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Synthesis of 4′-Carboxy-benzo-30-crown-10 and a Thermodynamic Study of Its Complexes with Thallium and Alkali Cations in Acetonitrile Solution

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Abstract. A synthetic procedure has been developed for the preparation of 4′-carboxy-benzo-30-crown-10. The formation of Na^+, K^+, Rb^+, Cs^+ and Tl^+ complexes with the large crown ether was investigated conductometrically in acetonitrile solution at various temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data. It was found that the stability of the complexes vary in the order $Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+$. The data obtained in this study support the existence of a 'wrap around' structure for the above complexes in solution. The enthalpy and entropy of complexation reactions were determined from the temperature dependence of the formation constants. In all cases, the complexes were enthalpy stabilized but entropy destabilized. The resulting $T\Delta S°$ vs. $\Delta H°$ plot showed a fairly good linear correlation, indicating the existence of an entropy-enthalpy compensation in the large crown complexation reactions.

Key words: 4′-carboxy-benzo-30-crown-10, thallium and alkali ion complexes, thermodynamic parameters, acetonitrile, conductance.

1. Introduction

Since the first synthesis of macrocyclic crown ethers by Pedersen [1], studies of these ligands and their metal ion complexes have received increasing attention [2, 3]. By variation of ring parameters and structural units such as ring size, number and type of donor atoms and nature of substituents, macrocyclic ligands which can

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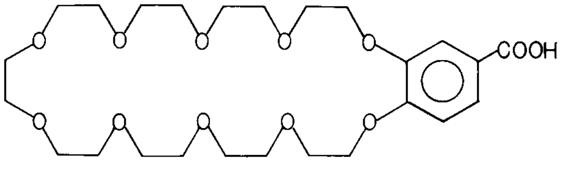
selectively bind cations, anions and even molecular compounds have been prepared [3, 4].

Among crown ethers, larger molecules (i.e. larger than 18-crown-6) are particularly interesting. These free macromolecules possess highly flexible geometries in solution, and thus can adapt their conformations for optimum complexation of guest species [5, 6]. Recently, it has been shown that large crown ethers may have substantial degrees of motional freedom even in the solid state [7, 8]. These large molecules, because of their high degree of flexibility and increased number of donating oxygen atoms in the macrocyclic ring, show two types of behavior. First, the ligand can twist itself around a metal ion of proper size to form a three-dimensional 'wrap around' complex in which all oxygen atoms of the ring are coordinated to the central cation [5, 6, 9–13]. Second, the macrocyclic ring can accommodate two cations if the repulsion forces are not too large, as in the case of Li^+, Na^+ and K^+ complexes with dibenzo-24-crown-8 [14–16] and dibenzo-30-crown-10 [17].

We have been interested in studying the influence of the nature and size of cations and the solvent properties on the interactions of metal ions with large crown ethers, capable of forming three-dimensional complexes with cations [6, 11, 12, 13, 18–22]. In this paper we report the first synthesis of a large crown derivative 4′-carboxy-benzo-30-crown-10 (COOH-B30C10, **I**) and a conductance study of the thermodynamics of its complexes with Na^+, K^+, Rb^+, Cs^+ and Tl^+ ions in acetonitrile solution.



I

Formula **I**.

2. Experimental

2.1. REAGENTS

Reagent grade nitrate salts of sodium, potassium, rubidium, cesium and thallium (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Reagent grade acetonitrile (Merck) was purified and dried by the previously described method [23]. The conductivity of the solvent was less than 1.0×10^{-7} S^{-1} cm^{-1}. 3,4-Dihydroxybenzaldehyde, triethylene glycol, 1,2-bis(2-chloroethoxy)ethane, thionyl chloride, silver oxide (all from Aldrich) were used as received. All other chemicals used were purchased from Merck or Fluka and used as received.

2.2. APPARATUS

The ^{13}C NMR spectra with ^{1}H noise decoupling were recorded on a Varian Gemini XL-200 spectrometer at 50.3 MHz. The ^{1}H NMR spectra were recorded on a Bruker AMX-400 spectrometer. All chemical shifts are reported in ppm downfield from TMS. The mass spectra were recorded on a VG7070E mass spectrometer. The high resolution mass spectra were obtained from a Kratos Concept II H instrument with a resolution of 8000 and ionization of 70 eV which was scanned at 10 s/dec and an ac voltage of 8 kV using perfluorkerocine (PFK) as reference.

Conductivity measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell, made of platinum black, with a cell constant of 0.8310 cm^{-1} was thermostatted at the desired temperature ±0.05 °C using a Phywe immersion thermostat.

2.3. PROCEDURE

In a typical run, 15 mL of a metal nitrate solution (5.0×10^{-5} M) was placed in a water-jacketed cell equipped with a magnetic stirrer and connected to the thermostated circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same metal ion concentration. The conductivity of the initial solution was measured after thermal equilibrium had been reached. Then a known amount of the macrocycle solution was added in a stepwise manner using a calibrated micropipette. The conductivity of the solution was then measured after stirring and thermal equilibrium establishment. Addition of the crown ether was continued until the desired ligand-to-cation mole ratio was achieved.

