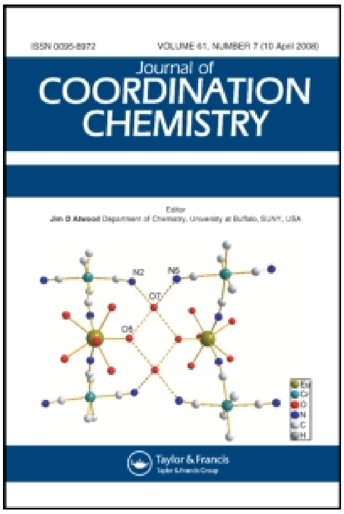

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COMPLEXES OF SODIUM, POTASSIUM, RUBIDIUM AND CESIUM PICRATES WITH BIS-CROWN ETHERS

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The complexation between alkali metal picrate salts and bis-crown ethers with benzo-12-crown-4, benzo-15-crown-5 and benzo-18-crown-6 moieties bridged by polyethylene glycol has been investigated by UV-visible spectroscopy. Since these bis-crown ethers are potential phase transfer reagents and catalysts in reactions, their abilities to transfer alkali picrates from solid phase or from aqueous solution into chloroform are used to gauge their complexing efficiencies towards alkali metal ions. It is found that there are at least two types of complexes formed between alkali picrates and bis-crown ethers in chloroform. One is the sandwich type of crown separated ion pair complexes present in the systems bis-benzo-12-crown-4 ethers–sodium picrate, bis-benzo-12-crown-4 ethers–potassium picrate, bis-benzo-15-crown-5-ethers–potassium picrate, bis-benzo-15-crown-5 ethers–rubidium picrate, bis-benzo-15-crown-5 ethers–cesium picrate, and bis-benzo-18-crown-6–cesium picrate. The other is the non-sandwich type of crown complexed tight ion pairs as encountered in the systems bis-benzo-15-crown-5–sodium picrate, bis-benzo-18-crown-6-ethers–sodium picrate, bis-benzo-18-crown-6 ethers–potassium picrate, and bis-benzo-18-crown-6 ethers–rubidium picrate. For those alkali metal cations that form sandwich type complexes, the extraction efficiencies from aqueous phase into chloroform by bis-crown ethers are much greater than that by the corresponding monomeric crown ethers. However, for those forming non-sandwich type complexes, the extraction constants by bis-crown ethers are slightly smaller than that by the corresponding monomeric crown ethers. The length of the bridge linking the two crown moieties also affects the extraction efficiencies. The selectivity orders of extracting alkali metal picrate from aqueous solution into chloroform are $K^+ > Rb^+ > Na^+ > Cs^+$ for bis-benzo-15-crown-5 ethers and $K^+ \sim Cs^+ > Rb^+ > Na^+$ for bis-benzo-18-crown-6 ethers, respectively.

INTRODUCTION

The sandwich type complex between potassium ion and benzo-15-crown-5 ether has been known for many years.[1] In order to increase the stability of the complex, bis-crown ethers with benzo-15-crown-5 moiety have been successfully synthesized and subsequently proven to be much better complexing agents for the potassium ion.[2] Furthermore, these bis-crown ethers can achieve better separation of an ion pair than the corresponding monomeric crown ethers. The increase in the interionic distance in an ion pair results in an increase in the reactivity of the anion in organic solvents of low polarity.[3]

The ability of forming stable sandwich type complexes depends on the relative sizes of alkali metal ions and the hole cavities of the crown ethers. Bearing this in mind, we have successfully synthesized a series of bis-crown ethers containing benzo-12-crown-4,[4] benzo-15-crown-5[5] and benzo-18-crown-6[5] moieties. The bridge chains consist of only ether functional group which ensures the stability of these bis-crown ethers in acidic or basic media. The structures of these bis crown ethers are depicted below.

