The Extraction of Alkali Metal Picrates with Dibenzo-18-Crown-6

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The distribution of alkali metal picrate complexes of macrocyclic polyether (dibenzo-18-crown-6) between water and benzene was investigated. The polyether-cation complexes were found to be of a 1: 1 stoichiometry. The formation of 2: 1 complexes was recognized for Rb and Cs in a large excess of the polyether. The extractability of complex cation-picrate ion-pairs decreases in this sequence: K>Rb>Cs>Na>Li. The values of the extraction constants (log K_{ex}) were determined to be 4.65, 3.75, and 3.07 for K, Rb, and Cs compounds respectively. The thermodynamic quantities for the extraction process were calculated from the change in the extraction constants with the temperature. The extraction reactions are all exothermic, accompanied by an entropy decrease.

Macrocyclic polyethers, widely investigated by Pedersen[1)] in the last decade, are known as ligands which can form fairly stable stoichiometric complexes with certain cations. It is quite noteworthy that some of these compounds have a great affinity even for alkali metals, though non-cyclic polyethers are commonly not considered strong complexing agents. The most stable complex is formed with a cation which fits well into the molecular cavity of a given ligand, whereas a stable complex is not formed if the ion is too large or too small to lie in the cavity. For instance, polyethers such as 18-crown-6 and its analogues, containing six oxygen atoms linked by six ethylene groups, have ether rings 2.6—3.2 Å[2)] in diameter; therfore, they complex with the potassium ion (ionic diameter, 2.66 Å) selectively. X-Ray analyses[3—5)] of crystalline complexes show that the metal cation is located in the center of the ether ring. Cations larger than the optimum size can not be accommodated well into the molecular hole, so they tend to form a 2: 1 or 3: 2 polyether-cation complex of a sandwich type.[2,6—8)]

As regards the extraction of an ion-pair species, it has been widely accepted that the extractability of the ion-pair increases with the bulkiness, indicating that the concept of water structure-enforced ion-pairing[9)] is applicable. Accordingly, a complex ion-pair species formed by the association of a complexed cation and a large anion, which is considered more hydrophobic and bulkier than an uncomplexed one, is expected to be more extractable.

The present work was undertaken in order to investigate the distribution equilibria and the dependence of the extractability on the size of the alkali metal picrate complexes.

Dibenzo-18-crown-6 was chosen as the complexing agent, since the properties of the polyether and the complexes formed with alkali metals had been well characterized.[1)] The picrate anion was chosen as the counter ion so that the ion-pair formed could be determined colorimetrically. Benzene was chosen as the solvent for its non-ionizing property, though it was not necessarily the best solvent. The analysis of the extraction equilibria may be facilitated by the use of non-ionizing solvents, since uncomplexed alkali metal picrates are scarcely extracted into the solvents and the complex ion-pairs do not dissociate in the solvents.

Experimental

Materials. Dibenzo-18-crown-6 was synthesized by the method of Pedersen[1)] from catechol and bis(2-chloroethyl)-ether. Recrystallization from benzene gave white, fibrous crystals. The polyether thus obtained had a melting point and an infrared spectrum identical with those of an authentic sample. The alkali metal picrates were prepared by adding a corresponding carbonate solution to an aqueous solution of picric acid; the resulting precipitates of caesium, rubidium, and potassium picrates were recrystallized from water, and the precipitates of sodium picrate, from a water-ethanol (1: 3) mixture. The sodium picrate was found to be monohydrate by means of a thermogravimetric method. Benzene of a guaranteed-grade was washed with a sodium hydroxide solution and then water, distilled, and saturated with water. The resulting water-saturated benzene was stored so as to prevent any dissolution of the carbon dioxide. Deionized water was carefully decarbonated by boiling and was saturated with benzene just before each experimental run in order to minimize the volume change on mixing.

Extraction Procedure. An aliquot of an aqueous alkali metal picrate solution and a lithium hydroxide solution (5×10^{-5} M) were transferred into a 50 ml centrifuge tube equipped with a well-grounded stopper and diluted to 20 ml with water (to give these final concentrations: Na and K< 10^{-2} M, Rb<3×10^{-3} M, and Cs<5×10^{-3} M). 20 ml of a benzene solution containing the polyether (<10^{-2} M) was then added. The resulting mixture was shaken in a thermostated water bath (10—30±0.1 °C) for 20 min and subsequently allowed to stand for 20 min to complete the phase separation. All the extractions were carried out at pH>6.7.