2.4. SYNTHESIS

2.4.1. *1,26-Dichloro-3,6,9,12,15,18,21,24-octaoxaoctadecane (**4**)*

A 250 mL round bottom two necked flask, equipped with a condenser and a dropping funnel, was charged with triethylene glycol (225 g, 1.5 mol), crushed pellets of sodium hydroxide (12 g, 0.3 mol) and heated to 80 °C while stirring under a nitrogen atmosphere for half an hour until most of the base was dissolved. 1,2-Bis(2-chloroethoxy)ethane (29.6 g, 0.15 mol) was added dropwise to the mixture through a dropping funnel over a period of 2 h keeping the temperature at about 90 °C. The reaction mixture was heated to 90 °C and then refluxed at 120 °C for 1 h and then cooled to room temperature. The water produced and the excess triethylene glycol were removed by evaporation at reduced pressure to obtain a viscous brown residue of nonaethylene glycol.

To the residue of nonaethylene glycol, excess (37.7 mL, 0.5 mol) thionyl chloride was added dropwise over a period of 60 min while cooling the flask in an ice bath under nitrogen. The mixture was stirred at room temperature for an hour and then warmed up and kept at about 70 °C for 5 h. The absence of any starting nonaethylene glycol was checked using ^{13}C NMR by following the known peak at about 60 ppm as an indication of the CH_2OH group. The excess thionyl chloride was removed at reduced pressure, the residue was cooled and poured into ice (50 g) and then washed with CH_2Cl_2(3 × 100 mL). The combined extracts were washed with saturated $NaHCO_3$ (3 × 20 mL), saturated NaCl (30 mL), water (2 × 30 mL) and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation at reduced pressure and fractional distillation was applied on the viscous crude product. The fraction boiling at 220–226 °C at 0.4 mm Hg was collected as pure product.

^{1}H NMR($CDCl_3$), δ_H(ppm): 3.75 (m), 3.60–3.70 (m).

^{13}C NMR($CDCl_3$), δ_c(ppm): 70.98, 70.22, 42.42. CIMS (m/z): M + 1 at 451 (85%), other peaks at 195 (22%) and 149 (100%).

2.4.2. *4′-Formylbenzo-30-crown-10 (***5***)*

3,4-Dihydroxy benzaldehyde (4.14 g, 0.03 mol) was dissolved with stirring in anhydrous acetonitrile (1500 mL) in a 2000 mL round bottom 2-necked flask, equipped with a condensor under a nitrogen atmosphere. K_2CO_3 (12.4 g, 0.09 mol), Cs_2CO_3 (0.1 g), and 1,26-dichloro-3,6,12,15,18, 21,24-octanonadodecane (14 g, 0.03 mol) dissolved in 100 mL acetonitrile were added to the flask and the reaction mixture was refluxed for 3 days. Upon cooling, the mixture was filtered, the solvent was removed by rotary evaporation and finally the crude product was purified by column chromatography on silica gel (grade 60, 230–400 mesh). Elution with ethyl acetate yielded 8.2 g (53% from starting aldehyde) of light yellow oily 4′-formylbenzo-30-crown-10.

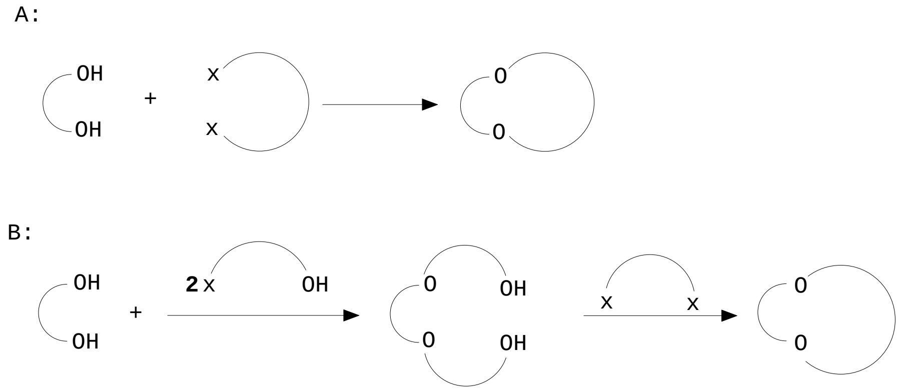
^{13}C NMR ($CDCl_3$), δ_C (ppm): 191.37 (CHO), 154.84, 149.66, 130.64, 127.22, 112.70, 111.96 (aromatic carbons); 71.50, 71.44, 71.26, 71.12, 70.12, 70.69, 69.97, 69.83, (O-CH_2-CH_2-O).

^{1}H NMR ($CDCl_3$), δ_H (ppm): 9.93 (s, 1H, CHO), 7.43 (d of d, J = 8.4 and 1.4 Hz, 1H), 7.41 (d, J = 1.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H) (aromatic protons); 4.22 (m, 4H), 3.93 (m, 4H), 3.78 (m, 4H), 3.60 (m, 4H), 3.55–3.50 (m, 20 H) (O-CH_2-CH_2-O).

CIMS (m/z): M + 1 at 517 (90%), other peaks at 243 (15%), 309 (45%), and 149 (100%).

2.4.3. *4′-Carboxybenzo-30-crown-10 (***6***)*

Ag_2O (7.4 g, 0.03 mol) was dissolved in 100 mL NH_4OH (1.1 m) in a 500 mL Erlenmeyer flask covered by aluminum foil and stirred for 5 min. To this solution, 4′-formylbenzo-30-crown-10 ether (7.4 g, 0.032 mol) dissolved in absolute ethanol (100 mL) was dropwise added. After a short period of time, the mirror started to form. The mixture was stirred for 10 h at room temperature, then filtered and washed with CH_2Cl_2 (4 × 50 mL). Evaporation of the solvent from the organic



Scheme 1.

phase gave 3 g of mostly unreacted aldehyde. The aqueous phase was then acidified to pH = 2 and washed with CH_2Cl_2 (4 × 50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation. The solid residue was kept under vacuum to yield 4.2 g (50%) of 4′-carboxybenzo-30-crown-10 ether, mp 30-32 °C.

