

A Conductance Study of 1 : 1 Complexes of Glyme-5, 18 Crown 6 and Tetraethylene Glycol bis Quinoline Ether with Alkali Metal Ions in Methanol/Water

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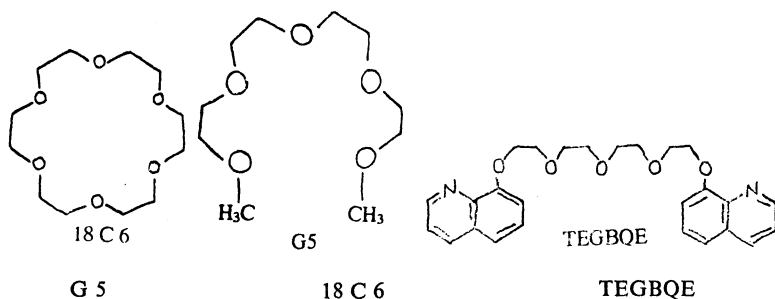
Conductivities of alkali metal picrates in the presence of glyme-5, 18 crown 6 and tetraethylene glycol bis quinoline ether (TEGBQE) were measured at 25°C in methanol water mixture. Formation constants and molar conductivities of the 1 : 1 complexes of these ligands with alkali metal ions in 70% methanol were determined. The $\log K_{ML^+}$ sequences of the alkali metal ions with pentaglyme, 18 C 6 and bis quinoline ether are $K^+ > Na^+ > Rb^+ \approx Cs^+ > Li^+$, $K^+ \gg Na^+ > Rb^+ > Cs^+$, $Na^+ > K^+ > Rb^+ > Cs^+ > Li^+$ respectively. This sequence for G 5 is consistent entirely with 18 C 6, but the order is different with TEGBQE. The complexes are less stable in case of non-cyclic ligands and selectivity is lost in going from cyclic to non-cyclic ligand. The TEGBQE complex may be entropy destabilised due to the two flexible arms.

INTRODUCTION

Macrocyclic polyethers, widely investigated by Pedersen and Lehn^{1,2} in 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. Cyclic ligands are highly powerful, so that it is rather difficult^{3,4} to understand the contributions related to the coordinative characteristics of M^+ during complexation and these ligands impose⁵ rather strong conditions with respect to the size of the cation to be complexed. Much emphasis is given to the non-cyclic multidentates and their complexing behaviour with alkali metal ions. Complexation reactions of crown compounds and their corresponding open chain analogues with metal ions have been studied from thermodynamic and kinetic point of view⁶. However, few data on solvation behaviour and structure in solutions of the resulting complexes have been reported.

The work described in this paper concerns the *in vitro* studies on-complexing behaviour of M^{2+} with special reference to cyclic as well as non-cyclic ligands. These ligands have been chosen in order to study the nature of interaction between the M^{2+} ions and the cyclic and non-cyclic

polyethers. TEGBQE with rigid donor and group fill the gap between glyme and common cyclic crown ether⁷.



EXPERIMENTAL

Materials-Ligands G-5, 18 C 6 and TEGBQE were obtained from Fulka and Co. and used without further purification. All metal picrates were prepared by adding an aqueous solution of metal carbonates, hydroxides to ethanolic solution of picric acid. All the picrates were recrystallised four times from ethanol and dried at 150°C in a vacuum oven. The method of purification of methanol⁸ was previously described. Middle 70% of distillate of the solvent was used. Conductivities of the purified methanol and water were less than 3×10^{-7} mhos.

The conductance measurements were made on a digital conductivity meter systronics NDC (732) model fitted with a water thermostated at $30^\circ\text{C} \pm .01^\circ\text{C}$. The conductivity cell used with cell constant 1.005 cm^{-1} . The values reported are the averages of three measurements.

