INFLUENCE OF ANIONS ON POTASSIUM AND SODIUM EXTRACTION WITH DIBENZO–18–CROWN–6
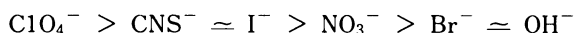
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Summary

A crown compound such as dibenzo-18-crown-6 (DBC) forms complexes with alkali metals. But the effect of anion on metal extraction with DBC is not so apparent. In the extraction of sodium and potassium ions with DBC, the degree of extractability is remarkably dependent on the anion in their metal salts, expressed as follows:

$$ClO_4^- > CNS^- \simeq I^- > NO_3^- > Br^- \simeq OH^-$$

The decreasing order is explained on the basis of the difficulty of the removal of these ions from the aqueous phase, which coincides with the increasing order of the Gibbs free energy of hydration.

1. Introduction

The crown compounds have been studied as selective complexing and extracting agents for metal ions (1-9). These materials form strong complexes particularly with metal ion such as sodium and potassium which fit well into the hole of the cyclic polyether ring. However, the influence of anions on the formation of complexes with crown and metal ions is not apparent except for halide ions (7).

In this report, the influence of anion on the solvent extraction of sodium and potassium was investigated by using dibenzo-18-crown-6 (DBC) in chloroform.

2. Experimental

Materials. DBC was obtained from Aldrich and was recrystallized three times from benzene solution before use. Analytical grade sodium and potassium salts were used. Chloroform was of pure grade freed from ethanol.

Extraction Procedure. Chloroform and water were pre-equilibrated with each other in order to minimize volume change during extraction. Extraction were performed using 45 ml cylindrical vials fitted with polyethylene thimble stoppers and plastic screw caps. Volume ratio 1 : 1 mixture of $8 \times 10^{-3} \sim 7 \times 10^{-2}$M (1M = 1mol dm^{-3}) DBC-chloroform solution and 5×10^{-2} M potassium or 1×10^{-1} M sodium salts aqueous solution were shaken together for one hour in a reciprocating shaker at room temperature $(20 \pm 1°C)$. Then the solutions were centrifuged in order to separate the phases and ali-

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quots of sample were removed from each phase for analysis. The eluted DBC in aqueous phase was determined by UV photometer. The extracted sodium or potassium ions in chloroform phase were determined as follows. After evaporating the chloroform from the organic phase, the solid metal complexes were dissolved in methyl isobutyl keton. The metal ion in the solvents was determined by atomic absorption spectrophotometer.

3. Results and Discussion

The extraction rate of the metal ion with the DBC chloroform solution was measured. Figure 1 shows the relationship between the distribution ratio and shaking time for the extraction of potassium thiocyanate.
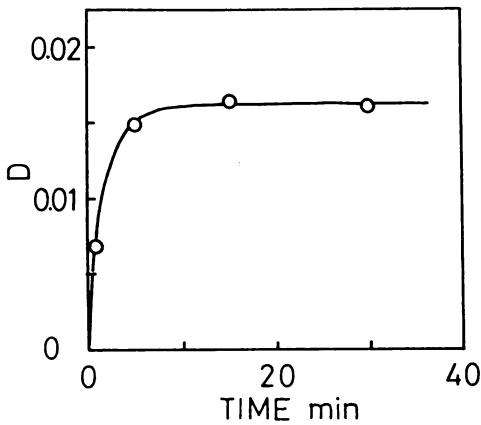

Fig. 1 Plots of distribution ratio D against shaking time for the extraction of KCNS by 0.03M DBC in chloroform.

The extraction of potassium salt with DBC chloroform solution was equilibrated within 10 minutes. Therefore, a one hour shaking time was carried out in subsequent equilibrium experiments.

The distribution ratio D of potassium or sodium salts has as a function of DBC contents $[L]_{(o)}$ in organic phase at equilibrium as shown in Figure 2 and 3, respectively.
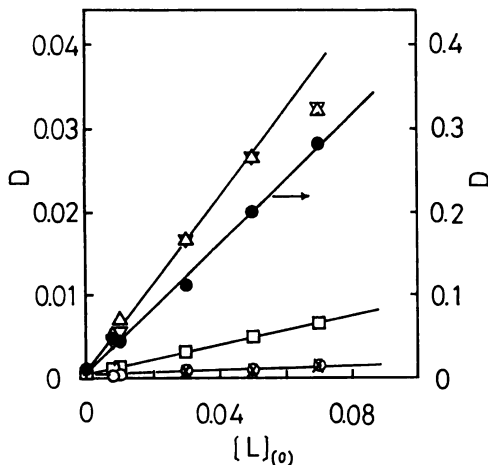

Fig. 2 Plots of distribution ratio D against DBC concentration in chloroform $[L]_{(o)}$ for the extraction of potassium salts : $KClO_4$ (●), $KI(\triangle)$, $KCNS(\triangledown)$, KNO_3 (□), KBr (×), and KOH (○).
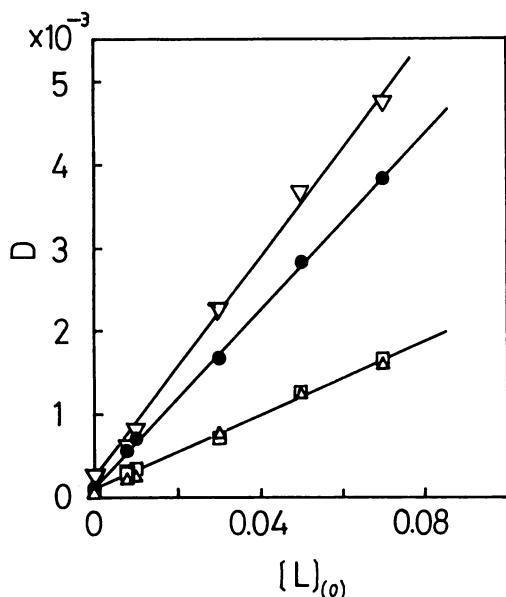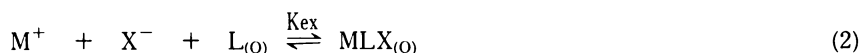
Fig. 3 Plots of distribution ratio D against DBC concentration in chloroform $[L]_{(o)}$ for the extraction of sodium salts : NaClO$_4$ (●), NaI (△), NaCNS (▽), and NaNO$_3$ (□).