^{13}C NMR ($CDCl_3$), δ_c (ppm): 170.72 (COOH), 153.55, 148.36, 124.75, 122.27, 115.13, 112.46, (aromatic carbons); 71.07, 71.01, 70.73, 70.63, 70.63, 70.58, 69.68, 69.53, 69.14, 68.89 (O-CH_2-CH_2-O).

^{1}H NMR ($CDCl_3$) (400 MHz), δ_H (ppm): 11.2 (broad s, 1H, COOH), 7.86 (d of d, J = 8.5 and 1.9 Hz, 1H), 7.60 (d, J = 1.9 Hz, 1H), 6.92 (d, J = 8.5 Hz, 1H); 4.18 (m, 4H), 3.89 (m, 4H), 3.75 (m, 4H), 3.62 (m, 4H), 3.59 − 3.52 (m, 20 H), 3.68 (broad s, 4H) (O-CH_2-CH_2-O).

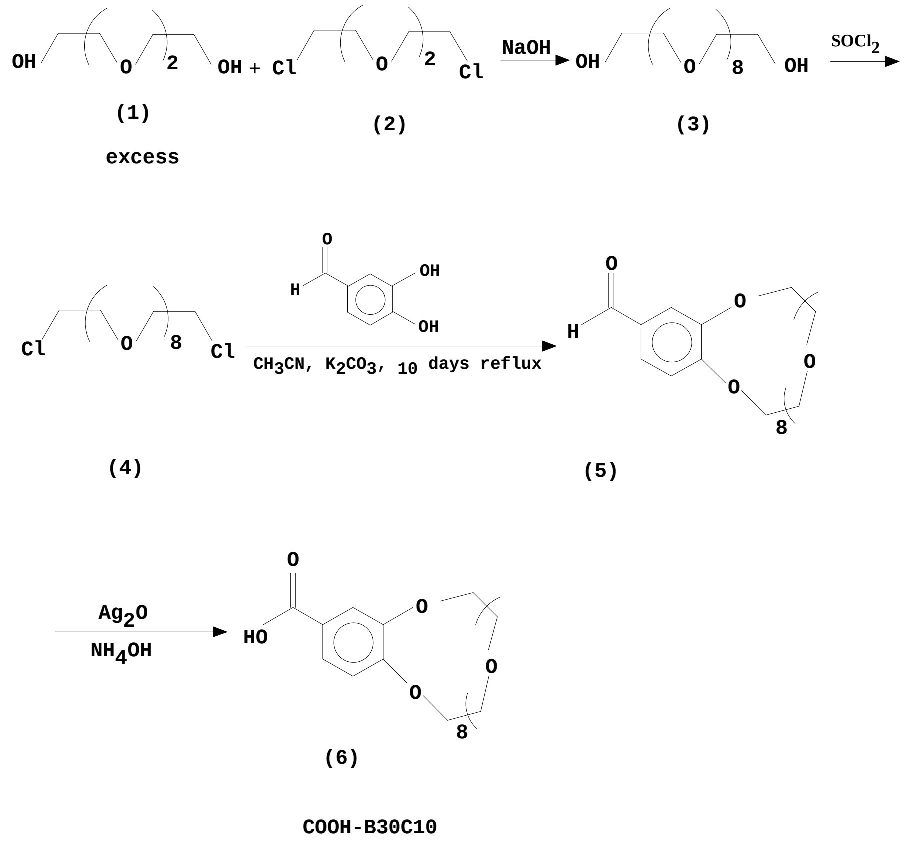
CIMS (m/z): M + 1 at 533 (8%), other peaks at 515 (100%), 471 (12%), 427 (14%), and 180 (18%).

3. Results and Discussion

3.1. SYNTHESIS AND CHARACTERIZATION OF COOH-B30C10

A few synthetic routes have been developed to prepare large crown ether rings, two of which are shown in Scheme 1. In route A, the whole ring is built up in one step, while in route B, part of a large ring is made first followed by the cyclization step. The synthesis route employed for the target large size crown COOH-B30C10 is shown in Scheme 2. The one step cyclization was used because of the fewer number of synthesis steps as well as the convenient synthesis method of the key cyclization step component, the dichloride **4**.

In order to synthesize the key dichloride component **4**, 1,2-bis (2-chloroethoxy)ethane was treated with triethylene glycol in the presence of sodium hydroxide. An excess amount of triethylene glycol was used to minimize the possible polymerization process between the two bifunctional group reagents. The



Scheme 2.

resulting nonaethylene glycol was then treated with thionyl chloride, as recently reported for the synthesis of heptaethylene glycol [24] to obtain **4**.

The cyclization step was carried out under dilute condition in acetonitrile as solvent using a mild base, potassium carbonate, in the presence of a catalytic amount of cesium carbonate. We have successfully applied such experimental conditions in the cyclization step of the synthesis of some B24C8 derivatives [8, 24]. However, the cyclization step was almost completed within 10 days to obtain the crown ether **5** in 53% yield, which is a relatively high yield for the synthesis of such a large ring size crown ether. Since it is well known that the chemical shift of carbons attached to chlorine in -CH_2CH_2Cl fragments is detectable at about 42 ppm [8, 24], the cyclization reaction was monitored by ^{13}C NMR which shows the disappearance of the signal corresponding to the terminal carbon of dichloride **4** at the expense of the production of **5**.

