− *Notes* −

Effect of Organic Cations and Solvents on the Ion-Pair Extraction of Boric Acid with Salicyl Alcohol

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Ion-pair extraction of boric acid with salicyl alcohol (H_2sal) has been studied using several organic cations such as trioctylmethylammonium chloride (TOMACl), tetrahexylammonium bromide (Hex_4NBr), and tetraphenylphosphonium bromide (Ph_4PBr) in various solvents. The extractability of boric acid was strongly dependent on the organic cations and solvents used and decreased in the order TOMACl > Hex_4NBr >> Ph_4PBr in almost all solvents for which the order was *o*-dichlorobenzene ≥ chlorobenzene > toluene > 1,2-dichloroethane > hexane > chloroform > methyl isobutyl ketone for TOMACl. The extracted species was found to be $TOMA^+ \cdot B(sal)_2^-$ in toluene from equilibrium analysis.

1. Introduction

Boron is an essential plant trace element and is widely used in various fields such as electronics, nuclear engineering, and organic synthesis. However, when humans and wildlife take boron, it causes an adverse gonad effect. Therefore, the World Health Organization recommends a boron level of 2.4 mg l^{-1} for drinking water. In general, the solvent extraction of boric acid is performed using aliphatic diol compounds in chloroform [1-3] as well as aromatic diol compounds in benzene, kerosene, and fatty alcohols [4-7]. An industrial extractant, 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylolphenol (CTMP), has been synthesized and used for the removal of boron from alkaline brine, but the extraction equilibrium is not well understood [8, 9]. In addition, only a few reports have dealt with the extraction equilibrium of boric acid with diol compounds [9-11].

In this paper, the effect of ion-pair reagents and organic solvents on the extraction of boric acid with salicyl alcohol (H_2sal) as the mother compound of CTMP was investigated, and the extraction equilibrium in the H_2sal–trioctylmethylammonium chloride (TOMACl)–toluene system was studied at pH 4−12.

2. Experimental

2.1 Reagents

A stock solution of boric acid was prepared by dissolving boric acid (Merck, Suprapur) in water. Salicyl alcohol (99.8 % purity) was obtained from Aldrich. Trioctylmethylammonium chloride, tetrahexylammonium

bromide (Hex$_4$NBr), and tetraphenylphosphonium bromide (Ph$_4$PBr) were of guaranteed reagent (GR) grade and were used without further purification. Chlorobenzene (CB), 1,2-dichloroethane (DCE), hexane (Hex), toluene (Tol), methyl isobutyl ketone (MIBK), and o-dichlorobenzene (DCB) were of GR grade and were used as obtained. Chloroform (CF) was washed twice with water before use. High purity deionized water (18.2 MΩ) processed by a Milli-Q system (Millipore) was used throughout this work. Other chemicals used were of analytical or GR grade.

2.2 Extraction procedure

An aqueous phase containing 4.0×10^{-4}–1.0×10^{-2} mol dm^{-3} boric acid and 1.0×10^{-1} mol dm^{-3} NaCl was shaken for 10 min with an equal volume of an organic phase containing 5.0×10^{-4}–1.0×10^{-1} mol dm^{-3} H$_2$sal and a 5.0×10^{-4}–1.0×10^{-2} mol dm^{-3} ion-pair reagent. After phase separation, the pH of the aqueous phase was measured with a pH meter (Horiba, F-52) equipped with a combination glass electrode (Horiba, 9611-10D). The boron concentration in the aqueous phase was determined spectrophotometrically using chromotropic acid [12], while that in the organic phase was determined in the same manner after back-extraction of boron with 1.0×10^{-1} mol dm^{-3} HCl. The percentage extraction (%E) and the distribution ratio (D) of boron were calculated from the concentrations in both phases.

