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Lithium Salt Effects on Extractions of 15-Crown-5, 18-Crown-6, or Their Silver(I) Complexes as Picrates

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The extractions of 15-crown-5, 18-crown-6, or their silver(I) or lithium(I) complexes as picrates from lithium salt solutions into chloroform have been studied at 25 °C. The extractions of these crown ethers were impaired by an increase in the lithium perchlorate or nitrate concentration. A small salting-out effect was observed in the presence of lithium chloride. The extraction of silver(I) was also impaired by the addition of lithium perchlorate or nitrate. In the lower-concentration region of the lithium salts, the extraction of silver(I) was affected more markedly than that of crown ether itself.

The extraction of metal ions with crown ethers and anions has been measured under uncontrolled ionic media, although the extraction from constant ionic media should be useful in keeping the activity coefficients of all species constant. This fact is mainly caused by the facts that the extraction with crown ethers has been measured in rather dilute solutions, and that such suitable background salts as sodium perchlorate, which is employed in most extraction systems, can not be used because any cations may interact with the crown ethers.

However, information on the effects of salt on the extraction is necessary to treat the data quantitatively or to attempt the extraction and separation of trace elements such as the uranyl ion from seawater or concentrated salt solutions.

Recently, Kolthoff has made a preliminary report on the effect of salt on the extraction into dichloromethane of 18C6 (18-crown-6) and of the ion pair between the potassium ion complexed with the ether and the picrate anion.[1] According to his report, the extraction of 18C6 increased in the presence of lithium chloride, while the extraction of the complexed potassium ion decreased.

The present paper will describe the effect of lithium nitrate on the extraction of 15C5(15-crown-5), B15C5 (benzo-15-crown-5), 18C6, and DB18C6 (dibenzo-18-crown-6) and will extend to the effects of such anions as chloride and perchlorate ions on the extraction of 15C5 and 18C6. The effects of salt on the extraction of crown ether itself will be compared with the effect on the extraction of an ion pair consisting of silver(I) or lithium(I), a crown ether, and a picrate ion.

Experimental

Reagents. The lithium chloride and nitrate were recrystallized from water. The lithium perchlorate was prepared from lithium carbonate and perchloric acid and was then recrystallized from water. The concentration of the stock solutions, prepared by dissolving the salts in deionized water, was determined from the balance between the weight of an aliquot of each stock solution and that after it had dried up. The chloroform was washed with deionized water just before use. The benzo-15-crown-5 and DB18C6 were recrystallized from heptane and benzene respectively. The other reagents were used without further purification. The concentration of 15C5 or 18C6 was checked from the balance between the weight of the solution and that after it had dried up.

Procedures. Distribution constants of crown ethers: a portion of a salt stock solution at a certain concentration between 0 and 3 M (M=mol dm^{-3}) and a certain amount of a 15C5 or 18C6 aqueous solution were placed in a stoppered glass tube, together with chloroform, agitated mechanically for 1 h, and centrifuged. Then, a portion of each phase was transferred into another glass tube containing lithium dipicrylamide (7×10^{-4} M), a potassium chloride aqueous solution for 18C6 or a sodium chloride solution for 15C5, and a given volume of chloroform. After both phases had attained distribution equilibria, the absorbance of each chloroform phase was measured at 460 nm. Lambert-Beer's law holds to at least 2×10^{-5} M for 18C6 and 4×10^{-5} M for 15C5.

The distribution constant of a crown ether was calculated from the ratio of the total concentration between the two phases:

$$K_D = [E]_o/[E], \tag{1}$$

where E denotes crown ethers and where the subscript "o" and the lack of a subscript denote the organic phase and the aqueous phase respectively.

The distribution constant of B15C5 or DB18C6 was determined in a similar way except that we then employed the chloroform solution and the concentrations in the two phases were determined by measuring the absorption at 275 nm directly.