Similar to the monomeric crown ethers, the IUPAC nomenclature system for these bis-crown ethers is very cumbersome.[1] For convenience in use, an abbreviated naming system for these bis-crown ethers is desirable. Since these bis-crown ethers contain benzo-12-crown-4, benzo-15-crown-5 or benzo-18-crown-6 moieties, respectively, a prefix "bis" is added in front of the corresponding monomeric crown moiety indicating the bis-crown ether families. The length of the bridge linking the two identical crown moieties can be indicated by the number of oxygen atoms present in the polyethylene ether chain, and this number is put in between the prefix "bis" and the name of the monomeric crown ether moiety. For example, the IUPAC name of compound I is 1,7-bis-[3′,4′-(1″,4″,7″,10″-tetraoxacyclododeca-2″-ene)-benzyl]-1,4,7-trioxaheptane and its abbreviated name is bis-3-benzo-12-crown-4.

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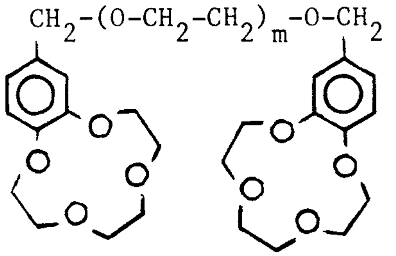
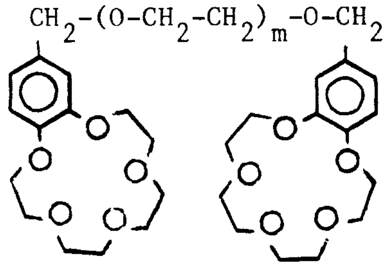
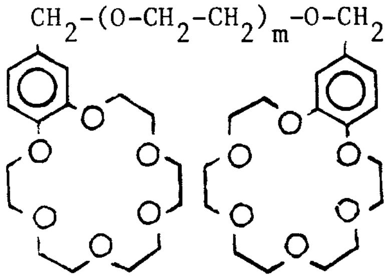


m = 2 I bis-3-benzo-12-crown-4
m = 3 II bis-4-benzo-12-crown-4



m = 0 III bis-1-benzo-15-crown-5
m = 1 IV bis-2-benzo-15-crown-5
m = 2 V bis-3-benzo-15-crown-5
m = 3 VI bis-4-benzo-15-crown-5



m = 1 VII bis-2-benzo-18-crown-6
m = 2 VIII bis-3-benzo-18-crown-6
m = 3 IX bis-4-benzo-18-crown-6

It is well known that ethers are useful as reagents in phase transfer reactions.[6] This is due to the formation of complexes between crown ethers and alkali metal salts. These complexes are more lipophilic and therefore can be transferred into the organic layer in the form of ion pairs. In this respect, the ability of transferring alkali salts from solid phase or from aqueous solution into organic solvent by crown ethers is the prime concern in this study. The picrate anion is widely used as a probe because its characteristic UV-visible absorption maximum ranging between 350 nm and 450 nm depends very much on the interionic distance of the crown complexed ion pair.[7]

EXPERIMENTAL

Bis-crown Ethers

The preparations of bis-benzo-12-crown-4 ethers,[4] bis-benzo-15-crown-5 ethers and bis-benzo-18-crown-6 ethers[5] have been described elsewhere. For comparison purpose, monomeric crown ethers with benzo-12-crown-4, benzo-15-crown-5 and benzo-18-crown-6 moieties were also used. 4′-Methylbenzo-12-crown-4 was synthesized according to the procedure described elsewhere.[4] 4′-Methylbenzo-15-crown-5 and 4′-methylbenzo-18-crown-6 were prepared according to the procedure described by Pedersen.[1]

Sodium Picrate

Excess amount of ethanolic sodium hydroxide solution was added slowly into ethanolic picric acid solution with stirring at room temperature. The reddish orange precipitate of sodium picrate was filtered and washed with 95% ethanol to remove the excess base. Pure salt was obtained by recrystallization twice in 95% ethanol and dried under vacuum at room temperature.

