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Polarographic Study of Thallium(I) Complexes with Large Crown Ethers in Binary Acetonitrile-Water Mixtures

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The complexation reactions between the Tl⁺ ion and large crown ethers dibenzo-30-crown-10 (DB30C10), dibenzo-27-crown-9 (DB27C9), dibenzo-24-crown-8 (DB24C8) and dibenzo-21-crown-7 (DB21C7) were studied in different acetonitrile-water mixtures at 25 °C using an a.c. polarographic technique. The stoichiometry and stability of the complexes were determined by monitoring the shift in peak potential of the polarographic waves of the metal ion against the crown concentration. In all solvent mixtures used, the stability of the resulting 1:1 complexes was found to vary in the order DC24C8 >> DB30C10 > DB21C7 > DB27C9 > DB24C8. There is an inverse relationship between the complex formation constants and the amount of water in the mixed solvent. In all cases, a linear relation was observed between log K_f and the mole fraction of acetonitrile in its mixtures with water.

INTRODUCTION

The first synthesis of macrocyclic crown ethers by Pedersen[1] and the discovery of their ability to strongly and selectively complex the alkali and alkaline earth cations have led to an extensive study of these ligands and their metal ion complexes.[2,3] Among the macrocyclic polyethers, large crown ethers (i.e. larger than 18-crown-6) possess interesting properties. Some of these ligands are very flexible molecules with enough oxygen atoms in their rings to enable them to twist around a metal ion of suitable size to envelop it completely and form a 'wrap around' complex in which all oxygen atoms of the ring are coordinated to the central cation. Evidence for the existence of such tri-dimensional structures both in solid state[4,5] and in solution[6-10] have been reported. Moreover, in some cases, the macrocyclic ring can accommodate two cations, if the repulsion forces are not so large, as in the case of Li⁺, Na⁺ and K⁺ complexes with dibenzo-24-crown-8[11,12] and dibenzo-30-crown-10.[6,9,13]

It was of interest to us to study the influence of the cation size (and nature) and solvent properties on the interactions of metal ions with large crown ethers.[6,7,14,15] Due to the special importance of Tl⁺ as a polarizable soft cation in biological and environmental processes,[16,17] in this paper we report a polarographic study of thallium complexes with dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8), dicyclohexyl-24-crown-8 (DC24C8), dibenzo-27-crown-9 (DB24C9) and dibenzo-30-crown-10 (DB30C10) in different binary acetonitrile-water mixtures at 25 °C. Structures of the ligands are shown in Fig. 1.

EXPERIMENTAL

Crown ethers DB24C8, DB30C10 (both from Merck) and DB27C9 (Parish) were purified and dried using pre-
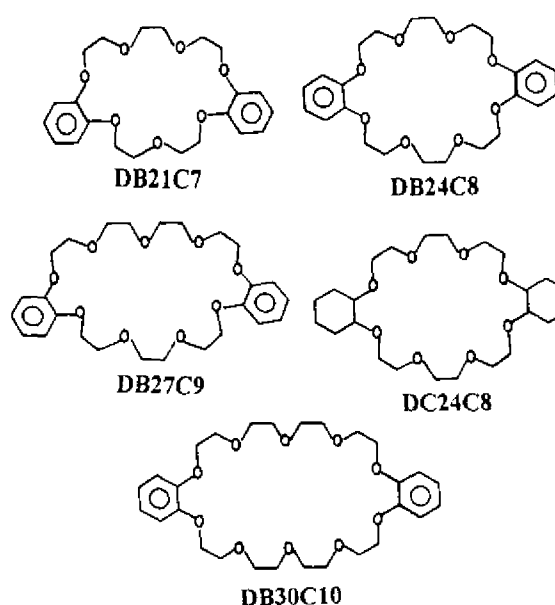

Fig. 1. Structure of the ligands.

viously reported methods.[7] DB21C7 (Parish) and DC24C8 (Fluka) were of the highest purity available and used as received. Reagent grade tetrabutylammonium perchlorate (TBAP, Merck) was recrystallized from pure acetone and vacuum dried for 24 h. HPLC grade acetonitrile (Merck) and doubly distilled deionized water were used to prepare the solvent mixtures by weight.

The polarographic measurements were carried out with a dropping mercury electrode (DME) in a three-electrode arrangement. The auxiliary electrode was a Pt wire with a considerably larger surface area than that of DME. A silver-silver chloride reference electrode was placed in 0.05 M TBAP solution and connected to the electrolyte. All the solutions were deaerated for 10 min with pure nitrogen and an inert atmosphere was maintained over the solutions during the reduction. All polarographic measurements were made with a Metrohm multipurpose instrument model 693 VA Processor equipped with a 694 VA Stand. The usual instrumental parameters were: drop time, 1 s; scan rate 6 mV/s; a.c. amplitude, 20 mV. All experiments were carried out at 25.0 ± 0.5 °C.