Tollen's reagent (Ag_2O + NH_4OH) [25] was chosen as oxidant to prevent any possible ether bond breakage during the oxidation process. The crown ether **6** was easily separated from unreacted starting aldehyde by simple acid-base chemistry at pH = 2. The melting point of the COOH-B30C10 product (**6**) (30–32 °C) was significantly increased in comparison with crown ether **5**, which is liquid at room temperature.

There is a good agreement between the ^{1}H and ^{13}C NMR spectra of the previously reported crown ether COOH-B24C8 [8, 22] with those obtained for COOH-B30C10. The aromatic region of COOH-B30C10 shows six distinct peaks in the ^{13}C NMR while its ^{1}H spectrum appears as an AMX spectrum with J values of 8.5 and 1.9 Hz. In the aliphatic region, the pattern of four protons in each O-CH_2-CH_2-O network represents an AA′BB′ spin system. The number of ^{1}H multiplets that can be resolved is four and the rest of the aliphatic protons result in the most shielded multiplet signal.

The molecular ion peak at m/z = 533 in the CIMS spectrum of the final product also suggested the formation of the desired crown ether. The presence of the base peak at m/z = 515 can be simply explained by considering the fact that the molecular ion can lose a water molecule.

3.2. CONDUCTANCE STUDIES

In order to evaluate the effect of adding COOH-B30C10 on the molar conductance of the metal ions used in acetonitrile solution, the conductivity at a constant salt concentration (5.0×10^{-5} M) was monitored while increasing the macrocycle concentration at various temperatures. The resulting molar conductance vs. COOH-B30C10/M^+ mole ratio plots at different temperatures are shown in Figure 1 and the influence of temperature on the conductance mole ratio plot of the COOH-B30C10-Cs^+ system is illustrated in Figure 2. It is immediately obvious that, in all cases studied, every mole ratio plot shows a rather large and continuous decrease in the molar conductance with an increase in the crown ether concentration. This behavior indicates that the complexed metal ions are less mobile than the corresponding solvated M^+ ions.

As seen from Figures 1 and 2, in most cases, and especially at lower temperatures, addition of the large crown ether to metal ion solution causes a continuous linear decrease in the molar conductance which begins to level off at mole ratios of greater than one, indicating the formation of a relatively stable 1 : 1 complex. However, in some cases such as Na^+ and Cs^+ ions, and at higher temperatures, although the molar conductance does not show any tendency for leveling off even at a mole ratio of about 3, the corresponding mole ratio plots show a considerable change in their slopes at a mole ratio of about one, emphasizing the formation of some weaker 1 : 1 complexes in solution.

The 1 : 1 binding of different M^+ ions used with COOH-B30C10, L, can be expressed by the following equilibrium