Determination of the Picrates. The concentrations of the picrates in the organic and aqueous phases were determined spectrophotometrically (Hitachi Spectrophotometer, Type 124) at 425 and 353 nm respectively with appropriate quartz cells 2—50 mm in length. The molar extinction coefficients, ε, of the complex ion-pairs in the organic phase were determined to be 9930, 9800, and 9600 for caesium, rubidium, and potassium compounds respectively. The ε values of the 2: 1 polyether-cation complexes for rubidium and caesium were virtually identical with those of the 1: 1 complexes. The ε value of the picrate ion in the aqueous phase was also determined to be 14400.

The Distribution Coefficient of the Polyether. A benzene solution containing the polyether (<5×10^{-3} M) was shaken with pure water under the conditions described above. The aqueous phase thus separated was concentrated by evaporation to less than one-third of its original volume in order to remove any dissolved benzene. The concentration of the polyether was then determined spectrophotometrically at 272 nm (ε= 5050). Measurements were carried out at five different temperatures, ranging from 10 to 30 °C.

Results and Discussion

Extraction Equilibria. The equilibrium between an aqueous solution containing the alkali metal cation, M^+, and the picrate anion A^-, and an organic solution containing dibenzo-18-crown-6, L, can be written as:

$$M_a^+ + L_o + A_a^- \rightleftarrows MLA_o$$

$$K_{ex} = \frac{[MLA]_o}{[M^+]_a[L]_o[A^-]_a} \tag{1}$$

where MLA denotes the complex ion-pair extracted in the organic phase; the molar concentrations are given in brackets. The overall extraction equilibrium can be analyzed in terms of the following four constituent equilibria.

i) Transfer of the uncomplexed polyether from the organic to the aqueous phase:

$$L_a \rightleftarrows L_o \qquad D^L = \frac{[L]_o}{[L]_a} \tag{2}$$

ii) Complexation of alkali metals with the polyether:

$$L_a + M_a^+ \rightleftarrows ML_a^+ \qquad K_a^{ML} = \frac{[ML^+]_a}{[L]_a[M^+]_a} \tag{3}$$

iii) Association of the complexed cations with the picrate anion:

$$ML_a^+ + A_a^- \rightleftarrows MLA_a \quad K_a^{MLA} = \frac{[MLA]_a}{[ML^+]_a[A^-]_a} \tag{4}$$

iv) Transfer of the complex ion-pairs from the aqueous to the organic phase:

$$MLA_a \rightleftarrows MLA_o \qquad D^{MLA} = \frac{[MLA]_o}{[MLA]_a} \tag{5}$$

Distribution Ratios of the Picrates. The distribution ratios of the picrates, q^A, was calculated from either the concentration in the organic phase, A, or that in the aqueous phase, $A^\circ-A$:

$$q^A = \frac{A}{A^\circ-A} \tag{6}$$

where the superscript o denotes the initial concentration. From the mass balances, the following relations can be obtained:

$$[A^-]_a = A^\circ - A - \frac{A}{D^{MLA}} = f(A) \tag{7}$$

$$[M^+]_a = M^\circ - A - g(A) \tag{8}$$

$$g(A) = \frac{A}{D^{MLA}}\left(\frac{1}{f(A)K_a^{MLA}}+1\right)$$

$$[L]_o = \frac{L^\circ-A-g(A)}{1+1/D^L} \tag{9}$$

The substitution of Eqs. (7)—(9) into Eq. (5) gives:

$$q' = \frac{A}{A^\circ-A-A/D^{MLA}}$$
$$= \frac{K_{ex}(L^\circ-A-g(A))(M^\circ-A-g(A))}{1+1/D^L} \tag{10}$$

The q' is related to q^A by the following equation:

$$\frac{1}{q'} = \frac{1}{q^A} - \frac{1}{D^{MLA}} \tag{11}$$

Assuming that $A^\circ-A \gg A/D^{MLA}$, $D^L \gg 1$, and $M^\circ-A$, $L^\circ-A \gg g(A)$, Eq. (11) can be reduced to:

$$q^A = K_{ex}(M^\circ-A)(L^\circ-A) \tag{12}$$

In the above formulations, complexes with other than the 1 : 1 stoichiometry are not considered; this exclusion is supported by the method of continuous variation (Fig. 1). The theory indicates that the maximum