3. Results and Discussion

3.1 Effect of ion-pair reagents and solvents

The extraction of 4.0×10^{-4} mol dm^{-3} boric acid with 4.0×10^{-3} mol dm^{-3} H$_2$sal and 4.0×10^{-3} mol dm^{-3} TOMACl, Hex$_4$NBr, or Ph$_4$PBr in various organic solvents was carried out. It was ascertained that equilibrium was readily attained within 5 min shaking time. Figure 1 shows the extractability of boric acid as a function of the aqueous phase pH. The %E value increases with increasing pH and reaches a maximum value at around pH 9 in all systems. The quantitative extraction of boric acid was achieved with TOMACl and Hex$_4$NBr in several solvents in the pH range from 8.0 to 9.5. Since the extraction efficiency strongly depends on both the ion-pair reagents and solvents, the %E values are compared at pH 8.0 in Table 1. The highest degree of extraction was obtained by TOMACl in DCB. The effect of the solvents on the extractability of boric acid was dependent on the ion-pair reagent used as follows; DCB ≥ CB > Tol ≥ DCE > Hex > CF > MIBK for TOMACl, DCB ≥ CB > DCE > Tol > CF > MIBK for Hex$_4$NBr, and DCE > CF ≥ DCB > MIBK > CB > Tol for Ph$_4$PBr. In all the systems, the solvents having higher dielectric constants like DCB and DCE

Figure 1.   Plots of %E for boric acid (4×10^{-4} mol dm^{-3}) as a function of pH. 4×10^{-3} mol dm^{-3} H$_2$sal; 4×10^{-3} mol dm^{-3} ion-pair reagent.   (a) TOMACl, (b) Hex$_4$NBr, (c) Ph$_4$PBr system. ○, DCB; ◐, CB; ●, Tol; ◆, DCE; ◆, Hex; ◇, CF; ✜, MIBK.

gave higher extractability. The difference between the ion-pair reagents, especially TOMACl and Ph$_4$PBr, is ascribable to their hydrophobicity. TOMACl is highly hydrophobic but Ph$_4$PBr is rather hydrophilic, as it dissolves in
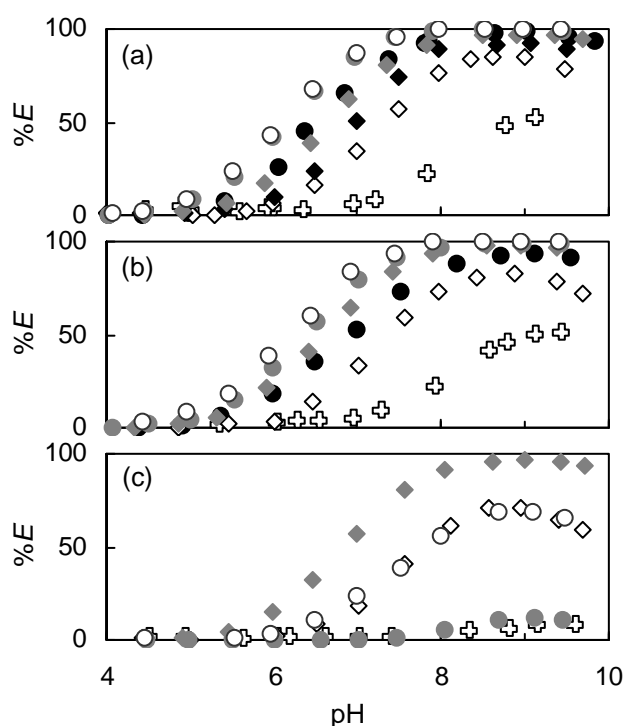
water [13, 14]. To understand such extraction behavior of boric acid, it is necessary to elucidate the extraction equilibrium and the extractable species.

3.2 Extraction equilibrium

The extraction equilibrium of boric acid was investigated in the H$_2$sal–TOMACl–toluene system over a wide pH range from 5 to 12. Figure 2 shows the log D–pH plot. At pH values lower than 8, the log D value linearly increases with increasing pH, while at pH values higher than 10, the log D value steeply decreases. The acid dissociation constants of B(OH)$_3$ and H$_2$sal were $K_{a,B(OH)_3} = 10^{-9.05}$ [15] and $K_{a,H_2sal} = 10^{-9.94}$ (spectrophotometrically determined in this work), respectively. Hence the extraction equilibrium can be separately discussed for pH values < 8 as well as for pH values > 11.

Since boric acid exists as B(OH)$_3$ in aqueous solution at pH < 8, if it forms an anionic complex with n molecules of H$_2$sal and is extracted with m molecules of TOMACl, the extraction equilibrium can be expressed by,

Table 1.   %E of boric acid at pH 8.0.