$$M^+ + L \overset{K_f}{=} ML^+. \tag{1}$$

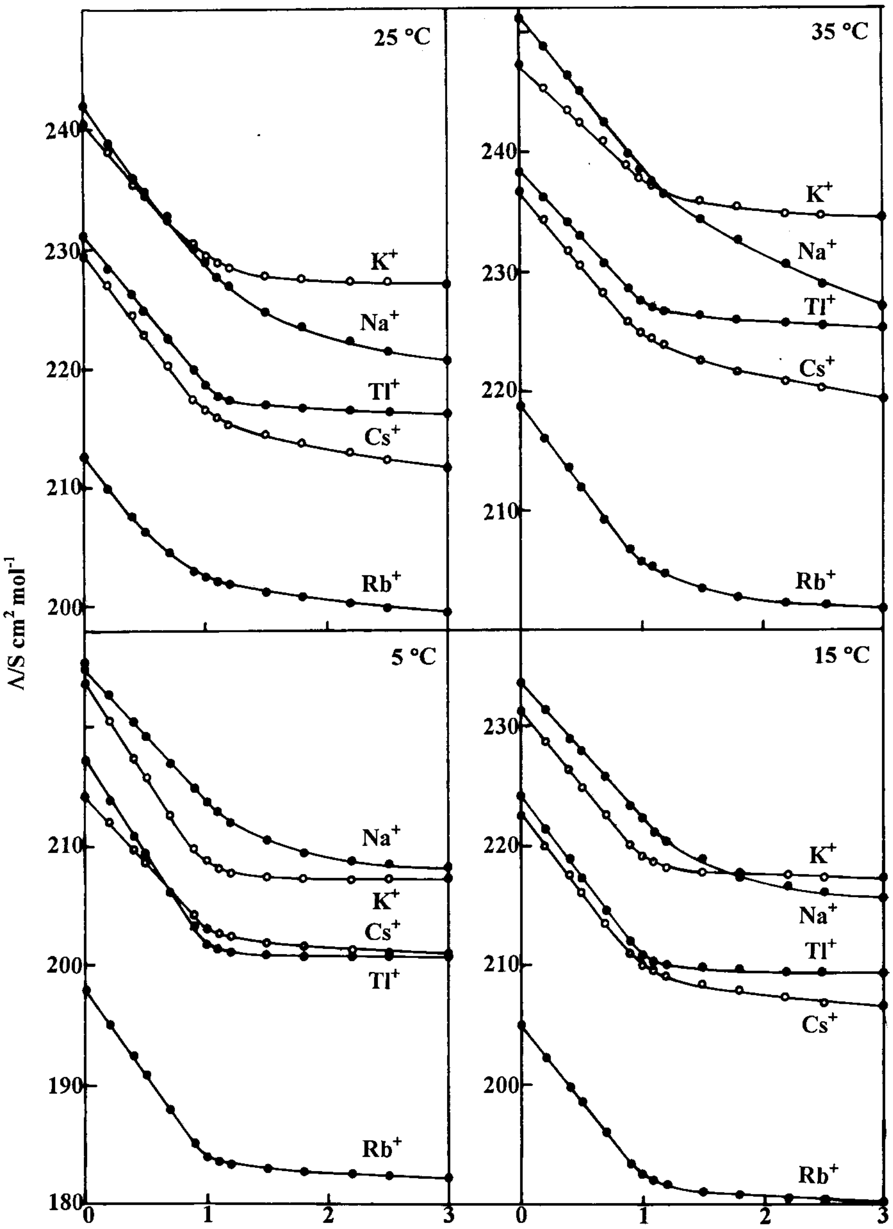


Figure 1. Molar conductance vs. mole ratio plots for different COOH-B30C10-M$^+$ systems in acetonitrile solution at various temperatures.

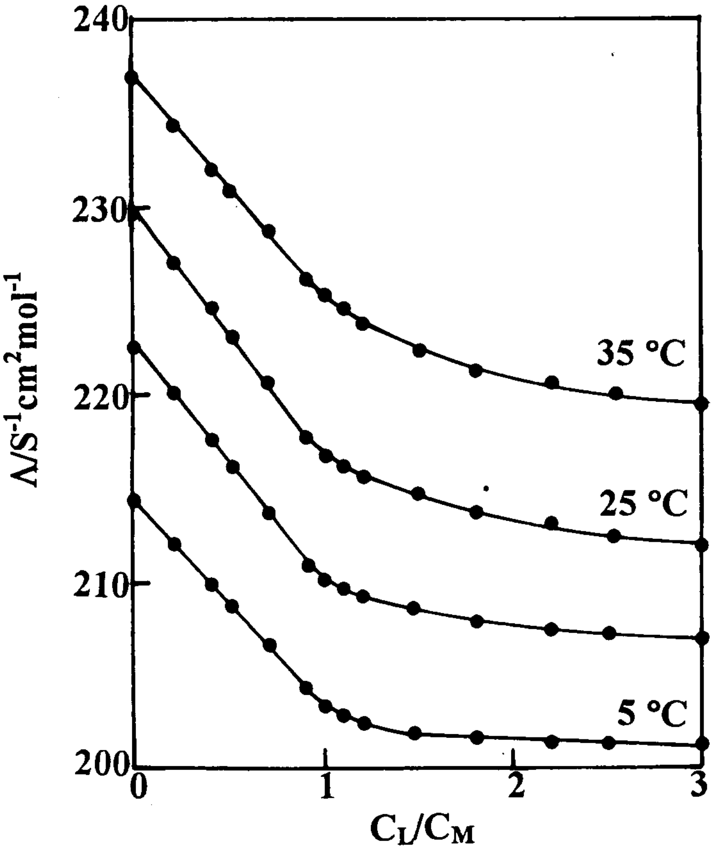


Figure 2. Molar conductance vs. mole ratio plots for the COOH-B30C10-Cs^+ system in acetonitrile solution at various temperatures.

The corresponding equilibrium constant, K_f, is given by

$$K_f = \frac{[[ML^+]}{[ML^+][L]} \times \frac{f(ML^+)}{f(M^+)f(L)} \tag{2}$$

where $[ML^+]$, $[M^+]$, $[L]$ and f represent the equilibrium molar concentrations of complex, free cation, free ligand and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, the activity coefficient of uncharged ligand, f(L), can be reasonably assumed as unity [22, 26–28]. The use of the Debye-Hückel limiting law for 1 : 1 electrolytes [24] leads to the conclusion that $f(M^+) \sim f(ML^+)$, so that the activity coefficients in Equation (2) cancel.

Thus, the complex formation constant in terms of the molar conductances, Λ, can be expressed as [30, 31]

$$K_f = \frac{[ML^+]}{[M^+][L]} = \frac{(\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]}. \tag{3}$$

Here, Λ_M is the molar conductance of the metal nitrate before addition of ligand, Λ_{ML} the molar conductance of the complexed ion and Λ_{obs} the molar conductance of the solution during titration. Rearrangement of Equation (3) results in

$$\Lambda_{obs} = \frac{\Lambda_M + K_f\Lambda_{ML}[L]}{1 + K_f[L]}. \tag{4}$$

The mass balance equations are given as

$$C_M = [M^+] + [ML^+] \tag{5}$$

$$C_L = [L] + [ML^+] \tag{6}$$

where C_M and C_L are the analytical concentrations of the metal ion and the ligand, respectively. Substitution of Equations (5) and (6) into Equation (2) and rearrangement yields

$$K_f[L]^2 + (1 + K_f(C_M - C_L))[L] - C_L = 0. \tag{7}$$

For evaluation of the formation constants from the molar conductance vs. C_L/C_M mol ratio data, a non-linear least-squares curve fitting program KINFIT was used [32] The program is based on the iterative adjustment of calculated values of Λ to observed values by using either the Wentworth matrix technique [33] or the Powell procedure [34] Adjustable parameters are the formation constant, K_f, and the molar conductance of the complexed ion, Λ_{ML}. The free ligand concentration was calculated from Equation (7) by means of a Newton-Raphson procedure. Once the value of [L] had been obtained, the Λ value was calculated from Equation (4) using the estimated values of the K_f and Λ_{ML} of the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values of Λ for all experimental points was minimized. The output of the program KINFIT comprises refined parameters, the sum-of-squares and the standard deviation of data.