Distribution ratio of Ag^{I} or Li^{I}: Silver nitrate, lithium picrate, 15C5, or 18C6, and various amounts of lithium nitrate or perchlorate were placed in a stoppered glass tube together with an equal volume of chloroform. The two phases were then agitated vigorously. The concentration of silver(I) distributed between the two phases was determined by means of atomic absorption spectrometry. The extraction with DB18C6 was measured in a similar way except that we then used a chloroform solution containing DB18C6. The amount of lithium(I) extracted into the organic phases was measured by means of emission spectrometry. The distribution ratio of silver(I) or lithium(I), D, was defined as:

$$D = [M(I)]_o/[M(I)]. \tag{2}$$

Results and Discussion

Effect of Lithium Salts on the Distribution Constants of Crown Ethers. The distribution constants of crown ethers between water and chloroform, K_{D0}, are listed in Table 1. Figure 1 shows the change in the distribution constants (K_D) of 15C5, B15C5, 18C6, and DB18C6 as a function of the lithium nitrate concentration when the distribution constant (K_{D0}) between water and chloroform was employed as a reference (K_D/K_{D0}). The introduction of a benzene ring into crown

Table 1. Distribution constants of crown ethers and extraction constants of silver(I) with picrate anion and the ethers between water and chloroform

Crown ether	log K_{Do}	log K_{ex_0}
18C6	0.8	4.6
DB18C6	3.9[a)]	3.3[a)]
15C5	0.9	4.4
B15C5	2.4	3.5[b)]

a) Taken from Ref. 2. b) Taken from Ref. 3.

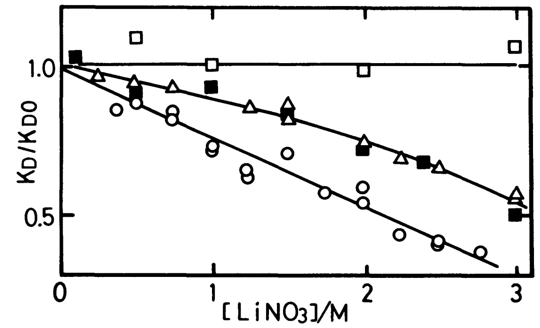

Fig. 1. The influence of $LiNO_3$ on the change in the distribution constant of 15C5 (○), 18C6 (△), DB18C6 (□), and B15C5 (■) when the distribution constant of each crown ether obtained from water was employed as a reference.
The total concentration of crown ether employed: 3.8×10^{-4} M (15C5), 1×10^{-4} M (18C6), 3×10^{-2} M (B15C5), and 1.8×10^{-2} M (DB18C6).

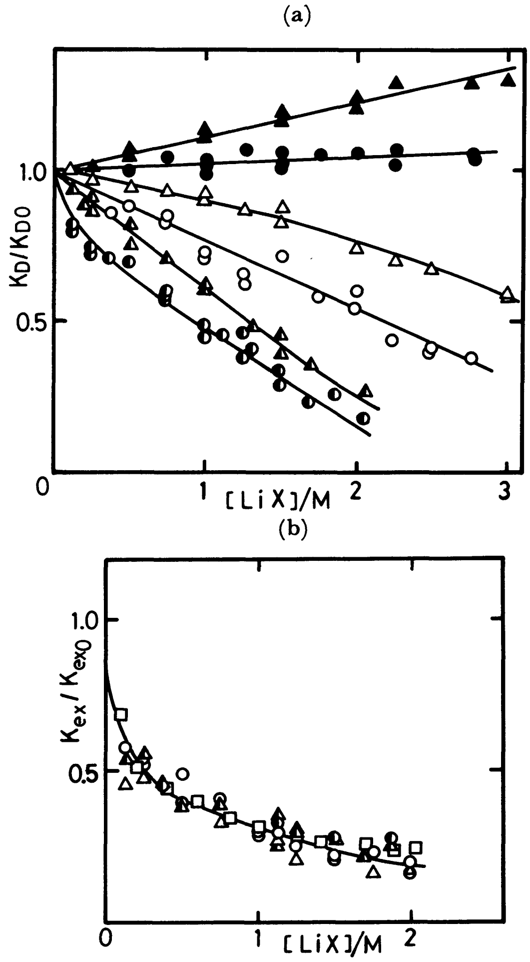

Fig. 2. Change in the distribution constant of crown ethers (denoted in Eq. 1) and the extraction constant of Ag^I with picrate ion and the crown ether (Eq. 5) by an addition of lithium chloride (closed symbols), nitrate (open symbols), or perchlorate (semiclosed symbols).
The K_{D0} and K_{ex_0} are listed in Table 1.
(a): The influence of lithium salts on the distribution constants of 15C5 (circles) and 18C6 (triangles).
(b): The influence of lithium salts on the extraction of Ag^I picrate with 15C5, 18C6 or DB18C6.
Aq phase: lithium salt solutions containing Ag^I of 5×10^{-5} M, 15C5 (circles) or 18C6 (triangles) of 1.1×10^{-3} M and 9.4×10^{-3} M lithium picrate. Org phase: $CHCl_3$ for 15C5 and 18C6 or $CHCl_3$ containing DB18C6 (squares) of 2.5×10^{-3} M.

