

## Studies on the Solvent Extraction of Metal Perchlorates. II. Extraction of Alkali Metal Perchlorates with Trioctylphosphine Oxide

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(Received December 12, 1979)

**Synopsis.** Solvent extraction of alkali metal ions in 1 mol dm<sup>-3</sup> sodium perchlorate ionic media with trioctylphosphine oxide (TOPO) in hexane was measured. The extraction improved in the order Li(I) > Na(I) > K(I) > Rb(I) > Cs(I). This was explained in terms of the higher ability of solvation with TOPO of the smaller ions. The chemical form of the extracted species was M(TOPO)<sub>n</sub><sup>+</sup>(ClO<sub>4</sub>)<sup>-</sup>, where *n* is three for Li(I), Na(I), and K(I) and three and four for Rb(I) and Cs(I).

Sodium perchlorate in aqueous solution is extractable with trioctylphosphine oxide (TOPO) in hexane but extraction was not effective.<sup>1)</sup> In the present investigation, the extraction of other alkali metal perchlorates with TOPO was measured under identical conditions. Factors affecting the extractions are discussed.

### Experimental

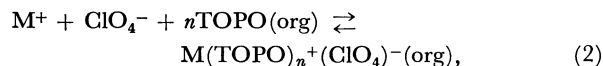
Hexane solution of TOPO and aqueous sodium perchlorate solution were prepared as reported previously.<sup>1)</sup> Lithium hydroxide of reagent grade was dissolved in water and the concentration was measured by titration with a standard acid solution. It was neutralized by perchloric acid, a standard sodium perchlorate solution being added in order to obtain 1.0 mol dm<sup>-3</sup> (Na, Li)ClO<sub>4</sub>. Potassium, rubidium, and caesium chlorides each of reagent grade were dissolved in water and the concentration was measured by titration with a standard silver nitrate solution. One mol dm<sup>-3</sup> (Na, M)ClO<sub>4</sub> solutions (where M<sup>+</sup> is the alkali metal ion) were prepared from a standard sodium perchlorate solution and the metal chloride solution. The concentration of potassium(I) was 0.025 mol dm<sup>-3</sup>, that of the other metal ions being 0.01 mol dm<sup>-3</sup>. The solutions except for that of lithium(I) thus contained a small amount of chloride but its effect on the extraction equilibrium was found to be negligible. The other reagents and procedures were the same as those in the previous work.<sup>1)</sup> The distribution experiments were carried out at 25 ± 0.3 °C. An aqueous perchlorate solution and an organic TOPO solution were placed in a glass stoppered tube, agitated vigorously and centrifuged. The metal in the organic phase was back-extracted with 1 mol dm<sup>-3</sup> nitric acid containing 0.1 mol dm<sup>-3</sup> of sodium nitrate which was added in order to reduce the error caused by back-extracted sodium perchlorate in flame photometry. The aqueous metal concentration was calculated from the initial aqueous and equilibrium organic concentrations.

### Results and Discussion

The distribution ratio of an alkali metal ion is defined by

$$D = [M(I)]_{\text{org}}/[M(I)] \quad (1)$$

where the subscript "org" denotes chemical species in the organic phase. Its extraction with TOPO can be written as



$$K_{\text{exn}}(M) = [M(\text{TOPO})_n^+(\text{ClO}_4)^-]_{\text{org}}/[M^+][\text{ClO}_4^-][\text{TOPO}]_{\text{org}}^n. \quad (3)$$

Dissociation of ion-pairs is negligible in solvents essentially nonpolar. The aqueous phase in the present study is neutral and therefore the extraction of perchloric acid should be negligible for statistical treatment. Since the solvation number of sodium perchlorate with TOPO is three,<sup>1)</sup> the following equations can be obtained.

$$\begin{aligned} [\text{TOPO}]_{\text{org, total}} &= [\text{TOPO}]_{\text{org}} + 3[\text{Na}(\text{TOPO})_3^+(\text{ClO}_4)^-]_{\text{org}} \\ &+ \sum n[M(\text{TOPO})_n^+(\text{ClO}_4)^-]_{\text{org}} \end{aligned} \quad (4)$$

$$\begin{aligned} &= [\text{TOPO}]_{\text{org}} + 3K_{\text{ex3}}(\text{Na})[\text{Na}^+][\text{ClO}_4^-][\text{TOPO}]_{\text{org}}^3 \\ &+ \sum nK_{\text{exn}}(M)[M^+][\text{ClO}_4^-][\text{TOPO}]_{\text{org}}^n. \end{aligned} \quad (5)$$

Thus the distribution ratio is given by

$$\begin{aligned} D &= \sum [M(\text{TOPO})_n^+(\text{ClO}_4)^-]_{\text{org}}/[M^+] \\ &= \sum K_{\text{ex}}(M)[\text{ClO}_4^-][\text{TOPO}]_{\text{org}}^n. \end{aligned} \quad (6)$$

By use of a least squares computer program and the value of extraction constant of sodium(I),<sup>1)</sup>  $K_{\text{ex3}}(\text{Na}) = 10^{1.01}$ , a successive approximation procedure was carried out by means of Eqs. 3—6, the "free" TOPO concentrations,  $[\text{TOPO}]_{\text{org}}$ , and the best-fit extraction constants of metal ion,  $K_{\text{exn}}(M)$ , being obtained. The "best-fit" with the data was obtained when extraction of only trisolvate was assumed for lithium(I) and potassium(I), as well as when extraction of both tri- and tetrasolvate was assumed for rubidium(I) and caesium(I). The extraction constants are given in Table 1. Figure 1 shows the log *D* vs. free TOPO concentration plot (the data of sodium(I) are taken from Ref. 1), the solid curves being calculated by introducing the values of constants in Table 1 into Eq. 6.

