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Ion Pair Extraction—Effect of Reagent Quantity on the Selectivity of Bromide-Chloride Separation

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Abstract

The calculated selectivity of anions extracted from an aqueous phase into an organic solvent by a quaternary ammonium compound is highly dependent on the quantity of the reagent. Selectivity increases with a decrease in quantity of the salt (from 2.2 to 21.2 for salt quantities of 1 and 0.02 mol, respectively, in the system discussed) but never exceeds a certain value (25 in the system discussed). The same trend is observed when the volume of the organic phase is reduced. Experimental data agree well with the calculated results.

INTRODUCTION

Chemical extraction of ions and salts from aqueous solutions by liquid ion exchangers in organic solvents is a common method in analytical chemistry (*1*, *2*) that has found numerous applications as a separation technology (*3*, *4*) as well as in synthesis (*5*, *6*).

Anions, for example, can be extracted from water by contact with an organic solvent containing lipophilic quaternary ammonium salt according to the general equation (*7*, *8*)

$$R_4N^+X^-(\mathrm{org}) + Y^-(\mathrm{aq}) \rightleftharpoons R_4N^+Y^-(\mathrm{org}) + X^-(\mathrm{aq}) \qquad (1)$$

where Y^- is the anion to be extracted from the aqueous phase. In a similar manner, cations were transferred to organic solvents by the application of

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soluble cation exchangers. An example is the extraction of the calcium cation by sulfonic acid salts (*4*):

$$2RSO_3Na(org) + Ca^{2+}(aq) \rightleftharpoons (RSO_3)_2Ca(org) + 2Na^+(aq) \quad (2)$$

Application of mixtures of liquid anion and liquid cation exchangers allowed the extraction of various salts into the organic phase (*4*). Sodium chloride can be extracted by hexane-mixed solutions of trilaurylamine and stearic acid according to the following mechanism:

$$R_3N^+HR'COO^-(org) + NaCl(aq) \rightleftharpoons R_3N^+HCl^-(org) + R'COO^-Na^+(aq) \quad (3)$$

where R is a C_{12} residue and R′ is a C_{18} residue. This principle was applied for the extraction and separation of a large number of salts (*4*).

Since the major application of the above systems is for separation of ionic substances, one should take into consideration two important properties of the extracting reagents, namely the extraction constant and the selectivity coefficient.

For a quaternary ammonium salt with the general formula Q^+X^- which is distributed between aqueous and organic phases, a stoichiometric extraction constant, E_{QX}, was defined as follows (*9, 10*):

$$E_{QX} = \frac{[QX]}{[Q^+][X^-]} \quad (4)$$

where [QX] is the concentration of the ion pair QX in the organic phase, and $[X^-]$ and $[Q^+]$ are the concentrations of the dissociated ions in the aqueous phase.

If a competitive ion pair extraction of more than one anion is taking place, an ion-exchange selectivity coefficient $K_{sel}^{X/Y}$ is defined (*11*):

$$K_{sel}^{X/Y} = \frac{[QX][Y^-]}{[QY][X^-]} = \frac{E_{QX}}{E_{QY}} \quad (5)$$

where X^- and Y^- are the competing anions in the aqueous phase and QX and QY are the corresponding ion pairs in the organic phase. E_{QX} determines to what extent the ion pair QX is distributed between the phases while $K_{sel}^{X/Y}$ reflects the selectivity of the organic phase cation for anion X^- over Y^-. The selectivity coefficients given in the literature are usually based on chloride as a reference ion (Y^-). Tables for E_{QX} and K_{sel}^{X/Cl^-} for various systems are available (*7, 11*).

From literature data it is apparent that both E_{QX} and K_{sel}^{X/Cl^-} are dependent on the structure of the quaternary cation, the nature of the anion, and the type of solvent.

While studying the separation of various anions by extraction with liquid anion exchangers, we have observed that the overall selectivity of the separation, namely the relative concentrations of the two ion pairs in the organic phase [QX]/[QY], depends not only on the above constants but also on the molar proportion of the extracting reagent to the extracted species (*12*). This phenomenon, not reported until now in the literature, will be calculated and demonstrated here for separation of bromide anion from chloride anion in aqueous solutions by extraction with tetra-*n*-butylammonium cation in chloroform

We believe that this phenomenon is general in nature and can be applied to similar systems of chemical extraction.