As shown in Figure 2 and 3, there is a linear relationship between D and $[L]_{(O)}$. This relationship can be considered as follows.

The metal salt, MX, can be extracted from the organic phase on the basis of the following equations

$$M^+ \ + \ X^- \ \overset{Kd}{\rightleftharpoons} \ MX_{(O)} \tag{1}$$

$$M^+ \ + \ X^- \ + \ L_{(O)} \ \overset{Kex}{\rightleftharpoons} \ MLX_{(O)} \tag{2}$$

where L, Kd and Kex are DBC ligand, distribution coefficient and extraction constant respectively, and the subscript O denotes the organic phase. On the other hand, uncomplexed DBC ligand in organic phase is eluted into the aqueous phase (eq. 3), and the complexation of metal ion with DBC is performed in aqueous phase (eq. 4)

$$L_{(O)} \ \overset{Kdl}{\rightleftharpoons} \ L \tag{3}$$

$$M^+ \ + \ L \ \overset{k}{\rightleftharpoons} \ M^+L \tag{4}$$

where Kdl is the distribution coefficient of DBC, and k is the formation constant of metal complex in aqueous phase.

The distribution ratio D can, therefore, be written as

$$D = \frac{[MX]_{(O)} + [MLX]_{(O)}}{[M^+] + [M^+L]} = \frac{Kd \ [X^-] + Kex \ [X^-] \ [L]_{(O)}}{1 + k \ Kdl \ [L]_{(O)}} \tag{5}$$

If the kKdl $[L]_{(O)}$ value is less than 1, the plot of D against $[L]_{(O)}$ gives a straight line as equation 6.

$$D = Kd \ [X^-] + Kex \ [X^-] \ [L]_{(O)} \tag{6}$$

It was known that the values of k were 14.6 and 46.5 l mol^{-1} for sodium and potassium ions respectively(5), and that the value of Kdl was $10^{-2.9}$(8). The DBC chloroform solution was prepared in the concentration from 8×10^{-3} to 7×10^{-2} M. Under the conditions of this experiment, the value of kKdl [L]$_{(O)}$ in the denominator of equation 5, threrefore, was negligible compared with 1. Consequently, Kex and Kd can be calculated from equation 6 by using the slope and intercept of the straight line in Figure 2 or 3, the mean value of anion concentration, which is the same as the metal ion concentration in the solution.
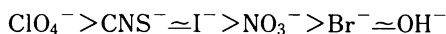
The equilibrium constants are summarized in Table 1.

Table 1   Extraction constants for extraction of potassium and sodium salts in aqueous
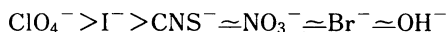solution with DBC chloroform at 20 ± 1 ℃

Salt	Kex/l^{2}mol^{-2}	Kd/l mol^{-1}	[X$^-$]/mol l^{-1} *
KClO$_4$	73.6±14.0	0.253±0.050	0.0458±0.0052
KCNS	10.4±0.3	0.010±0.001	0.0503±0.0011
KI	10.2±0.6	0.023±0.016	0.0502±0.0007
KNO$_3$	1.71±0.06	0.0057±0.0002	0.0511±0.0006
KBr	0.26±0.02	0.0023±0.0009	0.0513±0.0005
KOH	0.21±0.02	0.0063±0.0008	0.0494±0.0003
NaClO$_4$	0.51±0.01	0.0013±0.0005	0.1048±0.0004
NaCNS	0.68±0.04	0.0021±0.0002	0.0974±0.0015
NaI	0.23±0.01	0.0007±0.00005	0.0953±0.0003
NaNO$_3$	0.22±0.009	0.0009±0.00004	0.1012±0.0004

* Mean concentration of MX in aqueous solution after extraction.

As can be seen from Table 1, potassium salts are extracted in larger quantities than sodium salts, and their extractabilities are dependent remarkably on the anion in their metal salts. The extraction constant, Kex, decreases in the order given below, according to the anion in their metal salts.

$$ClO_4^- > CNS^- \simeq I^- > NO_3^- > Br^- \simeq OH^-$$

The distribution coefficient of metal ion, Kd, between organic and aqueous phases decrease also in the following order.

$$ClO_4^- > I^- > CNS^- \simeq NO_3^- \simeq Br^- \simeq OH^-$$

The decreasing order of Kex is almost similar to the increasing order of their Gibbs free energy of hydration in kJ mol^{-1} (10) : I$^-$ (-283), NO$_3^-$ (-300), Br$^-$ (-321) and OH$^-$ (-379) (11), no value for the thiocyanate anion. For ClO$_4^-$, it has been known that the value of hydration enthalpy is -289 kJmol^{-1} (12), and this value is nearly the value of its Gibbs free energy of hydration. Therefore, this effect of anion on the extraction of potassium is explained on the basis of the difficulty of

their removal from the aqueous phase.

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