Complexation of Macrocyclic Compounds with Silver Ions in Surfactant Media

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Abstract

This paper is a report on the complexation studies of silver ions with certain water soluble crown ethers viz., 15-crown-5, 18-crown-6, cyclam, diaza 15-crown-5 and certain water insoluble crown ethers viz., benzo 15-crown-5, dibenzodiaza 15-crown-4, dibenzyldiaza 18-crown-6 in some nonionic surfactants viz., polyoxyethylated alkyl phenol (TX 100), polyoxyethylene (20) sorbiton monolaurate (Tween 20), polyoxyethylene (20) sorbiton monoleate (Tween 80) and polyoxyethylated glyco monolauryl ether (Brij 35) by potentiometry. In addition, conductometry was also used to study the complexation of oxa crown ethers to compare the results obtained by potentiometry, which were found to be in good agreement with each other. The complexation studies indicate 1:1 complex formation between the silver ion and macrocycle, the $\log^{n+}_{ML}$ values being in the range 1 to 9.

Introduction

As of now, a large number of studies have been reported on metal-ligand complexation. Solvents are known to have a profound effect on the complexation phenomena. Solvent properties such as polarity, permitivity, solvation ability etc. effect the formation of complexes to a large extent [1–3]. Surface-active agents have also been found to affect the complexation phenomena in various ways. A number of spectrophotometric methods have been proposed in which cationic surfactants are used in conjunction with metallochromic reagents [4–6]. Goto *et al.* [7] found that in the spectrophotometric investigation of aluminium and iron with ferron, the addition of cationic surfactants greatly improves the linearity of the calibration curve and widens the useful pH range. The stepwise stability constants of the ferron complexes of aluminium and iron were determined in the presence and absence of the surfactants. Similar studies on the composition and stability of Ni(II), Cu(II), Mn(II), Gd(II) and Fe(II) complexes with certain chelating agents have been reported in relation with anionic surfactants [8, 9]. The formation of a yellowish brown complex between palladium (II) chloride and cephalosporins in the presence of sodium lauryl sulphate was used for the determination of cephalosporins [10]. Surfactants have also been found to influence the complexation reactions of cyclic polyethers with metal cations. The main reason for this being either the complexation of surfactant counterions with the crown ethers themselves [11, 12] or the localisation of the ligand or complex or both in the surfactant micelles [13].

Most of the above studies have involved ionic surfactants. The use of nonionic surfactants in such studies has been limited [14, 15]. Nonionics have a definite advantage over the ionics in that they are compatible with all other types of surfactants and their properties are little affected by changes in pH of the solution, also by virtue of their low CMC's they are effective in much lower concentrations.

Earlier, we had reported the use of organic solvents in binary mixtures with water for solubilization of the macrocyclic compounds and studied their effects on the stabilities of the complexes [16, 17]. As the presence of surfactants changes the solute properties of electrolytes, it would be interesting to study the effect of the surfactants on the metal ion complexation with macrocyclic compounds. Therefore, the present work was under taken to study the complexation of silver ions in surfactant media, with certain water soluble crown ethers viz., 15-crown-5 (15C5), 18-crown-6 (18C6), 1,4,8,11-Tetraazacyclotetradecane (cyclam), 1,4,10-Trioxa-7,13-diaza-cyclopentadecane (diaza 15C5) and some water insoluble crown ethers viz., benzo 15-crown-5 (B15C5), 5,6,14,15-Dibenzo-1,4-dioxa-8,12-diaza-cyclopentadeca-5,14-diene (dibenzodiaza 15C4), 7,16-Dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (dibenzyldiaza 18C6) solubilized with the help of some nonionic surfactants viz., polyoxyethylated alkyl phenol (TX 100), polyoxyethylene (20) sorbiton monolaurate (Tween 20), polyoxyethylene (20) sorbiton monoleate (Tween 80) and polyoxyethylated glyco monolauryl ether (Brij 35) by the potentiometric technique. In addition conductometric studies of the complexation behavior of silver with oxa crown ethers have also been taken up to compare the results obtained by potentiometry.

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MACROCYCLIC COMPOUNDS STUDIED IN THE PRESENT

INVESTIGATION
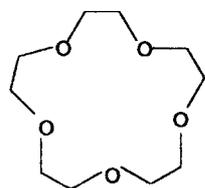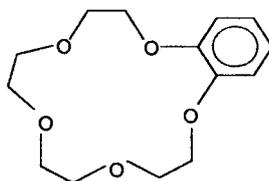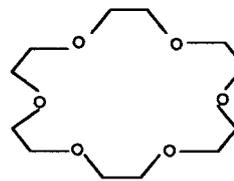
15C5   B15C5   18C6
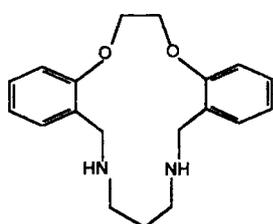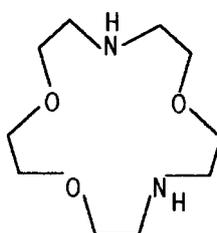
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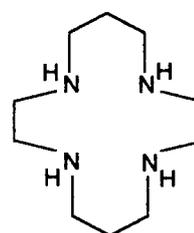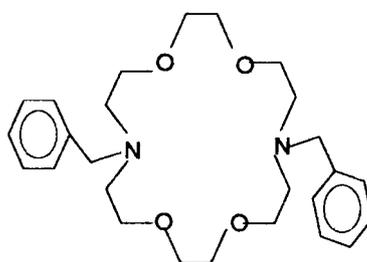
dibenzyldiaza 18C6

Scheme 1.