Potassium Picrate, Rubidium Picrate and Cesium Picrate

Excess amount of the corresponding aqueous alkali metal hydroxide solution was added slowly into the aqueous picric acid solution with stirring. Yellow crystals appeared immediately. The precipitate was filtered and washed with cold water to remove the excess base. Pure salt was obtained by recrystallization twice in distilled water and dried under vacuum at room temperature.

All salts were stored in the dark.

Dissolvation of Alkali Picrates in Chloroform by Bis-crown Ethers

A weighted amount of alkali picrate was stirred in 50 ml chloroform solution of known bis-crown ether concentration. Usually, it took about 10 hours to dissolve all alkali picrate crystals. The concentration of the bis-crown ether-alkali picrate complex was calculated based on the known volume of the solution and the exact amount of alkali picrate used. The UV-visible spectra in the range 340–450 nm were recorded using a Hitachi-323 UV-visible spectrometer. From the UV-visible spectrum, the molar absorptivity at the absorption maximum was determined for individual complex.

Extraction of Alkali Picrates from Aqueous Solution into Chloroform by Bis-crown Ethers

The efficiency of transferring alkali picrate salts from water into chloroform by each crown ether was evaluated from the extraction equilibrium constants. These constants were obtained by simple liquid-liquid extraction process.[7] The extraction was performed by vigorously shaking a 5 ml water saturated chloroform solution of known crown ether concentration with a 5 ml chloroform saturated aqueous solution of known alkali picrate concentration at room temperature. The concentration ranges of crown ethers and salts varied from 1.6×10^{-4} M to 6.3×10^{-4} M and from 1.0×10^{-3} M to 2.5×10^{-2} M, respectively. The concentrations of the crown ether-picrate complexes in the chloroform layer were calculated from the UV-visible spectra and the molar absorptivities previously determined.

RESULTS AND DISCUSSION

Characteristic UV-visible Absorptions and the Structures of the Complexes between Bis-crown Ethers and Alkali Metal Picrates in Chloroform

It is well known that, without the presence of crown ethers, alkali metal picrates do not dissolve in chloroform at room temperature.[7,8] The crown ethers which are used as the phase transfer reagents, can solubilize the solid salts into chloroform by the formation of stable complexes with the alkali ions. Upon stirring a solid alkali picrate salts in chloroform solution with a known concentration of bis-crown ethers, the salt starts to dissolve. If there is enough bis-crown ether, the salt will completely dissolve after about 10 hours stirring at room tem-

TABLE I

Absorption maxima (λ_{max} nm) of the complexes between bis-crown ethers and alkali picrates in chloroform at 20°C

Crown ether	Sodium picrate	Potassium picrate	Rubidium picrate	Cesium picrate
Bis-3-benzo-12-crown-4	362	365	–	–
Bis-4-benzo-12-crown-4	362	365	–	–
Bis-1-benzo-15-crown-5	356	378	378	376
Bis-2-benzo-15-crown-5	356	378	378	376
Bis-3-benzo-15-crown-5	356	378	378	376
Bis-4-benzo-15-crown-5	356	378	378	376
4'-methylbenzo-15-crown-5	356	365[a]	365[a]	364[a]
Bis-2-benzo-18-crown-6	362	365	365	378
Bis-3-benzo-18-crown-6	362	365	365	378
Bis-4-benzo-18-crown-6	362	365	365	378
4'-methylbenzo-18-crown-6	362	365	365	367[a]

[a] The crown ether is not in large excess in comparison with the corresponding salt. The absorption maximum can shift gradually to 378 nm in the presence of large excess of crown ethers.

perature. The criteria for completely solubilizing the salt are the availability of sufficient bis-crown ethers for complete complexation and the solubility of the complex in the solvent. For sandwich type complexes, the molar ratio of bis-crown ether to salt ([bis-crown ether]/[salt]) in the system must be slightly greater than one. In view of the long stirring time required, no attempt was made to establish the maximum solubility of these complexes in chloroform. However, there is no difficulty to achieve complex concentrations up to 5.0×10^{-2} M in chloroform at room temperature.

