Electrochemical Studies on Alkali-metal Complexes with the Small Macrocycle 1,4,7,10-Tetraoxacyclododecane. Polarographic and Potentiometric Determination of the Stability Constants in Propylene Carbonate

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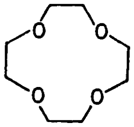
The electrochemical reduction of anhydrous alkali-metal perchlorates and of their complexes with 1,4,7,10-tetraoxacyclododecane (12-crown-4) has been investigated in propylene carbonate by normal polarography and potentiometry using a dilute amalgam pool electrode. Stability constants and stoicheiometries derived from partially irreversible polarographic waves corrected according to Gellings have been compared with potentiometric data. The ligand 12-crown-4 exhibits a high selectivity for Na^+ which forms 1 : 2 complexes (log $\beta_1 = 3.5 \pm 0.2$, log $\beta_2 = 6.31 \pm 0.04$). The stability constants of the 1 : 1 adducts with Li^+ (log $\beta_1 = 2.93 \pm 0.05$), K^+ (2.15 ± 0.05), Rb^+ (1.69 ± 0.04), and Cs^+ (1.43 ± 0.05) decrease with increasing ionic radius of the encapsulated ion.

THERE has recently been much interest in the study of the complexation of alkali-metal ions by macrocycles such as crown ethers or cryptands. A review[1] summarizes the present status of knowledge in this field and indicates that the complexation by a macrocycle depends essentially on the size and the rigidity of its internal cavity and on the electronegativity of its donor atoms. A highly selective complexation of the alkali-metal ions is thus possible with macrocycles of suitable size.

Polarographic[2-4] and calorimetric[5] investigations of the co-ordination properties of crown ethers have been restricted to macrocycles which are either larger or of the same size as the encapsulated ions. The primary aim of the present work was to determine the stability of complexes formed between the alkali-metal ions and a small twelve-membered macrocycle, 1,4,7,10-tetraoxacyclododecane also called 12-crown-4 (radius of the internal cavity, 0.57 Å).[6] To this end, the electrochemical behaviour of the adducts was investigated in propylene carbonate by polarography with a dropping mercury electrode (d.m.e.) and by potentiometry using dilute metal-amalgam pool electrodes (a.p.e.s).



The macrocycle 12-crown-4 is too small to accommodate any alkali-metal ion in its internal cavity. Nevertheless, this ligand can complex such ions, forming sandwich-type 1 : 2 adducts with sodium chloride and sodium hydroxide.[6] Complexes of 1 : 1 stoicheiometry with several lithium salts have also been obtained and their conformational behaviour in solution has been investigated.[7]

EXPERIMENTAL

All solutions and reagents were handled and stored in an inert dry atmosphere in a glove-box (less than 20 p.p.m. of water as monitored with a dewpoint meter). The macrocycle 12-crown-4 was synthesized according to Liotta and co-workers[8] and purified by distillation. Twice-recrystallized tetraethylammonium perchlorate (Fluka) was used as supporting electrolyte and was dried by heating overnight at 80 °C under vacuum. Alkali-metal perchlorates, except $Na[ClO_4]$ and $Li[ClO_4]$ (Fluka), were obtained by double decomposition of the chlorides (Merck) with perchloric acid and they were dried just before use at 80 °C under vacuum. Propylene carbonate (Merck) was purified according to Denat *et al.*[9] Final dehydration was achieved in the dry-box by elution through a column packed with 3 Å molecular sieves. The water content of the polarographic solution (Karl Fisher titration) was always less than 10 p.p.m. at the beginning, and never exceeded 40 p.p.m. at the end, of each series of measurements.