EXPERIMENTAL

Several batches of 100 mL of 0.1 *M* potassium bromide and 0.1 *M* potassium chloride (Fluka, analytical grade) solution were vigorously shaken with 100 mL of chloroform containing increasing concentrations of tetra-*n*-butylammonium hydrogensulfate (Aldrich, 98% purity). After phase separation the chloride and bromide concentrations in the aqueous phase were determined argentometrically and the bromide ion was determined separately using the Van der Meulen method.

RESULTS AND DISCUSSION

Consider a mixture of two anions X^- and Y^- in an aqueous solution which is contacted with an organic phase containing a quaternary ammonium compound Q^+Z^- where Z^- is an anion with a very low extraction constant.

After equilibrium is achieved we practically have two ion pairs in the organic phase, QX and QY, while in the aqueous phase we find the anions X^- and Y^- along with Z^- as well as some Q^+ (see Fig. 1). We assume, for the sake of simplicity, that no side reactions, namely association or dissociation of the ion pairs, are taking place in the organic phase (*8*) and that the aqueous phase is behaving as an ideal solution. E_{QX} and E_{QY} are defined in Eq. (4) and $K_{sel}^{X/Y}$ is defined in Eq. (5).

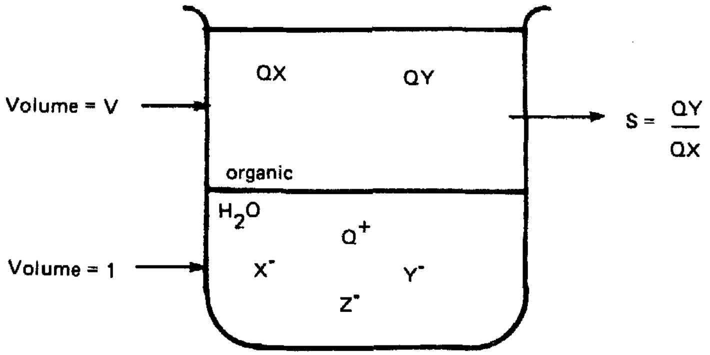

FIG. 1. Schematic representation of the extracting system. Quaternary ammonium compound, QZ, extracting X^- and Y^- anions from an aqueous into an organic phase.

The actual selectivity of the separation in the system S can be defined as follows:

$$S = [QX]/[QY] \tag{6}$$

where [QX] and [QY] are the concentrations of the ion pairs QX and QY, respectively, in the organic phase.

If n_i° is the initial number of moles of each component in the system and n_i is the number of moles of this component at equilibrium, we obtain by material balance:

$$n_{X^-} + n_{QX} = n^\circ_{X^-} \tag{7}$$

$$n_{Y^-} + n_{QY} = n^\circ_{Y^-} \tag{8}$$

$$n_{QY} + n_{QX} = n^\circ_{Q^+} \tag{9}$$

If V_{org} and V_{aq} are the volumes (in liters) of the organic and the aqueous phase, respectively, we can express Eqs. (7)–(9) as

$$V_{aq}[X^-] + V_{org}[QX] = n^\circ_{X^-} \tag{10}$$

$$V_{aq}[Y^-] + V_{org}[QY] = n^\circ_{Y^-} \tag{11}$$

$$V_{aq}[Q^+] + V_{org}[QX] + V_{org}[QY] = n^\circ_{Q^+} \tag{12}$$

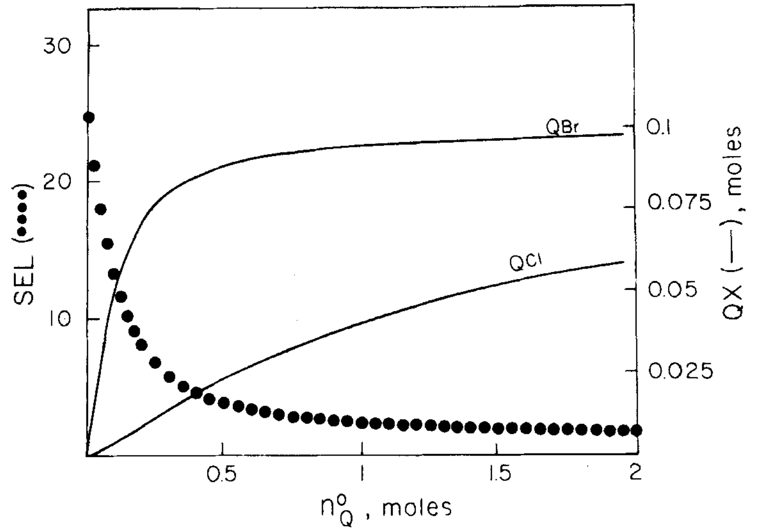

FIG. 2. Calculated selectivity of extraction and amounts of QCl and QBr extracted from a 0.1 *M* aqueous solution of each (initially) by QZ as a function of the total molar quantity of the quaternary ammonium cations in both phases. ($[Cl^-]_0 = [Br^-]_0 = 0.1$ *M*; organic phase = chloroform. Q^+ = tetrabutylammonium, Z^- = hydrogensulfate, $E_{QCl} = 0.78$, $E_{QBr} = 19.5$).