Determination of the formation constants of Tl^+-macrocycle complexes was based on the measurement of the shifts in E_p (peak potential) brought about by addition of an increasing amount of the ligands.[18] In the acetonitrile-water mixtures used, the reversible amalgam-forming reduction of the complexes results in a shift of the E_p to more negative values in accordance with the Lingane equation:[19]

$$\Delta E_p = E_p^{Tl\text{-macrocycle}} - E_p^{Tl} = -(RT/F)(\ln K_f$$
$$+ \, m \ln [macrocycle]_t) \tag{1}$$

where $E_p^{Tl\text{-macrocycle}}$ and E_p^{Tl} are the peak potentials of the complexed and free metal ions, respectively, m is the stoichiometry of the complex (i.e. macrocycle/cation ratio), K_f is the complex formation constant and $[macrocycle]_t$ is the analytical concentration of the macrocycle. In all experiments, the concentrations of TBAP (0.05 M) and Tl^+ (0.125-0.300 mM; 0.500 mM in cyclic voltammetry experiments) were kept constant and the concentration macrocycle added varied (10-25 mM). As is obious, the concentration of TBAP (0.05 M) taken was about 170-400 times higher than that of $TlNO_3$, in order to eliminate the migration effect and possible iR drop problem.

RESULTS AND DISCUSSION

To characterize the complexation equilibria of Tl^+ ion with the large crown ethers DB21C7, DB24C8, DC24C8, DB29C9 and DB30C10 in different acetonitrile-water mixtures, the cyclic voltammetric and polarographic measurements (both in a.c. and d.c. modes) were carried out under the same experimental conditions.

The polarograms obtained by the reduction of the free Tl^+ ion in different acetonitrile-water mixtures (with acetonitrile wt% of 100, 90, 80, 70 and 60) were all reversible, and quasireversible in the case of the complexed Tl^+ ion. The logarithmic analysis of the polarograms in d.c. and a.c. modes showed a linear dependence of log $(i_d - i)/i$ vs. $E_{d.c.}$ and log $[(i_p/i)^{1/2} \pm (i_p - i)/i]$ vs. $E_{d.c.}$, respectively, with the slopes of 60 ± 5 mV. The half-height potentials of the a.c. polarograms varied in the range of 90-105 mV. The reversibility of the reduction systems was also confirmed by cyclic voltammetry (see Fig. 2 as an example). All reduction waves were well defined and controlled by diffusion.

The large crown ethers used show no reduction wave within the available potential range. However, addition of the macrocyclic ligands to the Tl^+ solutions in 0.05 M TBAP resulted in the shifts of $E_{1/2}$ and E_p corresponding to the reduction of cations towards more cathodic values. In all Tl^+-
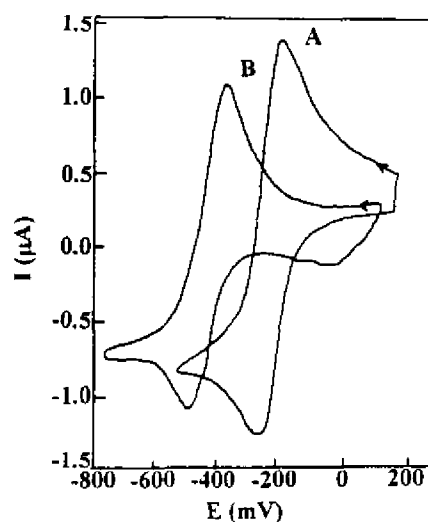

Fig. 2. Cyclic voltammograms of 0.5 mM Tl^+ ion and 0.05 M TBAP in acetonitrile solution in the absence (A) and presence (B) of 10 mM of DC24C8 at a scan rate of 100 mV/s.

Table 1. Formation Constants of Tl^+ Ion Complexes with Large Crown Ethers in Various Binary Acetonitrile-Water Mixture at 25 °C

Crown	wt% Acetonitrile	log K_f[a]				
		100	90	80	70	60
DB21C7		5.27 >5[b] 5.28[c]	4.25	3.77	3.14	2.62
DB24C8		4.80 4.81[b]	3.80	3.07	2.73	2.30
DC24C8		6.35	5.24	4.67	4.23	3.93
DB27C9		4.83	3.71	3.18	2.83	2.41
DB30C10		5.41 5.35[d]	4.16	3.67	3.31	2.95

[a] Standard deviations on log K_f values are within ± 0.05.
[b] Data taken from Ref. 7.
[c] Data taken from Ref. 30.
[d] Data taken from Ref. 31.