All polarographic experiments were carried out in propylene carbonate at 25 ± 0.1 °C and the data were collected with a PAR 170 polarograph equipped with a three-electrode cell. The drop time was fixed at 1 s. The reference cell was separated from the polarographic cell by a sintered glass diaphragm. The half-cell $Ag/Ag[ClO_4]$ (0.01 mol dm^{-3}) in propylene carbonate was used as a reference electrode, for it was shown to give stable and reproducible potentials.[10] In order to allow reliable comparisons with potentials measured in other non-aqueous media, all potentials were calculated using the reversible half-wave potential of the couple ferrocene–ferrocinium ion, $[Fe(C_5H_5)_2]$–$[Fe(C_5H_5)_2]^+$, in propylene carbonate as an internal reference.[11] It was verified that 12-crown-4 did not not influence the polarographic behaviour of the ferrocene–ferrocinium couple which, in any case, was added to the cell at the end of each series of measurements.

Potentiometric measurements were carried out at 25 ± 0.1 °C with a Fluke 8800A digital multimeter (input impedance 10^6 MΩ). Sodium and lithium-amalgam pool electrodes (a.p.e.s) were prepared just before use in the polarographic cell described above. Thus, solutions of $Li[ClO_4]$ or $Na[ClO_4]$ in propylene carbonate were reduced electrochemically with a mercury cathode and a platinum anode, the latter being separated from the measurement cell by sintered glass. The potential of the a.p.e. was then measured against a $Ag/Ag[ClO_4]$ (0.01 mol dm^{-3}) reference electrode after each addition of 12-crown-4. On standing, the potential drift of the working electrode was found to be negligible within the time required for the measurements, provided that the water content of the solvents was sufficiently low (<40 p.p.m.). Furthermore, a Nernstian

TABLE 1

Some polarographic parameters illustrative of the behaviour of the alkali-metal complexes with 12-crown-4 in propylene carbonate

Electrode reaction	10^3[M$^+$]	10^2[crown]	Slope [a]	$E_{\frac{1}{2}}$/V	
	mol dm^{-3}		mV	exptl.[b]	Gellings [c]
$Na^+ \longrightarrow Na$	0.88	0.00	61	2.607	
		0.33	70	2.681	2.668
		3.22	→140	2.866	2.788
$K^+ \longrightarrow K$	0.66	0.00	59	2.722	
		1.43	62	2.752	2.750
		3.99	63	2.776	2.771
$Rb^+ \longrightarrow Rb$	2.40	0.00	60	2.747	
		1.18	60	2.755	
		8.29	65	2.796	2.788
$Cs^+ \longrightarrow Cs$	3.84	0.00	59	2.772	
		1.50	60	2.779	
		9.54	62	2.805	2.802

[a] Slope = $\partial E/\partial \log [(i_d - i)/i]$. [b] Experimental half-wave potential *vs.* the ferrocene–ferrocinium couple. [c] Reversible half-wave potential calculated when necessary (slope $>$62 mV) by Gellings' method.[14]

behaviour of the a.p.e. was recorded for a large concentration range of Na or Li. No attempt was made to determine accurately either the metal content of the amalgam or the liquid-junction potential between the reference electrode half-cell and the solution, both of which were kept constant for each series of measurements.

RESULTS

In pure propylene carbonate, the reduction of potassium, rubidium, and caesium is reversible while sodium and lithium exhibit a quasi-reversible behaviour (Table 1). The half-wave potentials and the slopes $\partial E/\partial \log [(i_d - i)/i]$ are in good agreement with the results of Matsuura *et al.*[12] All reduction waves are well defined and controlled by diffusion: plots of i_d *versus* concentration of metal ion and of i_d *versus* $h^{\frac{1}{2}}t^{\frac{1}{6}}$ are straight lines with zero intercept (h is the height of the mercury column after correction for back pressure).

The macrocycle 12-crown-4 shows no reduction wave within the available potential range but an oxidation wave is recorded in the anodic region. This wave forms the new anodic limit of potential which is more negative than the limit measured in pure propylene carbonate. It is governed by diffusion and its height is proportional to the macrocycle concentration. Therefore it is assigned to the complexation by the macrocycle of the ions produced by electro-oxidation of the mercury electrode. A similar oxidation wave was recently reported for a diaza-cryptate in the same solvent.[13]