and if 1 liter aqueous solutions are used, we obtain:

$$[X^-] + V_{org}[QX] = n^{\circ}_{X^-} \tag{13}$$

$$[Y^-] + V_{org}[QY] = n^{\circ}_{Y^-} \tag{14}$$

$$[Q^+] + V_{org}[QX] + V_{org}[QY] = n^{\circ}_{Q^+} \tag{15}$$

Equations (13)–(15), combined with Eq. (4) which is expressed once for QX and once for QY, yield five equations with five unknowns.

We have solved these five equations for the system bromide–chloride in aqueous solution which is contacted with chloroform solution of tetra-*n*-butylammonium cation. For this solvent system, $E_{Bu_4NCl} = 0.78$ and $E_{Bu_4NBr} = 19.5$ (*7*, *8*). If the volumes of the two phases and the initial concentrations of Cl^-, Br^-, and Q^+ are known, then all the unknowns, namely $[Cl^-]$, $[Br^-]$, $[Q^+]$, [QBr], and [QCl], can be calculated

When the selectivity of the extraction S = [QX]/[QY] is calculated for a system where $n^{\circ}_{Cl^-} = n^{\circ}_{Br^-} = 0.1$ and $V_{org} = V_{aq}$ with varying quantities of $n^{\circ}_{Q^+}$, it was found that the selectivity is strongly dependent on the molar quantity of the extracting reagent.

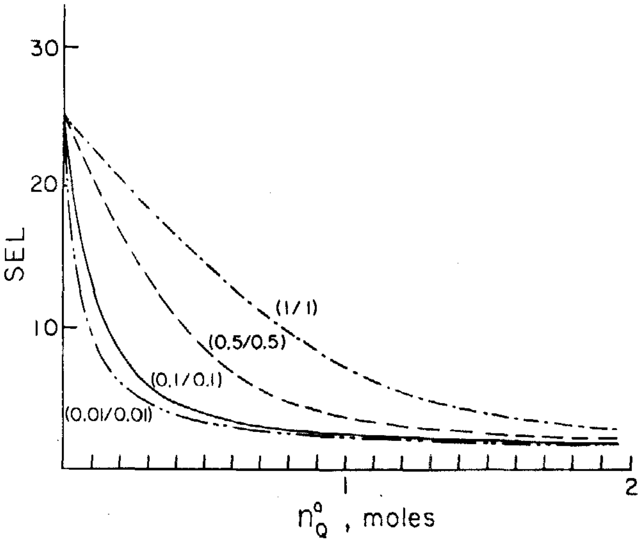

FIG. 3. The effect of total molar quantity of the extracting reagent (tetrabutylammonium hydrogen sulfate) on the calculated extraction selectivity for various initial amounts of Cl^- and Br^- (organic phase = chloroform, $E_{QCl} = 0.78$, $E_{QBr} = 19.5$).

The calculated results are presented in Fig. 2, where the selectivity is plotted versus varying quantities of $n_{Q^+}^o$. It can be seen that at high concentrations of the quaternary salt (above 1 *M*) the selectivity is smaller than 2, but when $n_{Q^+}^o$ decreases the selectivity increases up to 25 when $n_{Q^+}^o$ approaches zero:

$$S_{n_{Q^+}^o \to 0} = \frac{E_{QBr}}{E_{QCl}} = \frac{19.5}{0.78} = 25 \qquad (16)$$

This calculation shows that although the selectivity can be significantly increased by reducing the amount of the quaternary salt, it cannot be increased above the ratio of the extraction constants.

Figure 2 also presents the absolute values of QBr and QCl obtained for each quantity of quaternary cation applied. As can be expected when $n_{Q^+}^o$ is decreased, both [QBr] and [QCl] decrease while the proportion [QBr]/[QCl] increases.