macrocycle systems studied, the reduction waves of the complexed ion was found to be reversible (or quasireversible) and diffusion controlled. This reversible behavior indicates that the exchange between the free cation and its complexes is rapid on the measurement time scale, as expected.[20] Sample a.c. polarograms for Tl^+ ion in the presence of increasing concentration of DB21C7 is shown in Fig. 3. It should be noted that the observed decrease in peak current brought about upon addition of the macrocycle is most possibly a result of decreased diffusion of the complexed metal ion compared with that of the solvated cation

in solution.[21]

According to equation (1), the variation of ΔE_p as a function of log $[macrocycle]_t$ was linear for all cases studied (Fig. 4). The slopes of these straight lines gave a value of m $\cong$ 1, which suggests the formation of a 1:1 complex between Tl^+ ion and the large crowns used in solution. The formation constants of the resulting complexes were evaluated from the intercepts of the corresponding linear plots, and all K_f values are summarized in Table 1. The previously reported formations constants in pure acetonitrile solution are also included for comparison. As seen, there is a satisfactory
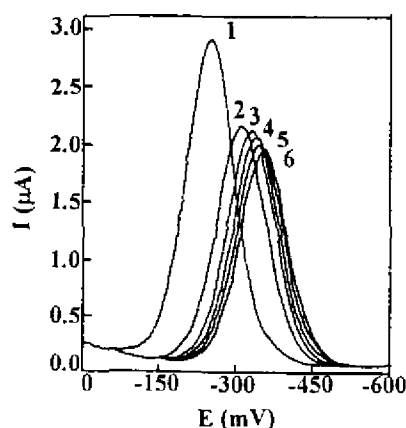

Fig. 3. a.c. polarograms of 0.125 mM of Tl^+ ion in acetonitrile solution in the presence of increasing concentration of DB21C7. Macrocycle concentration in mM is: (1) 0.0, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0, (6) 2.5.
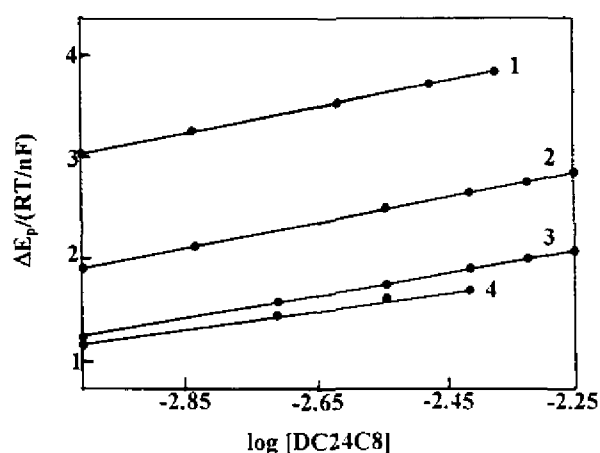

Fig. 4. Linear plots of $\Delta E_p/(RT/nF)$ vs. log [DC24C8] in different acetonitrile-water mixtures. Weight percent acetonitrile in the solvent mixtures is: (1) 100%, (2) 90%, (3) 80%, (4) 70%.

agreement between the log K_f values obtained in this work with those reported in the literature.

From the data given in Table 1 it is immediately obvious that, in all solvent mixtures used, the Tl^+ complex with DC24C8 is much more stable than that with the dibenzo-substituted large crown ethers used. It is well known that the presence of two cyclohexyl groups substituted on the crown ether's cavity can pump electrons into the ligand ring and thus increase the basicity of the oxygen atoms, while the flexibility of the macrocycle remains more or less the same as the unsubstituted crown. The result is the increased stability of the Tl^+-crown ether complex. On the other hand, the addition of two benzo groups to the macrocyclic ring lowers the stability of the Tl^+ complexes markedly. This be-

Fig. 5. Plots of log K_f vs. X_{AN} for Tl^+ ion complexes with (1) DC24C8, (2) DB30C10, (3) DB21C7, (4) DB27C9 and (5) DB24C8.

havior may be attributed to some combination of the inductive electron withdrawing property of the benzo groups, which weakens the electron-donor ability of the oxygen atoms of the ring, and reduced flexibility of the ligand which prevents to some extent the macrocyclic molecule warping itself around the cation.[14] Thus, the decreased stability of the Tl^+-dibenzocrowns in comparison with the Tl^+-DC24C8 is not surprising.[2,7]