The addition of 12-crown-4 modifies the reduction of the alkali-metal ions in propylene carbonate. The polarographic waves remain well defined and controlled by diffusion but they are shifted towards more negative potentials, indicating a complexation by the macrocycle. Moreover the presence of an excess of ligand gradually increases the irreversibility of the electron transfer at the d.m.e. For the purposes of illustration, some features of the polarographic waves are summarized in Table 1. When necessary, the reversible half-wave potentials were assessed by Gellings' method.[14] As can be seen from Table 1, the corrections for partial irreversibility are particularly important in the case of sodium. The stability constants and the stoicheiometries of the complexes with 12-crown-4 were derived from the amplitude of the polarographic shifts by DeFord and Hume's treatment.[15] Plots of F_i(L) as a function of the concentration of free ligand are in Figure 1.

The polarographic wave of the lithium adduct with 12-crown-4 did not lend itself easily to an analysis by both Gellings'[14] or Hale and Parsons'[16] methods. Either unreliable extrapolations or (and) inappropriate kinetic parameters for application of such treatments precluded the interpretation of the data. Consequently, the formation of the lithium adduct was investigated by potentiometry as described above. Moreover, the same technique was used for an analysis of the complexation of sodium by 12-crown-4 in order to assess the reliability of the Gellings' corrections [14]

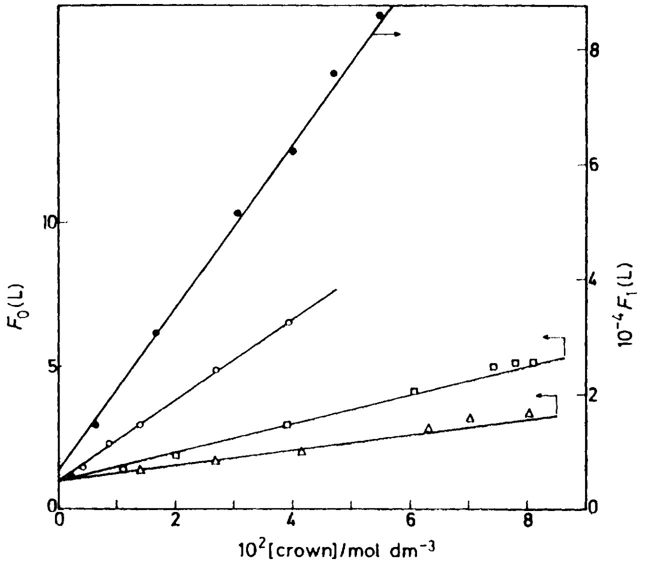


FIGURE 1 Analysis by DeFord and Hume's method [15] of the polarographic waves exhibited by the alkali-metal ion adducts with 12-crown-4. The functions F_0(L) and F_1(L) are plotted *vs.* the concentration of free ligand as computed by successive iterations:

$$F_0(\mathrm{L}) = \exp(nF/RT)[(E_{\frac{1}{2}}) - (E_{\frac{1}{2}})_c + (RT/2nF)\ln(D/D_c)] = 1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2; \;\; F_1(\mathrm{L}) = [F_0(\mathrm{L}) - 1]/[\mathrm{L}] = \beta_1 + \beta_2[\mathrm{L}]$$

Here [L] denotes the concentration of free crown and $(E_{\frac{1}{2}})$ and $(E_{\frac{1}{2}})_c$ are the half-wave potentials in the absence and in the presence of the complexing reagent. M = Na (●), K (O), Rb (□), or Cs (Δ)

TABLE 2

Cumulative stability constants of the alkali-metal complexes of 12-crown-4 in propylene carbonate

M^+	r^a/Å	log β_i	i
Li	0.68	2.93 ± 0.05 [b]	1
Na	0.97	3.6 ± 0.7 [c]	1
		6.17 ± 0.05 [c]	2
		3.5 ± 0.2 [b]	1
		6.31 ± 0.04 [b]	2
K	1.33	2.15 ± 0.05 [c]	1
Rb	1.47	1.69 ± 0.04 [c]	1
Cs	1.67	1.43 ± 0.05 [c]	1

[a] Ionic radius. [b] Determinated by potentiometry. [c] Determinated by polarography.