The absorption maxima (λ_{max} nm) of the complexes between bis-crown ethers and alkali picrates in chloroform at 20°C are listed in Table I. The accuracy of the recorded absorption maxima is within 0.5 nm. For convenience in comparison, data for the corresponding monomeric crown ether complexes are included in this Table.

There are at least two types of crown ether–alkali picrate complexes that exist in low polarity media. One is the non-sandwich type of crown-complexed tight ion pairs with an absorption maximum lying between 350 nm and 370 nm.[7] The other is the sandwich type crown separated ion pairs with an absorption maximum at 378 nm in chloroform[7] or at 380 nm in THF.[2] The complexes between bis-benzo-15-crown-5 ethers and sodium picrate in chloroform show an absorption maximum at 356 nm, regardless of the different lengths of the bridge linking the two crown moieties. This means that the complexed ion pairs in these system closely resemble that formed between the same salt and the corresponding monomeric crown ether, i.e. 4′-methylbenzo-15-crown-5. It is because the size of sodium ion is comparable with the diameter of the benzo-15-crown-5 cavity,[1] and therefore, the two crown moieties in the bis-crown ethers act as two individual crown units during complexation.

The absorption maxima of the complexes between sodium picrate and bis-benzo-18-crown-6 ethers are at 362 nm in chloroform, which coincide with the absorption maximum of the complex between the same salt and the monomeric crown ether, i.e., 4′-methylbenzo-18-crown-6. This phenomenon is similar to what has been observed in the bis-benzo-15-crown-5 system. Again, the bis-crown ethers simply provide two individual crown moieties for complexation.

Complexes between sodium picrate and bis-benzo-12-crown-4 ethers show absorption maxima at 362 nm which accidentally coincide with the absorption maximum of the complex between sodium picrate and 4′-methylbenzo-18-crown-6. This indicates that both complexes have very similar ionic distance and are in the form of tight ion pairs. Because of the small ring size of the benzo-12-crown-4 moiety, the sodium ion cannot be wrapped completely by these bis-crown ethers. The crown complex is therefore in the form of a V-shaped sandwich, with the sodium ion situated in between two crown moieties. This structure can provide enough space at the open end of the V-shaped sandwich for the picrate ion to pair with the sodium ion, resulting in a shorter interionic distance between sodium and picrate ions than that of a regular sandwich type complex.

In chloroform, two types of complexes between potassium picrate and bis-crown ethers containing different crown moieties are observed. The first type includes the salt complexes with bis-benzo-12-crown-4 ethers and bis-benzo-18-crown-6 ethers which show identical absorption maxima at 365 nm. In the case of bis-benzo-18-crown-6 ethers, the two crown moieties in the bis-crown ethers work as two individual units towards potassium ion and no sandwich type complexes are formed. In the case of bis-benzo-12-crown-4 ethers, similar to the sodium picrate case, formation of V-shaped structures with the potassium cation locating in between two crown ether moieties is expected. Based on the absorption maxima at 365 nm, these are inferred to be components of crown-complexed tight ion pairs. The second type consists of the salt complexes with bis-benzo-15-crown-5 ethers showing absorption maxima at 378 nm which coincide with the value found in the potassium picrate–polyvinylbenzo-15-crown-5 system.[7] Since the size of the potassium ion exceeds the diameter of the benzo-15-crown-5 cavity,[1] the two neighbouring crown moieties complex with one potassium ion simultaneously, leading to the formation of a sandwich complex. This type of structure has been known to exist in crown separated ion pairs with a characteristic absorption maximum at 378 nm in chloroform.[7]

Two types of complexes between rubidium picrate and bis-crown ethers are observed. Bis-benzo-18-crown-6 ethers and the salt form crown complexed tight ion pairs with absorption maxima at 365 nm, while bis-benzo-15-crown-5 ethers complex with the same salt leading to the formation of crown separated ion pairs showing absorption maxima at 378 nm. Bis-benzo-12-crown-4 ethers cannot solubilize rubidium picrate into chloroform at room temperature. Their rather poor complexation ability is probably due to the unfavourable size relationship between the cation and the crown ether cavities plus the lack of enough complexation sites provided by the benzo-12-crown-4 moieties.

