraction mechanism of 1,3-propanediol with phenylboronic acid and a quaternary ammonium salt

2.2 Reactive extraction

Phenylboronic acid and quaternary ammonium salts as described above were used as co-extractants. Organic solutions were prepared by dissolving the co-extractants in 1-octanol. Aqueous solutions were prepared by dissolving 1,3-propanediol diol of G.R. grade in deionized water. The pH of the aqueous solutions was adjusted by using a 0.5 mol/dm^3 NaOH-NaHCO_3 buffer. Aqueous and organic solutions of

equal volume (5 cm³) were then mixed in a vial tube and shaken at 303 K to attain extraction equilibrium. After the two phases were separated, the concentration of 1,3-propanediol in the aqueous solution was measured. The pH values of the aqueous solutions before and after equilibration were obtained using a Horiba F-71 pH meter.

1,3-Propanediol concentrations in the samples were determined by HPLC (Shimadzu LC-10ADvp) with a refractive index detector (Shimadzu RID-10A). Analyses were performed using a Shodex SUGAR SH-1011 (Showa Denko) column and a 5 mmol/dm³ H₂SO₄ solution as the mobile phase. The distribution ratio of 1,3-propanediol, *D*, was defined as the following equation.

$$D = \frac{C_0 - C_{aq}}{C_{aq}} \quad (1)$$

where *C*₀ and *C*_{aq} are the concentrations of 1,3-propanediol at the initial and equilibrium states.

Table 1. List of extractants used in this study

Quaternary ammonium salt	Abbreviation [N _{R1,R2,R3,R4}][X]	Quaternary ammonium salt	Abbreviation [N _{R1,R2,R3,R4}][X]
Decyltrimethylammonium bromide	[N _{1,1,1,10}][Br]	Didodecyldimethyl ammonium bromide	[N _{1,1,12,12}][Br]
Dodecyltrimethylammonium bromide	[N _{1,1,1,12}][Br]	Dihexadecyldimethyl ammonium bromide	[N _{1,1,16,16}][Br]
Tetradecyltrimethylammonium bromide	[N _{1,1,1,14}][Br]	Distearyldimethyl ammonium bromide	[N _{1,1,18,18}][Br]
Stearyltrimethylammonium bromide	[N _{1,1,1,18}][Br]		
Trioctylmethylammonium chloride (Aliquat 336)	[N _{1,8,8,8}][Cl]	Tetrapropylammonium bromide	[N _{3,3,3,3}][Br]
		Tetrahexylammonium bromide	[N _{6,6,6,6}][Br]
		Tetraoctylammonium bromide	[N _{8,8,8,8}][Br]

3. Results and Discussion

It is well known that 1,3-propanediol is extracted with phenylboronic acid and a quaternary ammonium salt via the following steps [3]. Firstly the phenylboronic acid dissolved in the organic phase was distributed into the aqueous phase, and the trihydroxy phenylboronate anion was esterified with 1,3-propanediol. After esterification, the boronate anion was extracted into the organic phase via an anion exchange reaction. These steps are illustrated as Scheme 1. To improve the extractability, the esterification between the boronate anion and 1,3-propanediol (step 2) and the anion exchange reaction between the boronate-diol anion and the counter anion of the quaternary ammonium salt (step 3) were studied. In this study, we focused on the anion exchange reaction and examined the effect of the quaternary ammonium salt on the overall extraction reaction.

3.1 Effect of the quaternary ammonium cation

We examined the effect of the quaternary ammonium cation on the extraction of 1,3-propanediol. In the previous study [3], we used Aliquat 336 ($[N_{1,8,8,8}][Cl]$) as the anion exchanger. Quaternary ammonium cations can be divided into two groups; a relatively symmetrical group ($[N_{1,1,n,n}]$ and $[N_{n,n,n,n}]$) and an unsymmetrical group ($[N_{1,1,1,n}]$ and $[N_{1,n,n,n}]$). Figure 1 demonstrates the effect of unsymmetrical (A) and symmetrical (B) quaternary ammoniums salts on the distribution ratio. The distribution ratio showed an increase with increasing pH. This suggests that the boronate anion is involved in the extraction reaction because the pK_a value of phenylboronic acid is 9.2 [3]. Evidently, the symmetrical quaternary ammonium cations produced a higher distribution ratio than the unsymmetrical ones, with the exception of $[N_{3,3,3,3}][Br]$. The electrostatic interaction of the symmetrical quaternary ammonium cations are known to be less than that of the unsymmetrical ones, due to the shielding effect of the alkyl chain [6]. Therefore in the present case, the hydrophobic solvation between the large cations and anions was considered to be the dominant factor rather than the electrostatic interaction.