ether seems to lessen the salt effect. The different basicity of each crown ether would be one of the reasons why the effects of salt on the extraction of different crown ethers are not similar, as was suggested by Long and McDevit[4)] with reference to the salt effect on simple molecules in aqueous solutions. Actually, the fact that the distribution constant of 15C5 changes more than that of B15C5 may be explained simply in terms of the higher basicity of 15C5. However, the extraction of 15C5 seems to be affected more markedly by the salt than that of 18C6, although 18C6 should be a little more basic than 15C5. If the difference in the effects of salt on different crown ethers is caused by the complexation of the ethers with the lithium ion in the background salt, the use of a more hydrophobic anion as a counter ion should improve the extraction. Figure 2-a shows the ratio of the distribution constants of 15C5 and 18C6 obtained from a salt solution to that of one obtained from water as a function of the lithium salt concentration. As may be seen from the figure, the anion effect does not seem to support the above expectation; *e.g.*, the value of the distribution ratio of 15C5 in the presence of 1 M lithium perchlorate is smaller than one-half the value of the distribution ratio in the absence of the salt, and in 2 M lithium perchlorate the value of the distribution ratio is only 20% of the value without the salt, while the presence of lithium chloride does not change the constant, although a rather large salting-out effect with lithium chloride was reported[1)] (*e.g.*, the distribution constant of 18C6 between water and dichloromethane, 4.5, increased to 7.4 even upon the addition of lithium chloride of only 0.4 M).

The tendency of the anion effect on the distribution constants of crown ethers is similar to that on the aqueous solutions of many nonelectrolytes, which was comprehensively reviewed by Long and McDevit.[4)] The anion effect may not, however, be quantitatively explained by their theory, since they indicated that the theory is essentially valid only for nonpolar nonelectrolytes. They reported that the order of anions which exert greater salting-out effects on nonelectrolytes in aqueous solutions is in the sequence of $Cl^- > NO_3^- > ClO_4^-$.

The order of destroying the water structure by salt anions was also reported to be $ClO_4^- > NO_3^- > Cl^-$ on the basis of the IR measurements of various aqueous solutions.[5] Therefore, the order of anions whose presence leads to greater salting-in effects in the present extraction system, $ClO_4^- > NO_3^- > Cl^-$, seems reasonable.

Furthermore, it was confirmed by measuring the lithium(I) concentration in the organic phases that the increase in the extraction of the crown ethers is not caused by the extraction of the lithium ion complexed with crown ethers: when the concentrations of lithium(I) extracted with 15C5 or 18C6 into chloroform from lithium salt solutions were measured, it was observed that the concentrations increased with the increase in the salt concentration in the sequence of $ClO_4^- > NO_3^- > Cl^-$, as is generally observed in the extraction system of ion pairs. On the other hand, lithium(I) was not extracted without crown ether. Therefore, strictly speaking, the concentration ratio of crown ethers between organic and aqueous phases should be described as $D_E = ([E]_o + [LiEX]_o)/[E]$ instead of Eq. 1. However, since even the concentration of lithium(I) in chloroform extracted from a 2 M lithium perchlorate solution containing 2.5×10^{-2} M 18C6 was less than 2×10^{-3} M, the proportion of $(LiE)^+ClO_4^-$ to the total crown ether in the organic phase would be 10% at a maximum under the present experimental conditions. Accordingly, the concentration ratio of the crown ether may be substantially represented as Eq. 1, and it may be concluded that the change in the distribution ratio of crown ether with the increase in the salt concentration is due to the change in the activity coefficients of crown ether, but not to the extraction of the lithium(I) complexed with crown ethers.

A simple method to determine activity coefficients using the solvent extraction method has previously been reported;[4,6] that is, the distribution constants of crown ethers, as represented by activity units, are always identical, as obtained either from water or from a salt solution:

$$\frac{\{E\}_o}{\{E\}} = \frac{\gamma_o[E]_o}{\gamma[E]} = \frac{\gamma_{0,o}[E]_{0,o}}{\gamma_0[E]_0}, \tag{3}$$

where γ or $[E]$ denotes a value obtained from a lithium salt solution and where the subscript "0" denotes a value obtained from water. Since γ_o can be essentially regarded as $\gamma_{0,o}$ when the crown ether concentration in the organic phases is not high, $\gamma/\gamma_0 = K_D/K_{D0}$. Therefore, the ratio of K_D to K_{D0} in Fig. 2-a should be nothing but the change in the activity coefficients of crown ether in lithium salt solutions at various concentrations.