Solvent	TOMACl	Hex$_4$NBr	Ph$_4$PBr
DCB	100	98	56
CB	99	97	5
Tol	94	84	0
DCE	93	94	91
Hex	89	——[a]	——[a]
CF	77	74	57
MIBK	25	23	3

[a] No data because of low solubility of the reagent.
Initial boric acid concentration, 4.0×10^{-4} mol dm^{-3}; initial H$_2$sal concentration, 4.0×10^{-3} mol dm^{-3}; initial ion-pair reagent concentration, 4.0×10^{-3} mol dm^{-3}.
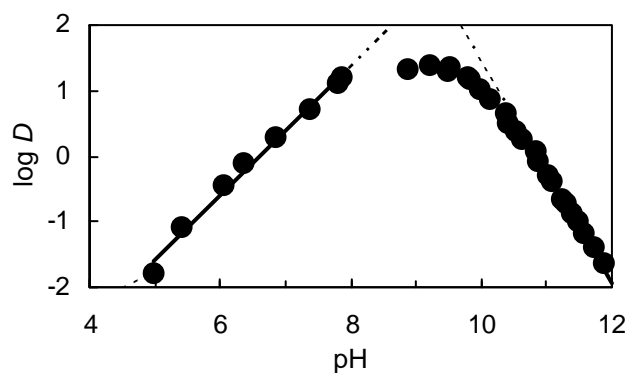

Figure 2.   Effect of pH on log D for boric acid (4×10^{-4} mol dm^{-3}). Solvent, toluene; 4×10^{-3} mol dm^{-3} H$_2$sal; 4×10^{-3} mol dm^{-3} TOMACl.

$$\text{B(OH)}_3 + n\text{H}_2\text{sal}_{org} + m\text{TOMACl}_{org} \rightleftharpoons m\text{TOMA} \cdot \text{B(OH)}_{3-x}(\text{sal})_{n,org} + (2n - x)\text{H}^+ + m\text{Cl}^- + x\text{H}_2\text{O} \quad (1)$$

$$K_{ex} = \frac{[m\text{TOMA} \cdot \text{B(OH)}_{3-x}(\text{sal})_n]_{org}[\text{H}^+]^{2n-x}[\text{Cl}^-]^m}{[\text{B(OH)}_3][\text{H}_2\text{sal}]_{org}^n[\text{TOMACl}]_{org}^m}, \quad (2)$$

where the subscript "org" refers to the organic phase. Since the distribution ratio of boric acid is given by $D = [m\text{TOMA} \cdot \text{B(OH)}_{3-x}(\text{sal})_n]_{org}/[\text{B(OH)}_3]$, the following equation is derived,

$$\log D = n\log[\text{H}_2\text{sal}]_{org} + m\log[\text{TOMACl}]_{org} + (2n - x)\text{pH} - m\log[\text{Cl}^-] + \log K_{ex}, \quad (3)$$

where [Cl$^-$] is kept at 0.10 mol dm^{-3} under the given conditions.

Figure 2 shows that the slope of the log D–pH plot at pH < 8 is 1.0, therefore $2n$-x = 1. The relationship between log D and log [H$_2$sal]$_{org}$ was examined at fixed pH and TOMACl concentration in toluene.   The equilibrium concentration of H$_2$sal in the organic phase was calculated using the distribution constant (K_{D,H_2sal}) determined in this work, i.e., $K_{D,H_2sal} = 10^{-0.33}$. Figure 3 shows that the log D–log [H$_2$sal]$_{org}$ plot gives a straight line with a slope of 1.9.

These results show that the values of n and x are 2 and 3 respectively. However, the log D–log [TOMACl]$_{total}$ plot did not give a straight line because of the aggregation of TOMACl in the organic solvent [16, 17]. Hence, the stoichiometry of the extracted species was confirmed by the mole ratio method. The extraction of 4.0×10^{-4} mol dm^{-3} boric acid was carried out with varying concentrations (0–1.0×10^{-3} mol dm^{-3}) of TOMACl in the presence of 4.0×10^{-2} mol dm^{-3} H$_2$sal at pH 8.81. Figure 4 clearly shows that the mole ratio of boric acid to TOMACl is 1 : 1 in the extracted species, therefore $m = 1$.