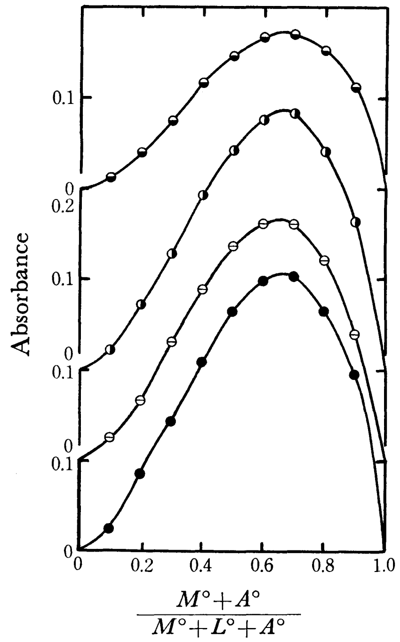

Fig. 1. The method of continuous variation.
Alkali metalpicrate complexes of dibenzo-18-crown-6,
●: Na, $M^\circ+L^\circ+A^\circ=3\times10^{-2}$ M, 50 mm cell.
◒: K, $M^\circ+L^\circ+A^\circ=1.5\times10^{-2}$ M, 2 mm cell.
◑: Rb, $M^\circ+L^\circ+A^\circ=9\times10^{-3}$ M, 50 mm cell.
⊖: Cs, $M^\circ+L^\circ+A^\circ=1.5\times10^{-2}$ M, 50 mm cell.
Temp.: 25 °C. Absorbances: org. phase, at 425 nm.

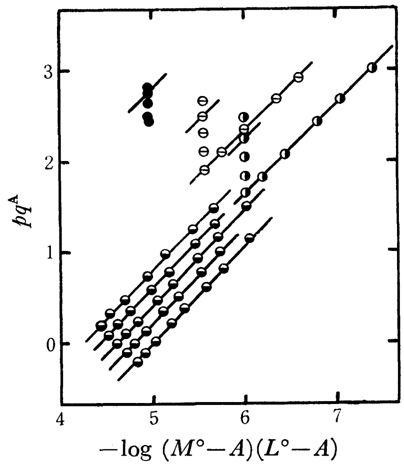

Fig. 2. Plots of pq^A against $-\log\,(M^\circ-A)(L^\circ-A)$. The symbols used are identical with those in Fig. 1. The vertically-arrayed five points are those obtained at the different temperatures: 30, 25, 20, 15, and 10 °C (from top to bottom).

extraction occurs when equimolar solutions of alkail metal salts and the polyether are added to a system. The equimolar composition corresponds to the point of 2/3 on the abscissa of Fig. 1. As can be expected from Eq. (12), a linear relationship exists between pq^{A} and $-\log(M^\circ - A)(L^\circ - A)$ values (Fig. 2), indicating that each ion-pair is of the 1: 1 stoichiometry. The values of the extraction constants, K_{ex}, calculated from the plots in Fig. 2 are given in Table 1. Since the extractability of the complex sodium ion-pair was so small that the molar extinction coefficient could not be determined, it was assumed that $\varepsilon = 9800$, the average value of the other alkali metal compounds.

TABLE 1. EXTRACTION CONSTANTS AND THERMODYNAMIC QUANTITIES

MLA	L	NaLA	KLA	RbLA	CsLA
$\log K_{\mathrm{ex}}$	2.9[a)]	2.2[b)]	4.65	3.75	3.07
ΔH°(kcal/mol)	2.0	−8.9[b)]	−16.3	−16.4	−16.0
ΔS°(e.u.)	20	−20[b)]	−33.4	−37.8	−39.6

a) $\log D^{\mathrm{L}}$ value. b) Estimated value.

The value of K_{ex} for the potassium compound shows that about a half of the potassium is transferred into the benzene phase, when the same volumes of the polyether (10^{-2} M) and the picrate (10^{-2} M) solutions are equilibrated at 25 °C. Figure 3 shows that dibenzo-18-crown-6 is highly selective for potassium, as had been expected.