Complexation between cesium picrate and bis-benzo-18-crown-6 ethers is very similar to that between potassium picrate and the bis-benzo-15-crown-5 ethers. The cesium complexes showing absorption maxima at 378 nm in chloroform exist in the form of crown separated ion pairs. The complexes between cesium picrate and bis-benzo-15-crown-5 ethers show absorption maxima at 376 nm, close to the absorption maxima of crown separated ion pair complexes (378 nm), and quite distinct from that (364 nm) of crown complexed tight ion pair formed between cesium picrate and 4′-methylbenzo-15-crown-5. Therefore, these complexes are considered to be the sandwich type of crown separated ion pairs. Similar to the case for rubidium picrate, there is no complex formation between cesium picrate and bis-benzo-12-crown-4 ethers in chloroform at room temperature.

Extraction of Alkali Metal Picrates from Aqueous Solution into Chloroform by Bis-Crown Ethers

The alkali picrates, though not directly soluble in chloroform, can be extracted into organic solvents from aqueous solution by crown ethers.[7] The overall extraction equilibrium can be expressed as.[7]

$$M^+_{aq} + Pi^-_{aq} + Cr_{org} \underset{}{\overset{Ke}{\rightleftharpoons}} CrM^+, Pi^-_{org} \qquad (1)$$

where M^+_{aq} and Pi^-_{aq} denote the alkali cation and picrate anion in aqueous phase, and Cr_{org} and CrM^+, Pi^-_{org} are, respectively, the crown ether and crown ether-picrate complex in chloroform. It has been shown that in chloroform the crown ether alkali picrate complexes exist in the form of ion pairs at or above the concentration of 5×10^{-5} M[7]. The extraction constant Ke is therefore given by the following expression

$$Ke = \frac{[CrM^+, Pi^-_{org}]}{\gamma^2_{\pm}[M^+_{aq}][Pi^-_{aq}]\{[Cr_{org}]_0 - [CrM^+, Pi^-_{org}]\}} \qquad (2)$$

where $\gamma^2_{\pm}$ is the mean activity coefficient of the picrate in water, $[Cr_{org}]_0$ is the initial crown ether concentration in chloroform, and $[CrM^+, Pi^-_{org}]$ is the crown ether picrate complex concentration in chloroform which measurable by UV-visible spectroscopy.[7] $[M^+_{aq}]$ and $[Pi^-_{aq}]$ can be considered as the initial salt concentration in aqueous solution because, in our extraction experiments, always less than 5% of the initial salt was extracted into the chloroform layer.

Eq. (2) for calculating the Ke value is valid only when the stoichiometric ratio between bis-crown ether and metal cation is 1:1. This includes the cases of complex formation between potassium picrate–bis-benzo-15-crown-5 ethers, rubidium picrate–bis-benzo-15-crown-5 ethers and cesium picrate–bis-benzo-15-crown-5 ethers as well as cesium picrate–bis-benzo-18-crown-6 ethers. All these complexes are of the sandwich type and absorb at 376–378 nm. Slight modification of Eq. (2), however, is needed for the cases of complex formation between sodium picrate–bis-benzo-15-crown-5 ethers, sodium picrate–bis-benzo-18-crown-6 ethers, potassium picrate–bis-benzo-18-crown-6 ethers, and rubidium picrate–bis-benzo-18-crown-6 ethers. In these cases, UV-visible spectroscopic data reveal that the two crown moieties of the bis-crown ethers act as two individual crown units towards the metal ions. As a result, the initial concentration of crown ether $[Cr_{org}]_0$ in Eq. (2) should be twice the initial concentration of the bis-crown ethers, i.e., $[Cr_{org}]_0 = 2 \times$ [bis-crown $ether_{org}]_0$. Similar approaches have been reported when using the polymer and copolymers of vinyl benzo-18-crown-6 and styrene as cation carriers in studies of ion transfer process through liquid membrane[7].