It is most probable that the interactions between the TOPO solvated metal ion and the perchlorate ion in the organic phase are electrostatic, viz., the extracted species are ion-pairs. The present results differ from those of extraction into polar solvents in

TABLE 1. SUMMARY OF EXTRACTION CONSTANTS OF ALKALI METAL PERCHLORATES WITH TOPO IN HEXANE<sup>a)</sup>

	log $K_{\text{ex3}}$	log $K_{\text{ex4}}$
Li(I)	2.29 ± 0.13	nil
Na(I) <sup>b)</sup>	1.01 ± 0.14	nil
K(I)	0.57 ± 0.22	nil
Rb(I)	0.06 ± 0.10	0.99 ± 0.17
Cs(I)	-0.17 ± 0.21	0.95 ± 0.18

a) Aq phase 1 mol dm<sup>-3</sup> (NaClO<sub>4</sub>), temp 25 °C. Limit of error is 3σ. b) Value taken from Ref. 1.

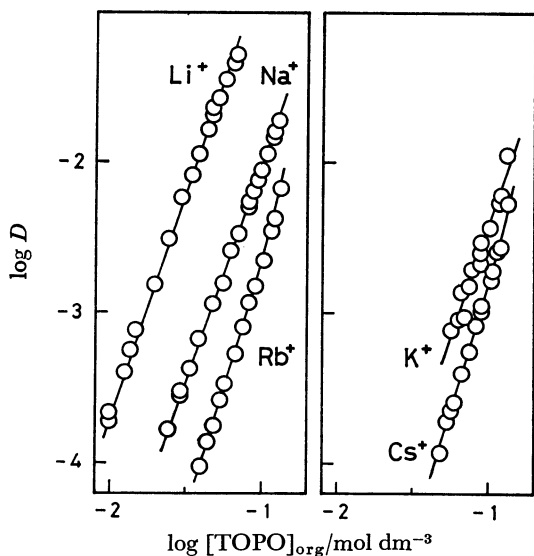


Fig. 1. The distribution ratio of alkali metal as a function of "free" TOPO concentration. The data of sodium(I) are taken from Ref. 1. Org. phase: hexane containing TOPO. Aq phase: Li(I);  $0.010 \text{ mol dm}^{-3}$   $\text{LiClO}_4 + 0.99 \text{ mol dm}^{-3}$   $\text{NaClO}_4$ , Na(I);  $1.0 \text{ mol dm}^{-3}$   $\text{NaClO}_4$ , K(I);  $0.025 \text{ mol dm}^{-3}$   $\text{KCl} + 0.975 \text{ mol dm}^{-3}$   $\text{NaClO}_4$ , Rb(I) and Cs(I);  $0.01 \text{ mol dm}^{-3}$  of chloride +  $0.99 \text{ mol dm}^{-3}$   $\text{NaClO}_4$ . The solid curves are calculated by means of Eq. 6 and the values in Table 1.

which the solvation of metal ions is weaker than that with TOPO and in which at least a partial dissociation of the extracted ion-pairs is expected. For example, the extraction of sodium(I), potassium(I), rubidium(I), and caesium(I) as ion-pairs with tetraphenylborate ion into nitrobenzene was found to be better in the increasing order of the ionic size of the metal ion.<sup>2)</sup> This type of extraction order often found in many other similar ion-pair extraction systems<sup>3)</sup> is explained in terms of lower hydration and higher hydrophobic tendencies of large metal ions and in some cases also of their higher tendency to dissociate in the organic

phase. The opposite extraction order in the present system can be explained in terms of the order of the formation of TOPO solvates. Although the size of the central metal ions in the TOPO solvates differs, the overall molar size of the solvated cations in the ion-pairs should be similar when the solvation number is the same, the effect of the molar size on the extraction (or the hydrophobic tendencies) should thus be similar. For this reason, best extraction of lithium(I) should be due to its highest tendency to be solvated with TOPO. Even though it is hydrated most strongly among these alkali metal ions in the aqueous phase, its small ionic size is also favorable for solvation with TOPO. The hydration interferes with extraction while TOPO solvation enhances it. However, the fact that the smaller the ionic size, the better the extraction indicates that the stronger solvation with TOPO overcomes the unfavorable stronger hydration. Thus although the metal ions are extracted as ion-pairs, the order of extraction is similar to that with  $\beta$ -diketones reported by Healy.<sup>4)</sup> It seems reasonable that the less strongly solvated larger ions, rubidium(I) and caesium(I), have space to accept one more TOPO molecule and are extracted also as tetrasolvates.

No quantitative work seems to have been carried out on the extraction equilibria of these metal perchlorates with solvating type solvents such as TOPO in nonpolar solvents.

The authors are grateful to Messrs. Yuichi Ishida and Kenji Ohira for their assistance in experiments.

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