From the results obtained above, the extraction equilibrium can be written as follows,

$$B(OH)_3 + 2H_2sal_{org} + TOMACl_{org} \rightleftharpoons TOMA \cdot B(sal)_{2,org} + H^+ + Cl^- + 3H_2O . \tag{4}$$
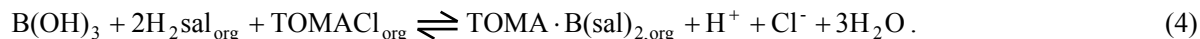
Thus boric acid forms the complex B(sal)$_2^-$ with two molecules of H$_2$sal which then acts as a bidentate ligand and is extracted by ion exchange with the Cl$^-$ of TOMACl. This complex formation between boric acid and H$_2$sal in aqueous solution and the structure of the complex have been studied by ^{11}B NMR as reported in a recent paper [18].

On the other hand, boric acid and salicyl alcohol exist as B(OH)$_4^-$ and Hsal$^-$ respectively in the aqueous phase at pH 11–12. If boric acid is extracted as the same species, B(sal)$_2^-$, the extraction equilibrium can be written as,

$$B(OH)_4^- + 2Hsal^- + TOMACl_{org} \rightleftharpoons TOMA \cdot B(sal)_{2,org} + 2OH^- + Cl^- + 2H_2O \tag{5}$$
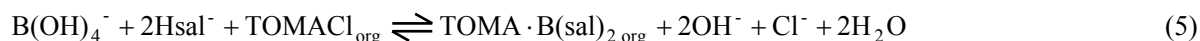
$$K_{ex}' = \frac{[TOMA \cdot B(sal)_2]_{org}[OH^-]^2[Cl^-]}{[B(OH)_4^-][Hsal^-]^2[TOMACl]_{org}} . \tag{6}$$

Since the distribution ratio of boric acid is given by $D = [TOMA \cdot B(sal)_2]_{org}/[B(OH)_4^-]$, the following equation is derived,

$$\log D = 2\log[Hsal^-] + \log[TOMACl]_{org} - 2pH - \log[Cl^-] - 2\log K_w + \log K_{ex}', \tag{7}$$
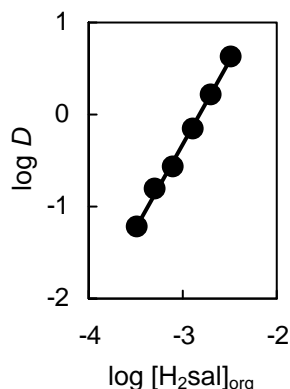

Figure 3. Effect of the H$_2$sal concentration in toluene on log D for boric acid at pH 6.39 ± 0.03. Initial TOMACl concentration, 4×10^{-3} mol dm^{-3}; initial boric acid concentration, 4×10^{-4} mol dm^{-3}.
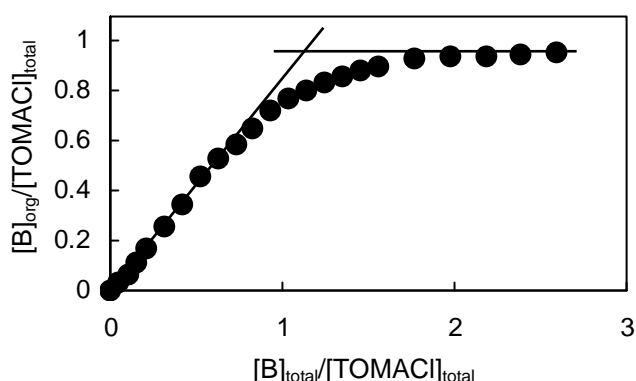
Figure 4. Mole-ratio plot at pH 8.81 ± 0.03. Initial H$_2$sal concentration, 4×10^{-2} mol dm^{-3}; initial boric acid concentration, 4×10^{-4} mol dm^{-3}; solvent, toluene.

where K_W stands for the ionic product of water. In Fig. 2, the log D–pH plot gave a straight line with a slope of -1.7 at pH > 11, which is reasonably close to the theoretical value of 2. Even if a part of Hsal$^-$ exists as TOMA$^+$·Hsal$^-$ in the organic phase, the [H$^+$] dependency is not affected at all.

In conclusion, boric acid forms a tetrahedral anionic complex, B(sal)$_2^-$, with salicyl alcohol and is extracted as the ion pair complex, TOMA$^+$·B(sal)$_2^-$, which is probably the most stable among the other organic cations used because TOMA$^+$ having a methyl group does not cause severe steric hindrance in the ion-pair formation and, furthermore, is most hydrophobic. Consequently, it can be extracted into chlorobenzene, toluene, and even hexane which is a nonpolar solvent.

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