(Figure 2). On examining the results presented in Table 2 it can be seen that very good agreement is achieved between the stability constants obtained by potentiometry and those obtained by polarography after correction for the partial irreversibility of the electrode reaction. No potentiometric investigations were performed for K^+, Rb^+, and Cs^+ on account of the nearly reversible polarographic behaviour exhibited by these ions at the d.m.e. under our experimental conditions.

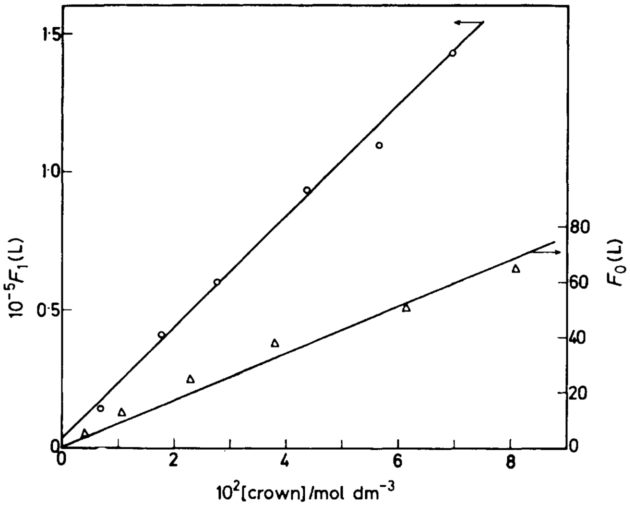


FIGURE 2 Analysis as in Figure 1 of the reduction of the adducts of Na (O) and Li (△) with 12-crown-4 (potentiometric data). Details as in Figure 1 except for F_0 (L) = exp(nF/RT)-($E - E_c$) where E and E_c are potentials of the amalgam pool electrode in the presence and in the absence of 12-crown-4

DISCUSSION

The utility of the electrochemical methods for an investigation of the stability of alkali-metal complexes with crown macrocycles has already been demonstrated by a few authors.[2-4] One feature of the present work should be specially noted: the partially irreversible polarographic waves of alkali-metal ions can be reliably interpreted by Gellings' method [14] as shown by the consistency between the stability constants of the sodium adducts deduced from potentiometric and polarographic measurements (Table 2).

The stability constants listed in Table 2 show that sodium forms a very stable adduct of 1 : 2 stoicheiometry. The metal is probably complexed in a sandwich-type configuration similar to the solid-state structure of the sodium adducts recently described by van Remoortere and co-workers.[6] In contrast, lithium forms a simple 1 : 1 adduct. This behaviour was anticipated since two macrocycles could not be accommodated in the co-ordination sphere of lithium. Indeed, the small ionic radius of this metal would constrain the oxygen atoms of the two cycles of an hypothetical sandwich complex to be in closer contact than allowed by the van der Waals radii.

van Remoortere and co-workers [6] reported that solid 1 : 2 complexes can also be prepared with KCl and RbCl. These complexes are isomorphous with the sodium–12-crown-4 sandwich adduct. At variance with this observation, the large alkali-metal ions in solution in propylene carbonate appear to form only 1 : 1 complexes, the stability constants of which decrease when the ionic radius of the encapsulated ion increases. The difference between the solution and solid-state behaviour of 12-crown-4 is tentatively ascribed to a competition between this ligand and propylene carbonate for the co-ordination of the large alkali-metal ions. In the solid 12-crown-4 sandwich complex of sodium,[6] lone-pair electrons of the oxygen atoms are directed toward the metal ion. Furthermore, all ethylene groups in the macrocycle are fully staggered. The sodium adduct is thus very stable and the macrocyclic effect largely overcomes that of solvation by propylene carbonate molecules. On the other hand, the two macrocycles in the sandwich complex are moved further apart when the radius of the complexed ion increases. A conformational rearrangement of the ligand would thus be required if the oxygen lone-pair electrons are to remain directed towards the metal. Also ion–dipole interactions decrease from Na^+ to Cs^+ in accord with decreasing charge density on the ion. It is thus expected that both the macrocyclic effect and the solvation effect weaken on going from Na^+ to Cs^+. The former effect is apparently altered more drastically thus allowing the solvent to compete more effectively with 12-crown-4 for co-ordination of the metal ion and leading to the formation of 1 : 1 adducts only with the large alkali-metal ions.