A sample computer fit of the molar conductance vs. crown/metal mole ratio data is shown in Figure 3. The assumed 1 : 1 stoichiometry for the resulting complexes was further supported by the fair agreement between the observed and calculated molar conductances. It should be noted that, in acetonitrile as a solvent of intermediate donor number (DN = 14.1) and dielectric constant (ϵ = 38.0) [35], it was assumed that the association to ion pairs is negligible under the highly dilute experimental conditions used [36]. The macrocycle concentration in solution was also sufficiently low ($<1.4 \times 10^{-4}$ M) to avoid corrections for viscosity changes [13, 28]. All calculated formation constants are summarized in Table I. The available formation constants for the corresponding complexes with dibenzo-30-crown-10 (DB30C10) in acetonitrile solution [13] are also included for comparison.

In order to achieve a better understanding of the thermodynamic behavior of complex formation between COOH-B30C10 and alkali ions in acetonitrile, it is

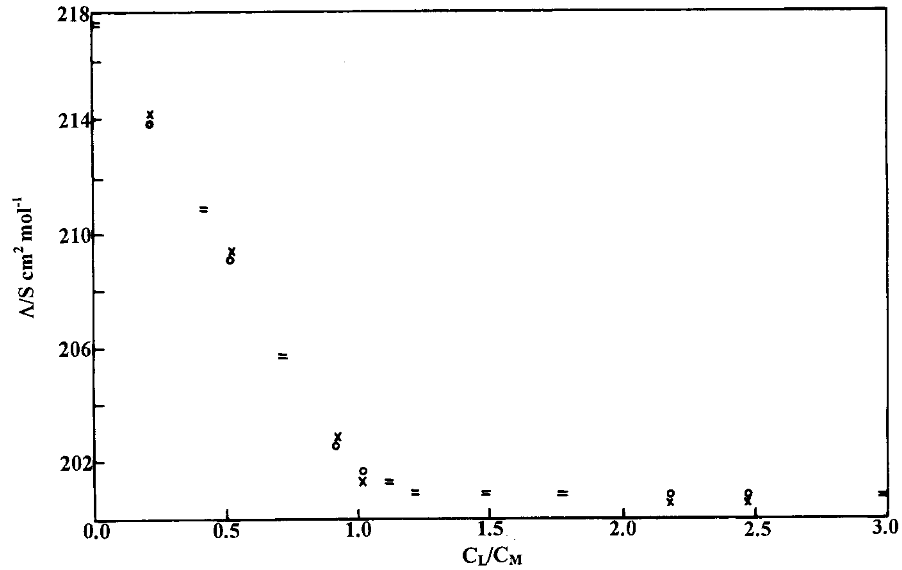


Figure 3. Computer fit of molar conductance-mole ratio data for COOH-B30C10-Tl^+ in acetonitrile at 5 °C: (×) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

Table I. Formation constants of different COOH-B30C10-M^+ complexes in acetonitrile solution

Ligand	Temperature (°C)	log K_f				
		Na^+(1.02)[a]	K^+ (1.38)	Rb^+ (1.52)	Cs^+ (1.67)	Tl^+ (1.50)
COOH-B30C10	5	4.42 ± 0.03	6.11 ± 0.11	5.79 ± 0.11	5.16 ± 0.08	6.34 ± 0.12
	15	4.25 ± 0.06	5.66 ± 0.08	5.38 ± 0.06	4.90 ± 0.07	5.90 ± 0.06
	25	4.01 ± 0.06	5.31 ± 0.03	5.06 ± 0.06	4.63 ± 0.06	5.52 ± 0.12
	35	3.82 ± 0.03	4.96 ± 0.05	4.78 ± 0.06	4.39 ± 0.04	5.06 ± 0.06
DB30C10[b]	25	3.14	4.63	4.76	3.81	5.15

[a] Ionic radius in Å, ref. 2.
[b] Ref. 13.

useful to consider the enthalpic and entropic contributions to these reactions. The influence of temperature on K_f values, as deduced from Figures 1 and 2 and Table I, is that the stability of the complexes decreases as the temperature is increased. Such a temperature dependence indicates that the complexation of these cations with COOH-B30C10 is an exothermic process. The thermodynamic quantities ΔH° and ΔS° were evaluated from the corresponding log K_f-temperature data by applying a linear least-squares analysis according to the Van't Hoff equation

$$2.303 \log \mathrm{K_f} = -\frac{\Delta H^\circ}{\mathrm{RT}} + \frac{\Delta S^\circ}{R}. \tag{8}$$

Table II. Enthalpy and entropy values for different COOH-B30C10-M^+ complexes in acetonitrile solution

Cation	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (J mol^{-1} K^{-1})
Na^+	33.4 ± 0.9	35 ± 3
K^+	67.2 ± 0.7	125 ± 2
Rb^+	55.0 ± 0.7	87 ± 2
Cs^+	42.3 ± 0.2	53 ± 1
Tl^+	70.6 ± 0.8	132 ± 2

Plots of log K_f vs. 1/T for all complexes studied were linear (Figure 4). The ΔH° and ΔS° values were determined in the usual manner from the slopes and intercepts of the plots, respectively, and the results are summarized in Table II. As readily seen from Table I, in the case of each cation, COOH-B30C10 forms a more stable complex than does DB30C10. This is likely due to the introduction of an extra electron withdrawing benzo group in the DB30C10 molecule which reduces both the donicity of its donating oxygens atoms and its flexibility in solution. However, the role and effects of the carboxyl group introduced on cation binding cannot be neglected. The existence of a carboxyl group, as an electrophilic substituent, on the 4′-position of the benzo ring may influence the stability of the resulting COOH-B30C10-M^+ complexes, not only via the electronic effects but also via the acid-base interactions.