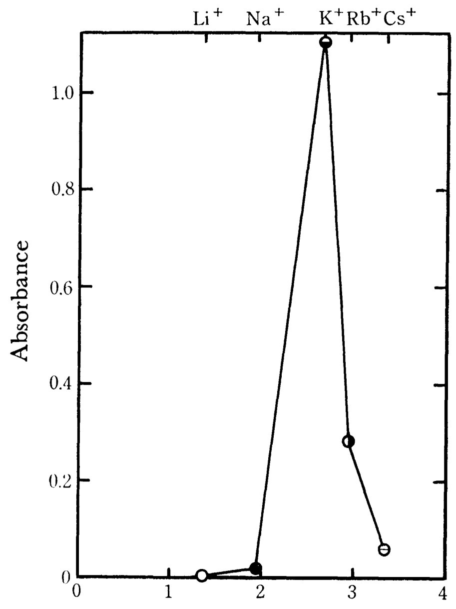

Fig. 3. Extractabilities of alkali metal picrate complexes of dibenzo-18-crown-6 at 25 °C.
M°, L°, $A^\circ = 10^{-3}$ M. Absorbances: org. phase, at 425 nm with 50 mm cell.

When the polyether was present in excess ($L^\circ/M^\circ > 5$), a plot of pq^{A} against $-\log(M^\circ - A)(L^\circ - 2A)^2$ was found to be linear for rubidium and caesium. The implication of such a relationship can easily be understood by assuming a further complexation of complex ion-pair with the polyether:

$$\mathrm{L_o + MLA_o \rightleftharpoons ML_2A_o} \quad K_{\mathrm{o}}^{\mathrm{ML_2A}} = \frac{[\mathrm{ML_2A}]_{\mathrm{o}}}{[\mathrm{L}]_{\mathrm{o}}[\mathrm{MLA}]_{\mathrm{o}}} \tag{13}$$

The existence of such an ion-pair has been demonstrated with some polyethers in the solid state[2,6–8)] or in a methanol solution.[10)] This may support, though not directly, the above assumption. The overall extraction equilibrium can also be formulated as:

$$\mathrm{M_a{}^+ + 2L_o + A_a{}^- \rightleftharpoons ML_2A_o}$$

$$K'_{\mathrm{ex}} = \frac{[\mathrm{ML_2A}]_{\mathrm{o}}}{[\mathrm{M^+}]_{\mathrm{a}}[\mathrm{L}]_{\mathrm{o}}{}^2[\mathrm{A^-}]_{\mathrm{a}}} \tag{14}$$

The values of $\log K_{\mathrm{ex}}'$ were determined from the plots to be 6.5 and 5.6 for the rubidium and caesium compounds respectively. The corresponding association constants, $K_{\mathrm{o}}^{\mathrm{ML_2A}}$, of the rubidium and caesium ion-pairs can be calculated to be $10^{2.7}$ and $10^{2.5}$ respectively by dividing K_{ex}' by K_{ex}. These values are of a magnitude similar to that of the stability constant obtained by Frensdorff[10)] in methanol ($[\mathrm{CsL_2}]/[\mathrm{CsL}][\mathrm{L}] = 10^{2.92}$).

No ion-pair of the $\mathrm{ML_2A}$ type was found with potassium, not even in a large excess of the polyether ($L^\circ/M^\circ < 18$).

Since the umcomplexed polyether is sparingly soluble in water (about 10^{-5} M at room temperature), it seems reasonable to assume that the ion-pair of $\mathrm{ML_2A}$ type can not exist in the aqueous phase, not even when the polyether is present in a large excess in the organic phase.

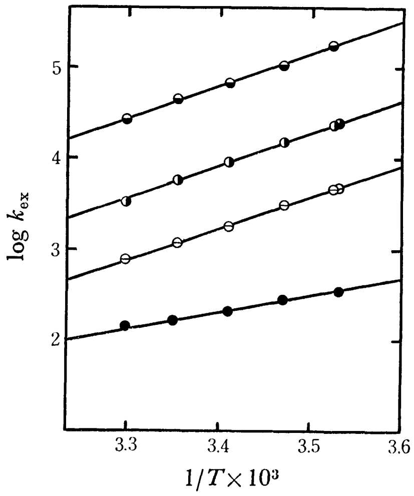

Fig. 4. Plots of $\log K_{\mathrm{ex}}$ against $1/T$.
The symbols used are identical with those in Fig. 1.