The absence in solution of 1 : 2 complexes with the largest alkali-metal ions could be a general feature of the complexation by small- and medium-size crown ethers. Izatt *et al.*[5] recently reported that benzo-15-crown-5 forms sandwich 1 : 2 complexes with Na^+ and K^+ but not with Cs^+ in 70% methanol–30% water mixtures.

The selective complexation of Na^+ by 12-crown-4 warrants special attention and is illustrated in Figure 3. The difference between the complexation of Na^+ on the one hand and of K^+ or Rb^+ on the other is of the same order or higher than the difference reported for bicyclic macrocycles,[17] the cavity size of which can be engineered to perform a particular complexation at the cost of a laborious synthesis. For comparison purposes, the percentage of complexation of the alkali-metal ions by the bicyclic [2.2.1] cryptand in water and 95% methanol–

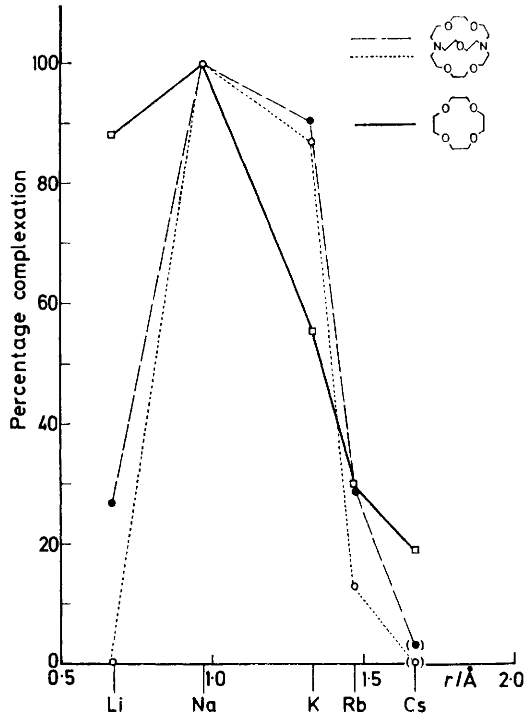


FIGURE 3 Percentage of complexation of the alkali-metal ions by 12-crown-4 in propylene carbonate (——) (this work) and by the bicyclic [2.2.1] cryptand in water (– – – –) and in 95% methanol–5% water (· · · ·).[17] Concentrations: each metal ion, 10^{-1} mol dm^{-3}; ligand, computed so as to achieve 99.5% complexation of sodium

5% water[17] is also given in Figure 3. The percentage of complexation of a 0.1 mol dm^{-3} metal solution is defined below where [M] and [L] denote the free alkali-metal ion and ligand concentrations. The total con-

$$\% \text{ complexation} = 100\,\frac{[\mathrm{Me}](\beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2)}{10^{-1}}$$

centration of each ligand was selected so that 99.5% of the sodium ion was complexed; the properties of the macrocycle are therefore easily compared. Among the bicyclic macrocycles, the cryptand 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane exhibits the same peak selectivity[17] for sodium as displayed by 12-crown-4. However, the tetraoxa-polyether favours sodium over potassium to a larger extent. Other cryptands such as the bicyclic derivatives 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane and 4,7,10,16,19,24,27-heptaoxa-1,13-diazabicyclo[11.8.8]nonacosane afford a somewhat better selectivity for sodium than 12-crown-4 but potassium is then the best complexed ion.

The easily synthesized 12-crown-4 was not expected to be such a selective complexing agent of sodium in view of the small dimensions of its internal cavity. The present work thus indicates that a consideration of only the relative dimensions of an ion and of a macrocycle does not necessarily indicate the most selective complexation.

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