From the data given in Table I, it is seen that the stability of COOH-B30C10 complexes in acetonitrile solution vary in the order $Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+$. For large crown ethers such as DB30C10 and COOHB30C10, which are capable of forming three-dimensional ‘wrap around’ complexes with metal ions [5, 6, 9–13], the size of the cation is expected to influence strongly the extent of the complexation reaction. According to the observed stability order, as well as the previous reports [6, 9, 13], metal ions with ionic radii of about 1.4 to 1.5 Å (i.e. K^+, Rb^+ and Tl^+ ions) seem to have the most convenient size to fit properly inside the cavity formed by twisting of the large crown, with all ten ether oxygens of the ring participating in the bond formation with the central cation [9, 10] In the case of larger cations such as the Cs^+ ion, the complete three-dimensional structure cannot be formed and only some of the donating oxygen atoms of the ring can bind to the cation; consequently a weaker complex results. On the other hand, if the ring size is much larger than the cation, as in the case of the Na^+ ion, the large crown ether can still form the ‘wrap around’ structure, but in this case the oxygen atoms of the ligand will have to be in close proximity and the resulting repulsive force will weaken the complex. However, the thermodynamic stability constant is not just a measure of absolute binding strength, as determined by the proper fitting of the cation inside the twisted large crown structure, but a measure of the

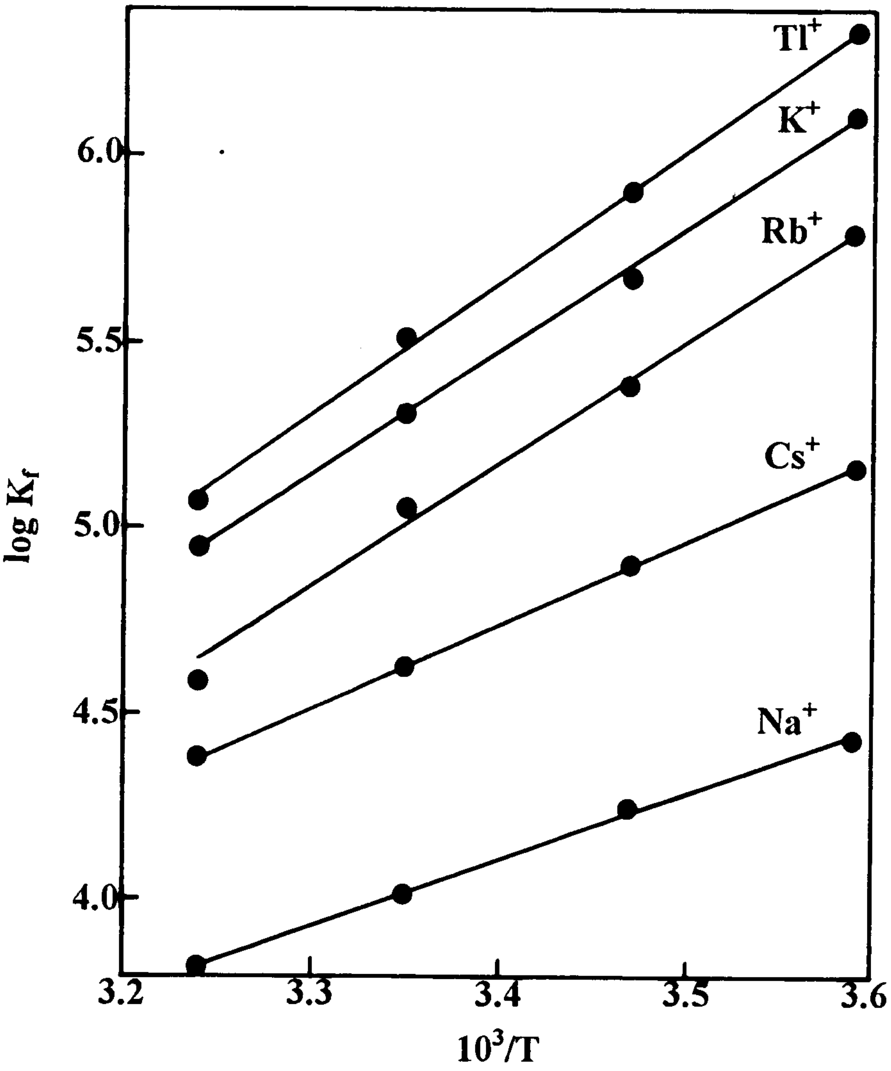


Figure 4. log K vs. 1/T plots for the 1 : 1 complexation of Na^+, K^+, Rb^+, Cs^+ and Tl^+ with COOH-B30C10 in acetonitrile solution.

relative strength as compared to the ionic solvation as well as the ligand-solvent interactions [4, 37]. Thus, the maximum stability for a given metal ion complex results from a balance between the binding and solvation energies.

Although the Tl^+ ion has an ionic radius very close to that of the Rb^+ ion (see Table I), the stability of its COOH-B30C10 complex is exceptionally higher than that of the COOH-B30C10-Rb^+ complex. This is most probably because Tl^+ ion is bound in the complexes by an ion-dipole interaction with a covalent contribution [38].