Effect of the Salts on Extraction of the Ion Pair of Ag^I or Li^I with the Crown Ethers and the Picrate Ion. When silver(I) is distributed between aqueous solutions containing a crown ether and a picrate ion and chloroform, the extraction equilibrium and the extraction constant can be described as:

$$M^+ + E_{(o)} + A^- \rightleftarrows ME^+A^-_{(o)},$$

$$K_{ex} = \frac{[ME^+A^-]_o}{[M^+][E]_o[A^-]}, \tag{4}$$

$$= D[E]_o^{-1}[A^-]^{-1}, \tag{5}$$

where $[E]_o = [E]_{total}/(1 + 1/K_D)$ and the values of K_D at the different salt concentrations were obtained from Fig. 2-a.

Figure 2-b shows the change in the extraction constant of silver(I) as a function of the concentration of the background lithium salt when the extraction constant obtained from an aqueous solution containing no lithium salt was employed as the reference. The extraction of silver(I) also lessens upon the addition of lithium salts. It does not seem that there is a big difference with the sort of salt added or the sort of crown ether used as an extractant, although the extraction of the crown ether itself is affected by them, as may be seen in Fig. 2-a. Moreover, it is also observed that the addition of a small amount of the salt leads to a larger change in the extraction of silver(I) than in the extraction of the crown ethers. For example, the rate of the change in the extraction of the crown ethers to the extraction from a no-salt aqueous solution is only 5—20% upon the addition of the salts of 0.3 M, while that of silver(I) may be more than 50%.

The extraction constants of lithium(I) are plotted as a function of the salt concentration in Fig. 3. The extraction constants were calculated by using Eq. 5. The extraction constants of lithium(I) do not seem to change greatly with an increase in the salt concentration or with the sort of salt. The extraction with 18C6 would, though, be a little better than that with 15C5. The distribution ratio in the absence of a lithium salt such as nitrate or perchlorate could not be determined, because the amount of lithium(I) extracted into chloroform was too small to be determined.

As has been mentioned above, the salting-in effect with background salts on the extraction of the ion pairs can not be explained in terms of the decrease in the crown ether concentration which is effective in forming extractable complexes in aqueous phases. The different salt effect on the extraction of silver(I) from that of lithium(I) may suggest that cations may be affected by

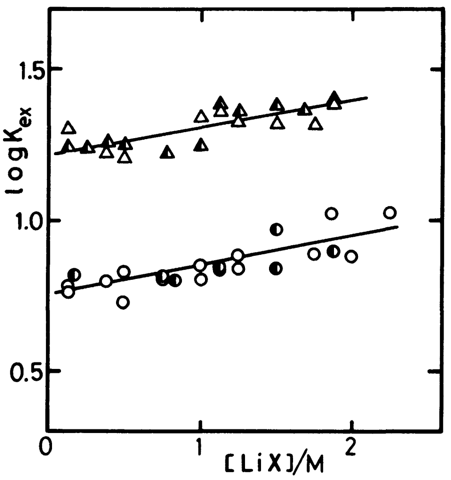

Fig. 3. The influence of lithium nitrate or perchlorate on the extraction constant of Li^I with 18C6 or 15C5 and picrate ion as a function of lithium salt concentration.
All symbols are the same in Fig. 2. The log D was around -4.

the background salt, because picrate ion is common to these systems. Besides, a metal ion trapped in a crown ether would not be as greatly affected as an untrapped metal ion. Salt effects on the extraction of an ion pair would thus be caused by a complex combination of many factors. Further information will be necessary before a detailed discussion of the salt effects on the ion pair extraction will become possible.

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References

1) I. M. Kolthoff, *Can. J. Chem.*, **59**, 1548 (1981).

2) Y. Hasegawa, N. Iizima, and T. Sekine, *J. Inorg. Nucl. Chem.*, **43**, 633 (1980).

3) Y. Hasegawa *et al.*, unpublished data.

4) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

5) G. R. Choppin and K. Buijs, *J. Chem. Phys.*, **39**, 2042 (1963).

6) Y. Hasegawa and T. Sekine, *Bull. Chem. Soc. Jpn.*, **38**, 117 (1965).