Figure 1. Extraction of 1,3-propanediol with unsymmetrical (A) and symmetrical (B) quaternary ammonium cations

3.2 Effect of the quaternary ammonium salts counter-anion

In order to promote the anion exchange between the counter anion of the quaternary ammonium salt and the boronate complex anion, we prepared quaternary ammonium fluorides and hydroxides. These salts have smaller association constants than chloride and bromide salts [7].

Figure 2 shows the extraction of 1,3-propanediol with quaternary ammonium fluoride (A) and hydroxide (B). As expected, the distribution ratios with fluoride and hydroxide salts were larger than those of the original salts. It is confirmed that the salts having small association constants with the quaternary ammonium salts give larger distribution ratios. The distribution ratio with fluoride increased with increasing pH (similar to Figure 1). On the other hand, the distribution ratio with hydroxide increased with

pH and further increases in the pH value caused a reduction in the distribution ratio because of an increase in the anion exchange reaction with hydroxide ions in the aqueous phase. The distribution ratio with $[N_{8,8,8,8}][OH]$ increased roughly twofold compared to that of Aliquat 336 reported in the previous paper [3]. However, even with the optimized quaternary ammonium salt, the distribution ratio remained below 0.5. In the extraction of mono-saccharides with the same extraction system, the distribution ratio with Aliquat 336 and phenylboronic acid was greater than 5 [8]. This is due to the large difference in the formation constants for polyol complexes with phenylboronic acid [9]. Because of this, the effect of boronate on the formation of the 1,3-propanediol complex will be examined in the near future.

Figure 2. Extraction of 1,3-propanediol with quaternary ammonium fluorides (A) and hydroxides (B)

4. Conclusion

In this study, phenyl boronate and quaternary ammonium salts were used to extract 1,3-propanediol from an aqueous solution, and the effects of the quaternary ammonium cation and counter anion on the extraction were examined. Symmetrical quaternary cations resulted in a higher distribution ratio compared with unsymmetrical ones. This suggests a contribution of hydrophobic solvation. Quaternary ammonium fluoride and hydroxide salts (which have smaller association constants than commercially available quaternary ammonium salts), also showed a higher distribution ratio. It was found that the distribution ratio of symmetrical quaternary ammonium hydroxides such as $[N_{8,8,8,8}][OH]$ increased roughly twofold, in comparison to that of Aliquat 336.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 25420813 and MEXT-Supported Program for the Strategic Research Foundation at Private Universities.

References

- 1) R. K. Saxena, P. Anand, S. Saran, J. Isar, *Biotechnol. Adv.*, **27**, 895-913 (2009).

- 2) Z. L. Xiu, A. P. Zeng, *Appl. Microbiol. Biotechnol.*, **78**, 917-926 (2008).
- 3) M. Matsumoto, A. Kado, T. Shiraki, K. Kondo, K. Yoshizuka, *J. Chem. Tech. Biotechnol.*, **84**, 1712-1716 (2009).
- 4) M. Matsumoto, K. Nagai, K. Kondo, *Solvent Extr. Res. Dev. Jpn.*, **22**, 209-213 (2015).
- 5) G. Kyuchoukov, M. Marinova, J. Albet, J. Molinier, *Ind. Eng. Chem. Res.*, **43**, 1179-1184 (2004).
- 6) S. Motomizu, S. Hamada, K. Toei, *Bunseki Kagaku*, **32**, 648-653 (1983).
- 7) V.V. Egorov, E.M. Rakhman'ko, Chemical Problems of the Development of New Materials and Technologies, O.A. Ivashkevich (Ed.), Minsk, pp. 340–367(2003).
- 8) M. Matsumoto, K. Ueba, K. Kondo, *Sep. Purify. Technol.*, **43**, 269-274 (2005).
- 9) D. S. Tarbell, E. J. Longosz, *J. Org. Chem.*, **24**, 769-774 (1959).