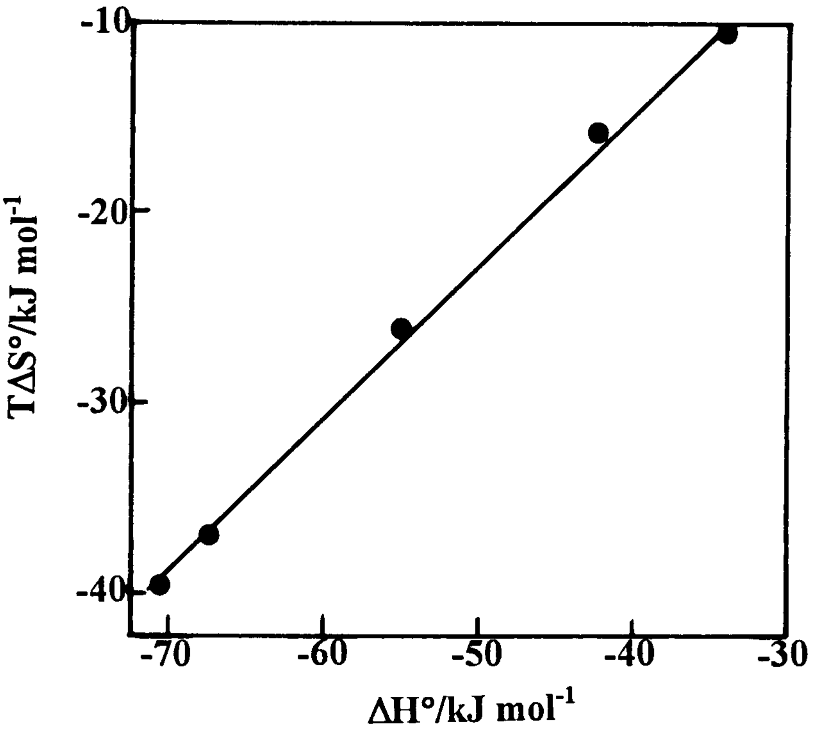


Figure 5. Plot of TΔS° vs. ΔH° for 1 : 1 complexation of Na^+, K^+, Rb^+, Cs^+ and Tl^+ with COOH-B30C10 in acetonitrile solution.

The thermodynamic data given in Table II show that, in all cases, the complexes are enthalpy stabilized but entropy destabilized. It should be noted that similar behavior was previously observed for most of the macrocyclic complexes studied in nonaqueous solvents [1, 2, 6, 12, 21, 26, 27]. It has been reasonably assumed that the decrease in entropy upon complexation is related to a change in the conformational entropy of the macrocyclic ligands, from a rather flexible structure in the free state to a rigid three-dimensional conformation in the complexed form [6, 12, 21]. The degree of macrocyclic flexibility in the free state would vary with its size as well as the macrocycle-solvent interaction [4, 37].

It is interesting to note that the ΔH° values obtained in this study emphasize the complex stability sequence $Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+$, which is in accord with the stability order obtained from values of log K_f at 25 °C. However, the trend observed in ΔS° values is opposite to that obtained from the stability constant data. Although the COOH-B30C10-Tl^+ and COOH-B30C10-K^+ complexes are entropically the most destabilized complexes in the series, their exceptionally large negative ΔH° values compensate for this destabilization to make them the most stable complexes in the series.

It is noteworthy that there is a fairly linear relationship between the $T\Delta S^\circ$ and ΔH° values obtained for alkali and thallium ion complexes with COOH-B30C10 in acetonitrile solution (Figure 5). The regression equation for the $T\Delta S^\circ$ vs. ΔH° plot is in the form

$$T\Delta S^\circ = T\Delta S^\circ_0 + \alpha\Delta H \qquad (9)$$

with $T\Delta S^\circ_0$ = 17.1 kJ mol^{-1}, α = 0.80 and the regression coefficient r = 0.998. Such a linear relationship between $T\Delta S^\circ$ and ΔH° has already been reported for the complexation of metal ions with various types of ligands in different solvent systems [39-41]. It is interesting to note that the $T\Delta S^\circ_0$ and α values reported from the $T\Delta S^\circ$-ΔH° plot constructed based on 207 data points for 1 : 1 complexation of mono-, di- and tri-valent cations with crown ethers of different cavity sizes are 10.0 kJ mol^{-1} and 0.76, respectively [39]. Equation (9) suggests that the entropic change consists of two components. The first component is independent of the enthalpy change ($T\Delta S^\circ_0$) and the second one is proportional to it ($\alpha\Delta H^\circ$). The proportionality factor, α, might be considered as a quantitative measure of the enthalpy-entropy compensation. The α value of 0.80 indicates that only 20% of the increase in ΔH° contributes to the increase in the complex stability.

The positive $T\Delta S^\circ_0$ value of 17.1 kJ mol^{-1} (the intrinsic entropic gain) emphasizes that the complex formation is favored even in the absence of any enthalpic gain (i.e. ΔH° = 0). This intrinsic entropic gain indicates the fundamental role of the solvent properties in the process of complex formation. Since, during the ‘wrap around’ complexation of a M^+ ion by a COOH-B30C10 molecule, most of the coordinated solvent molecules are replaced by the donating oxygen atoms of the macrocyclic ligand, even when the cation-macrocycle binding is weak, the increased degree of freedom due to the desolvation of the cation may result in some positive entropic gain. In other words, the $T\Delta S^\circ_0$ value indicates to what extent the solvation shell is replaced by the macrocycle’s donating groups. However some contributions from the COOH-B30C10-M^+ solvation as well as some possible interaction between solvent molecules and the free macrocycle [4] to the observed entropy changes cannot be neglected.

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