Comparison of the data given in Table 1 indicates that the stability of the Tl^+ complexes with dibenzocrowns used varies in the order DB30C10 > DB21C7 > DB27C9 > DB24C8. Although DB21C7 with a cavity size of 3.4-4.3 $Å$[22] provides the best fitting condition for Tl^+ ion (with an ionic size of 3.08 $Å$),[23] its Tl^+ complex is less stable than that with DB30C10 with the largest cavity size in the series. However, the ion-in-the-hole model[2] has limited usefulness in predicting the stability of the metal ion complexes of large crown ethers such as DB30C10. The increased number of ring atoms as well as the increased flexibility of the macrocyclic molecule make it difficult to define a fixed cavity diameter for the ligand. Actually, it has been shown that large crown ethers such as DB30C10 can twist around a cation of suitable size (such as K^+, ionic size 2.86 $Å$) to from a tridimensional 'wrap around' complex in which all oxygen atoms of the ring participate in the bond formation with the central cation.[4-7] A thallium ion, with about the same ionic size as potassium ion, seems to fit properly inside the twisted DB30C10 molecule to form a rather stable 'wrap around' complex.

The DB24C8 falls between the above two cases (i.e. DB30C10 and DB21C7); it possesses neither enough flexibility to form a three-dimensional 'wrap around' structure nor a suitable cavity size for the formation of a stable two-dimensional complex with all eight donating oxygens participating in the bond-formation with the Tl^+ ion. Since the cavity of DB24C8 is larger than the ionic size of Tl^+ ion,[2,22,23] it is more likely that a two-dimensional complex is formed in which only a part of the donor sites are bound to the Tl^+ ion.[2,7] Thus the resulting complex would be the least stable of the four. On the other hand, the increase both in the number of binding sites and the flexibility of DB27C9, in comparison with DB24C8, will result in some higher stability of its complex with the Tl^+ ion over the Tl^+-DB24C8 complex.
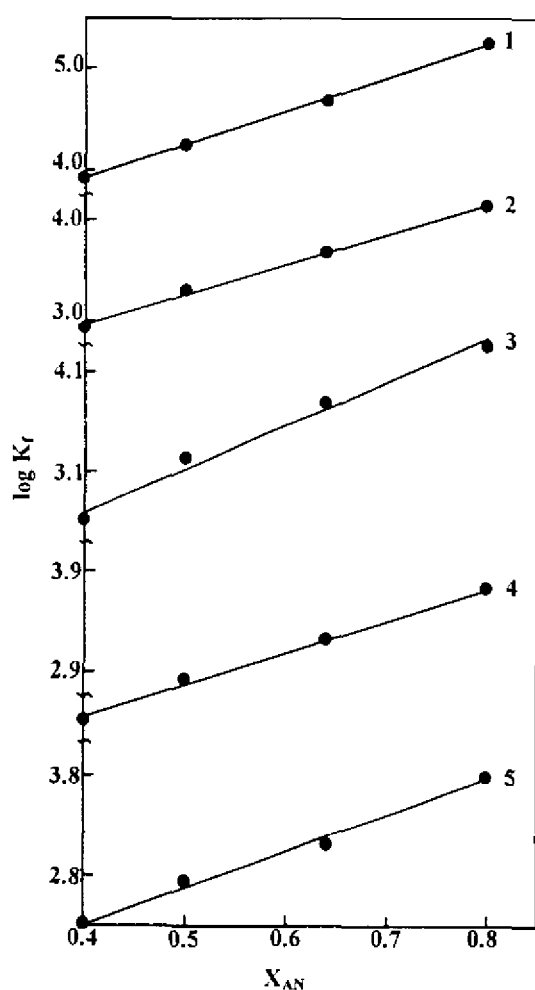
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The data shown in Table 1 illustrate clearly the important influence of the solvent properties in the complexation reactions. In all cases, the stability of the Tl^+ complexes decrease drastically with increasing weight percent of water in the mixed solvent. It has been shown that the solvating ability of the solvent, as expressed by the Gutmann donicity number,[24] plays a fundamental role in complexation reactions. Water is a solvent of high solvating ability (DN = 33),[25] which can compete strongly with the macrocyclic ligands for the Tl^+ ion. Thus, it is not unexpected that the addition of water to acetonitrile as a relatively low donicity solvent (DN = 14.1)[24] will decrease the extent of interaction between the ligands' donating atoms and the Tl^+ ion.

In addition, the lower dielectric constant of acetonitrile (38.0) compared with that of water (78.5) would also cause the electrostatic contributions to the bond formation to be decreased with an increasing percentage of water in the acetonitrile-water mixtures.

It is interesting to note that, in all cases studied, there is actually a linear relationship between log K_f and the mole fraction of acetonitrile, X_{AN}. In the mixed solvents, the same trend has already been reported for a variety of complexes in different binary mixtures.[26-29] It seems reasonable to assume that the preferential hydration Tl^+ ion is mainly responsible for such a monotonic dependence of the stability constants on the solvent mixture composition.

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