The effect of the original concentrations of the anions ($n_{Cl^-}^o$ and $n_{Br^-}^o$) in the aqueous phase on the selectivity is shown in Fig. 3. The same trend is

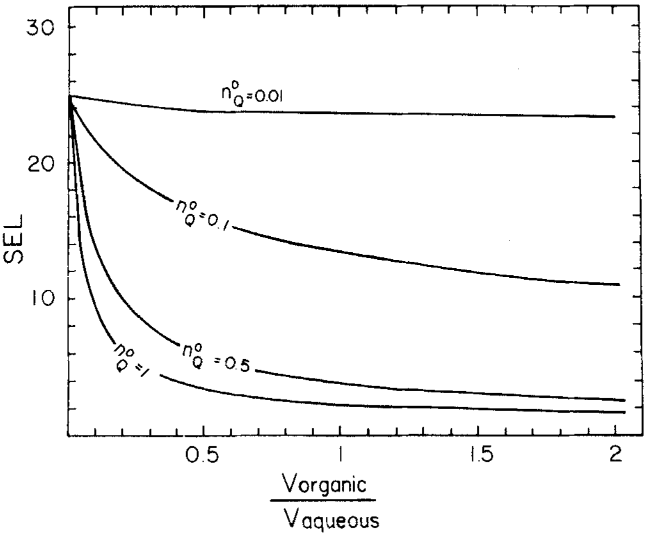

FIG. 4. Effect of the volumes ratio (V_{org}: V_{aq}) on the calculated extraction selectivity as affected by various n_Q^o values. ($[Cl^-]_0 = [Br^-]_0 = 0.1$ *M*, QZ = tetrabutylammonium hydrogen sulfate, organic phase = chloroform, $E_{QCl} = 0.78$, $E_{QBr} = 19.5$).

observed at all concentrations, but selectivity decreases more sharply with increasing $n_{Q^+}^o$ when the amount of the anions is smaller.

When plotting the selectivity S as a function of the volume of the organic phase, V_{org} (with V_{aq} defined as unit volume), a similar trend is observed particularly at high $n_{Q^+}^o$ values (Fig. 4). When V_{org} is reduced the selectivity increases and, again, approaches the value of 25 as $V_{org} \rightarrow 0$. The selectivity is strongly influenced by V_{org} when $n_{Q^+}^o$ is high since for low $n_{Q^+}^o$ values it is already close to 25.

Experimental studies were carried out using tetra-*n*-butylammonium hydrogen sulfate in chloroform to extract aqueous solution containing 0.1 *M* potassium bromide and 0.1 *M* potassium chloride. Equal volumes of the two phases were used.

In four experiments we have changed the concentration of the ammonium salt and measured, after equilibration, the concentration of Cl^- and Br^- in the water phase. From these data the concentrations of QCl, QBr, and Q^+ as well as S could be calculated. We assume that the bisulfate ion is not extracted at all in the presence of the halide ions due to its low extraction constant. The experimental and calculated data are presented in Table 1. The figures in the table are in good agreement with those shown in Fig. 2.

TABLE 1
Extraction of 0.1 *M* KBr and 0.1 *M* KCl in Aqueous Solution by Various Quantities of Tetra-*n*-butylammonium Hydrogensulfate in Chloroform. Equal Volumes of Aqueous Phase and Chloroform Are Used. Concentrations in m*M*

Expt.	$n^{\circ}_{Q^+}$	[Cl⁻]	[Br⁻]	[Q⁺]	[QCl]	[QBr]	S
1	50	29.4	0.0	20.6	67.6	104.0	∞
2	100	57.8	4.5	26.3	39.2	98.5	13.0
3	200	81.1	21.4	97.5	15.9	81.6	3.79
4	500	92.4	50.1	35.8	4.6	52.9	1.84

CONCLUSIONS

It has been shown that low quantities of extracting reagent are needed to obtain higher selectivity of extraction of two competing ions. Alternatively, low volumes of the organic phase will give the same results. It should be noted, however, that when working under conditions of high selectivity, only a small fraction of the anion mixture can be separated (see Fig. 2). This disadvantage can be overcome by operating the extraction process in a system which is continuously in a transient state. Two examples for such systems are phase transfer catalysis and liquid membrane technology with an ion-exchange carrier. In these two examples we have an extracting reagent present in small, catalytic quantities operating in a cycle for extracting anions from one phase to another. It is clear from our result that working with such systems with very low carrier concentrations can lead to very interesting separation processes. Application of this principle in both liquid membranes and phase transfer catalysis will be published.

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