The procedure for obtaining complex formation constant K_{ML} was just the same as that described by Takeda⁹. 200 ml of metal salt solution ($4 \times 10^{-4} \text{ M}$ – $5 \times 10^{-4} \text{ M}$) in 70% methanol was placed in beaker and the conductance (A_{MX}) of the solution measured. A step by step increase in the ligand concentration was affected by a rapid transfer of 4 ml instalment of ligand solution ($2 \times 10^{-3} \text{ M}$ – $5 \times 10^{-3} \text{ M}$) to the beaker, until the total concentration of the ligand was approximately 5 times as large as that of alkali metal salt. The conductance was measured after each addition of the ligand solution. The A_{MXL} value is estimated from the A values at the point of large $[L] t/[M] t$ ratios. Using these A_{MX} and A_{MXL} values, the $[L]$ is calculated and the K_{ML} is calculated using following formula.

$$K_{ML} = \frac{(A_{MX} - A)[L]}{(A - A_{MXL})[L]} \quad A_{MX} = \text{Molar conductance of salt solution}$$

$$[L] = [L] t - \frac{[M]t (A_{MX} - A)}{(A_{MX} - A_{MXL})} \quad A = \frac{k}{[M]t}$$

$$A_{MXL} = \text{Conductance of complex}$$

$[L]_t$ = Ligand concentration

$[M]_t$ = Metal ion concentration.

RESULTS AND DISCUSSION

Behaviour of G-5, 18 C 6 and TEGBQE Complexes in Solution

In this study, it is assumed that the association between a cation and an self established picrate anion is negligible and ligand forms the 1 : 1 complex with an alkali metal ion. The $\log K_{ML}$ values of the complexes studied are summarised in Table 1, and the plots were drawn for molar conduc-

TABLE 1
Log (K_{ML}/mol^{-1}) VALUES OF G 5, 18 C 6 AND TEGBQE-ALKALI METAL
ION COMPLEXES IN 70% METHANOL AT 25°C

	G 5	18 C 6	TEGBQE
Li ⁺	3.33 ± .01	—	2.80 ± .06
Na ⁺	3.42 ± .04	3.42 ± .04	3.90 ± .06
K ⁺	3.68 ± .05	4.07 ± .03	3.48 ± .02
Rb ⁺	3.37 ± .02	3.66 ± .02	3.40 ± .02
Cs ⁺	3.36 ± .4	3.13 ± .01	3.32 ± .03

tivity ΔV s $[L]_t/[M]_t$ ratio. The variation of $\log K_{ML}$ with ionic radius is shown in Fig. 1.

The molar conductivity ΔV s $[L]_t/[M]_t$ plots of all the metals with G-5 and TEGBQE shows an increase in Δ with an increase in the ligand concentration. This indicate that these complexes are more mobile than a free metal ion. In the case of lithium with 18 C 6 system, there is a negligible change in Δ in spite of an increase in the crown ether concentration. Consequently the complex formation constants could not be determined in this case. When the complex is unstable or the mobilities of the complex and the corresponding alkali metal ion are equal, conductometric determination of the complex formation constant is impossible. In the case of 18 C 6 system there is a decrease in Δ with an increase in ligand concentration except the case of sodium, which shows an increase.

It can be from concluded the plots of molar conductivity ΔV s $[L]_t/[M]_t$ ratio, that no clear breaking point is observed at $[L]_t/[M]_t = 1$, whereas reverse holds⁹ for 18 C 6. This is attributed largely to much lower stabilities of G 5 and TEGBQE complexes as compared to the 18 C 6 alkali metal ion complexes (Table 1). Hinz and Margerum proposed that a cyclic ligand, being much more compact, is less solvated