The extraction constants Ke of alkali metal picrate salts by bis-crown ethers for the system H_2O–$CHCl_3$ at 20°C were determined by varying the initial concentrations of the two species in both phases. The average Ke values for individual system together with the standard deviations are listed in Table II. For comparison, extraction constants of the monomeric crown ethers, 4′-methylbenzo-15-crown-5 and 4′-methylbenzo-18-crown-6, are also included.

By comparing the extraction constants between bis-crown ethers and the corresponding monomeric crown ethers for the alkali metal picrates, it is found that the extraction efficiencies of bis-crown ethers are definitely much better than that of the corresponding monomeric crown ethers for systems involving sandwich type complexes. For example, bis-1-benzo-15-crown-5 is about 100 times more effective than 4′-methylbenzo-15-crown-5 in extracting potassium picrate from aqueous phase into chloroform phase. The increase in number of binding sites for the cation in bis-crown ethers is responsible for the big difference in the extraction constants. The extraction constants for bis-crown ethers are, however, slightly smaller than the corresponding monomeric crown ethers when the com-

TABLE II

Extraction constants Ke of alkali metal picrates by bis-crown ethers for the H_2O–$CHCl_3$ system at 20°C

Crown ether	Na^+Pi^- ($\times10^{-4}M^{-2}$)		K^+Pi^- ($\times10^{-4}M^{-2}$)		Rb^+Pi^- ($\times10^{-2}M^{-2}$)		Cs^+Pi^- ($\times10^{-4}M^{-2}$)	
	Ke	standard deviation	Ke	standard deviation	Ke	standard deviation	Ke	standard deviation
Bis-1-benzo-15-Crown-5	0.24	0.17	4.5	0.59	2.6	0.33	0.16	[b]
Bis-2-benzo-15-crown-5	0.24	0.14	2.3	0.32	0.89	0.20	0.10	[b]
Bis-3-benzo-15-crown-5	0.23	0.05	3.5	0.86	1.6	0.26	0.16	[b]
Bis-4-benzo-15-crown-5	0.23	0.09	3.9	0.69	1.5	0.16	0.17	[b]
4′-Methylbenzo-15-crown-5	0.37[a]		0.042[a]		0.034	0.003	0.012	[b]
Bis-2-benzo-18-crown-6	0.21	0.012	14	2.1	5.9	1.4	8.5	2.1
Bis-3-benzo-18-crown-6	0.16	0.00	13	0.29	5.2	1.0	11	3.6
Bis-4-benzo-18-crown-6	0.18	0.008	17	1.7	5.8	0.54	15	2.3
4′-Methylbenzo-18-crown-6	0.23[a]		23[a]		6.9	0.28	1.4	0.17

[a] Ref. 7

[b] Due to low solubility of cesium picrate in water and small extraction constants, only one measurement was made.

plexes are not of the sandwich type, such as crown-complexed tight ion pair complexes. As mentioned before, the two crown moieties of the bis-crown ether act as two individual units in complexing, similar to two independent monomeric crown ethers. Therefore, the extraction constants of these bis-crown ethers in this case should be very close to those of their corresponding monomeric species. The slightly smaller extraction constants are probably due to the repulsion between the two cations bound to the two crown moieties of the same bis-crown ether molecule.