Thermodynamic Quantities. The values of the extraction constants increase monotonously with a decrease in the temperature. A plot of $\log K_{\mathrm{ex}}$ against $1/T$ shows a straight line for each alkali metal (Fig. 4). The value of the enthalpy change, ΔH°, was calculated from the slope. The value of the entropy change, ΔS°, was calculated from the corresponding ΔH° and K_{ex} values by using these thermodynamic relations: $\Delta G^\circ = -RT\ln K_{\mathrm{ex}}$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

It can be seen that the entropy contribution, $T\Delta S^\circ$, to the free energy change, ΔG°, is smaller than the thermal effect and has the same sign. There is no significant difference in $\Delta H°$, but the negative values in $\Delta S°$ apparently increase in going from sodium to caesium compounds. The thermodynamic quantities, $\Delta H°_{(15)}$ and $\Delta S°_{(15)}$, for the

$$M_a^+ + L_a + A_a^- \rightleftarrows MLA_o \qquad (15)$$

process were obtained by subtracting the $-\Delta H°_{(2)}$ and $-\Delta S°_{(2)}$ values from the corresponding $\Delta H°$ and $\Delta S°$ values: K, $\Delta H°_{(15)} = -14.3$ kcal/mol and $\Delta S°_{(15)} = -13.4$ e.u.; Rb, -14.4 and -17.8; and Cs, -14.0 and -19.6. The values of $\Delta H°_{(5)}$ and $\Delta S°_{(5)}$ can also be calculated in a similar way if the quantities of the association processes in the aqueous phase represented by Eqs. (3) and (4), $\Delta H°_{ass}$ and $\Delta S°_{ass}$, are known, or *vice versa*, but neither of the quantities is easy to obtain because of the very low solubility of the polyether in water. The thermodynamic quantities for the association processes of dicyclohexyl-18-crown-6 have been reported by Izatt *et al.*:[11] K, $\Delta H°_{ass} = -3.88$ kcal/mol and $\Delta S°_{ass} = -3.8$ e.u.; Rb, -3.33 and -4.2; and Cs, -2.41 and -3.7. If the values of $\Delta H°_{ass}$ and $\Delta S°_{ass}$ for dibenzo-18-crown-6 are assumed to be identical with dicyclohexyl-18-crown-6, the values of $\Delta H°_{(5)}$ and $\Delta S°_{(5)}$ may be calculated to be about -11 kcal/mol and -10—-16 e.u. respectively for each alkali metal.

From the above discussion, it follows that the association processes in the aqueous phase play only a minor role in determining the magnitude of the entropy change associated with the overall extraction process, and that the difference in $\Delta S°$ values is determined to a large extent by the difference in $\Delta S°_{(5)}$ values. A plot of $\Delta S°_{(15)}$ against the reciprocal of the cation radius was found to be linear, indicating that the magnitude of $\Delta S°_{(15)}$ is a result largely of electrostatic interaction as well as the relative hydration and number of product and reactant species. The trend in $\Delta S°_{(15)}$ values is consistent with Krasnov's observation:[12] for the extraction of triphenylmethane dye salts by chloroform, the larger the cationic radius, the more negative the distribution entropy becomes.

Though the effect of solvent polarity on the extractability of complex ion-pairs was not investigated systematically, a preliminary test has shown that polar solvents, such as isobutyl methyl ketone and nitrobenzene, give rise to an enhanced extractability. This observation is consistent with the results obtained by Frensdorff:[13] the extractability of the potassium picrate complex of dicyclohexyl-18-crown-6 decreases in this solvent sequence: methylene chloride>trichlorotrifluoroethane>*n*-hexane. Methylene chloride ($K_{ex} = 10^{5.85}$)[13] is found to be better than benzene ($K_{ex} = 10^{4.65}$) as a solvent of the potassium picrate complex of dibenzo-18-crown-6.

Thus, dibenzo-18-crown-6 and its analogues will be considered promising reagents for the separation and extraction of potassium.

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