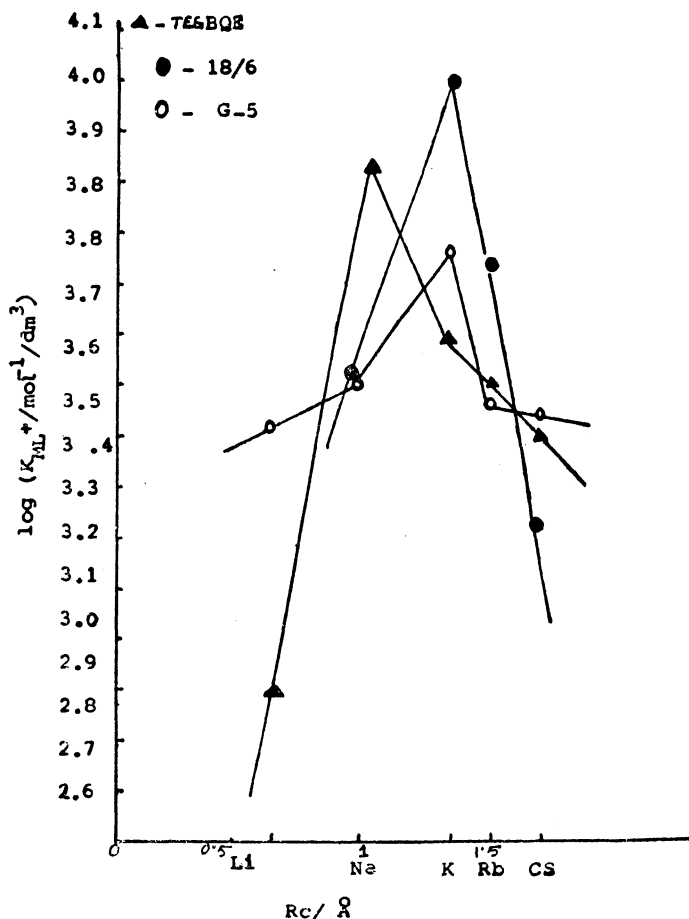


Fig. 1. Plots of $\log K_{ML}$ at 25°C Vs Crystal ionic radius of alkali metal
 ○ G 5, ▼ TEGBQE, ● 18 C 6

than a noncyclic and consequently less energy is expanded at its desolvation step¹⁰.

Stability of G 5, 18 C 6 and TEGBQE Complexes

The difference in $\log K_{ML}$ values of G 5, TEGBQE between neighbouring alkali metal ions in the periodic table is smaller than that of 18 C 6. The difference between the largest and the smallest $\log K_{ML}$ values of G 5 and TEGBQE complexes among alkali metal ions is smaller than that of 18 C 6. Selectivity of 18 C 6 for K⁺ shows the size fit correlation, while TEGBQE has two relatively flexible arms with rigid donor and groups and six donor ether oxygens. TEGBQE may trap the alkali metal ion with two arms and adopt the most favourable conformation according

to the size of alkali metal ion at the complexation reaction. The sequences of $\log K_{ML}$ values for these G 6, 18 C 6 and TEGBQE are $K^+ > Na^+ > Rb^+ \approx Cs^+ > Li^+$, $K^+ \gg Na^+ > Rb^+ > Cs^+$, $Na^+ > K^+ > Rb^+ \gg Cs^+ > Li^+$ respectively. The selectivity of TEGBQE for Na^+ indicates that size and shape of pseudocyclic cavity formed by two flexible arms at ortho position may be most suitable for Na^+ than for other ions. Since Na^+ is smaller than K^+ , Na^+ may attract the two flexible arms of TEGBQE more strongly than K^+ , resulting in more efficient complex by shielding of Na^+ in the complex by the two arms from surrounding solvent molecules. Since G 5 and TEGBQE are flexible, the entropy contribution seems to play a more dominant role in destabilising the complexes with these ligands compared to the 18 C 6 complexes.

Cyclic structure and greater number of donor atoms enhances the stability as well as selectivity in the case of 18 C 6 complexes. Also because of the presence of an appreciable interaction among the hetero atom lone pair orbitals and the metal ion. The result of this interaction is to produce a relatively higher energy H.O.M.O (higher occupied molecular orbitals) which makes them softer ligands than would have been expected in the absence of orbital interaction¹¹. While π electrons of the donor end groups greatly enhance the stability of the complex through pseudocyclic conformation¹².

Thus we can conclude that selectivity is lost in going from cyclic to noncyclic ligand although stability and selectivity can be enhanced and altered by attaching rigid donor sites to simple glycols.

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