For the sandwich type of complexes, the length of the bridge linking two crown moieties can slightly affect the extraction constants. For example, in the system of potassium picrate extracted by bis-benzo-15-crown-5 ethers, the highest Ke value of 4.5×10^4 M^{-2} is found for bis-1-benzo-15-crown-5 and then a drop to the minimum Ke value of 2.3×10^4 M^{-2} for bis-2-benzo-15-crown-5 is recorded. As the length of the bridge increased, the Ke values rise again for bis-3-benzo-15-crown-5 and bis-4-benzo-15-crown-5. The same trends are also observed for rubidium and cesium picrates extracted by these bis-crown ethers. The drop in extraction constants from bis-1-benzo-15-crown-5 to bis-2-benzo-15-crown-5 is due to the fact that the bridge oxygen atoms are not available for complexation. By examining CPK models of these bis-crown ethers, the bridge oxygen atoms are tied up on the benzylic carbons and cannot come close to the cavity of the crown moieties where complexation takes place. Due to the higher flexibility of bis-2-benzo-crown-5, it would lose more entropy than bis-1-benzo-15-crown-5 in forming sandwich complexes. As a result, the smaller extraction constant for bis-2-benzo-15-crown-5 is not unreasonable. In the case of bis-3-benzo-15-crown-5 and bis-4-benzo-15-crown-5, again by examining CPK models of these ethers, the bridge chains are flexible enough to allow the bridge oxygen atoms (except the benzylic bound oxygen atoms) to approach the complexation sites and participate in complexation of the cation. The contribution from these oxygen atoms can facilitate the formation of sandwich type complexes and thus slightly increase the extraction constants.[2]

In the case of cesium picrate, bis-benzo-15-crown-5 and bis-benzo-18-crown-6 ethers form the same type of complexes, i.e., sandwich type of crown-separated ion pairs. However, the extraction constants Ke for bis-benzo-18-crown-6 ethers are approximately 100 times larger than that of bis-benzo-15-crown-5 ethers. This big difference in Ke values can be rationalized by the fact that the size of the cesium ion is so large that ten oxygen atoms around the smaller cavities of bis-benzo-15-crown-5 ethers are not enough to coordinate the cation. Bis-benzo-18-crown-6 ethers which have larger cavities and higher numbers of oxygen atoms can wrap around the cesium ion and, therefore, form stable complexes.

Based on the extraction constants, the order of selectivity of transferring alkali metal picrates from aqueous phase into chloroform by bis-crown ethers is different from that by their corresponding monomer species. For bis-benzo-15-crown-5 ethers, the selectivity order is

$K^+ > Rb^+ > Na^+ > Cs^+$,

whereas, for the monomeric 4′-methylbenzo-15-crown-5 not in large excess, the order is

$Na^+ > K^+ > Rb^+ > Cs^+$.

For bis-benzo-18-crown-6 ethers, the order is

$K^+ \sim Cs^+ > Rb^+ > Na^+$,

whereas, for the monomeric 4′-methylbenzo-18-crown-6 not in large excess, the order is

$K^+ > Rb^+ > Cs^+ > Na^+$.

Although bis-3-benzo-12-crown-4 and bis-4-benzo-12-crown-4 can solubilize sodium picrate and potassium picrate into chloroform by forming the corresponding complexes, they cannot extract these salts from aqueous phase into chloroform layer. As mentioned before, no detectable amount of complexes between bis-benzo-12-crown-4 ethers and rubidium picrate or cesium picrate in chloroform was found. The weak phase transfer abilities of bis-benzo-12-crown-4 ethers are probably due to the lack of enough complexing sites and unsuitable cavity size for complexation.

An interesting phenomenon found in this study is that the most effective phase transfer reagents for potassium and cesium picrates from aqueous phase to chloroform phase are bis-benzo-18-crown-6 ethers. The extraction constants are not significantly different for both salts. They are about $1.0 \times 10^5\ M^{-2}$. However, the structures of the complexes involved in the phase transfer process are quite different. For the potassium salt, they are crown complexed tight ion pairs. For the cesium salt, they are crown separated ion pairs. In other words, the anions are in different ionic environments even though the same anion is involved in these complexes. Hence, one would expect that in phase transfer reactions, the reaction rate and, possibly, the reaction mechanism may be different. The behavior of the anions catalyzed by bis-crown ethers is currently being investigated in this laboratory. The preliminary result indicates that there is, indeed, a difference in catalytic effect between bis-crown ethers and their corresponding monomers.

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