Experimental section

Apparatus

A Mettler Toledo DL53 autotitrator with automatic temperature compensation (ATC) was used for standardization of silver nitrate solutions, potentiometric and conductivity measurements. The probes used were silver electrode with Ag/AgCl reference electrode (DM 141-SC) and conductometric sensor with ATC (Inlab 710).

Reagents

The crown ethers, 15-crown-5 (Fluka), benzo-15-crown-5 (Aldrich), 18-crown-6 (Aldrich), 1,4,8,11-tetraazacyclotetradecane (Fluka), 1,4,10-trioxa-7, 13-diazacyclopentadecane (Fluka), 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (Fluka) and 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Fluka) were of reagent grade (purity $\geq$ 99%) and used as received.

The surfactants, polyoxyethylated alkyl phenol (TX 100), polyoxyethylene (20) sorbiton monolaurate (Tween 20), polyoxyethylene (20) sorbiton monoleate (Tween 80) and polyoxyethylated glyco monolauryl ether (Brij 35) were of reagent grade (purity $\geq$ 99%) and used as received.

All solutions were prepared in surfactant solutions (1% by mass). Experimental solutions were prepared by appropriate dilutions. Stock solutions of silver nitrate were

standardized by titrating against sodium chloride on the DL 53 autotitrator, before use.

Procedure for potentiometry

The silver indicator electrode (DM 141-SC) with an inbuilt Ag/AgCl reference electrode was used for all measurements involving Ag(I) ions. The potentials of the silver ion solutions, with and without ligands in surfactant media were recorded and their difference used for calculation of stability constants [16, 18]. As a general procedure, the emfs were noted every 2 minutes. The potentials recorded were the average of the last two observations, which normally agreed to within ± 0.1 mV and the measured cell potentials were reproducible to ± 0.5 mV.

Procedure for conductometry

All measurements were done as before [16, 18] at 25.0 $\pm$ 0.1 °C, using the conductometric sensor Inlab 710 (with ATC), which was calibrated regularly with the Mettler Toledo standard solutions. All molar conductivities were calculated after correcting for the solvent conductivity. The uncertainty in the measurement of conductivities was ± 0.1 μS.

Step 1. The surfactant solution (1% by mass) was placed in the cell and the conductance was measured. A step-by-step increase in the metal ion concentration was affected by means of the autotitrator. After each addition, followed by mixing, the system was allowed to stabilize and a reading, which didn't change, by ± 0.2 μS over a span of 10 min was recorded.

Step 2. The metal nitrate solution ($\sim 1 \times 10^{-3}$ M) in 1% surfactant was placed in the cell and the conductivity was measured. The crown ether solution (~ 0.02 M) was added to the cell in small increments until the total concentration of the crown ether was approximately 2 to 3 times as large as that of the metal nitrate. The conductivity was measured after each addition as above.

Theory

The equations [16, 18] used for calculation of stability constants are described briefly as follows:

Conductometric study of crown ether complexation with silver nitrate

The complexation of a metal ion (M) with crown ether (L) may be represented as

$$\underset{\alpha[M]_t}{M^{n+}} + \underset{[L]_t-(1-\alpha)[M]_t}{L} \rightleftharpoons \underset{(1-\alpha)[M]_t}{ML^{n+}}, \tag{1}$$
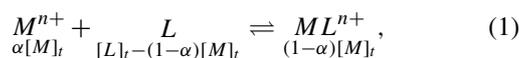
where $[M]_t$, $[L]_t$ and α are the total concentration of cation, the total concentration of crown ether and the fraction of uncomplexed cation, respectively. Accordingly the thermodynamic stability constant K'^{n+}_{ML} is given by

$$K'_{ML^{n+}} = [ML]f_{ML^{n+}}/[M]F_{M^{n+}}[L]f_L, \tag{2}$$

where $[ML]$, $[M]$ and $[L]$ are the concentrations of complexed cation, uncomplexed cation and uncomplexed crown ether, respectively, while $F_{ML^{n+}}$, $f_{M^{n+}}$ and f_L are the corresponding activity coefficients. The concentration stability constant $K_{ML^{n+}}$, which is reported, since $f_{ML^{n+}}$ and $f_{M^{n+}}$ are unknown, is given by

$$\begin{aligned} K_{ML^{n+}} &= K'_{ML^{n+}}f_{M^{n+}}/f_{ML^{n+}} = [ML]/[M][L] \\ &= (1-\alpha)/\alpha[L], \end{aligned} \tag{3}$$

where f_L is assumed to be unity.

The conductivity (κ) of a solution containing metal nitrate and crown ether is written as

$$\kappa = \kappa_{MXn} + \kappa_{MLXn}, \tag{4}$$

where κ_{MXn} and κ_{MLXn} are the conductivities of metal nitrate and metal crown ether nitrate, respectively. The respective molar conductivities are given by

$$\Lambda_{MXn} = \kappa_{MXn}/[M] = \kappa_{MXn}/\alpha[M]_t \tag{5}$$

$$\Lambda_{MLXn} = \kappa_{MLXn}/[ML] = \kappa_{MLXn}/(1-\alpha)[M]_t. \tag{6}$$

Equation (4) may be written in terms of molar conductance (Λ) by considering the total concentration $[M]_t$ via Equations (5) and (6), to give

$$\Lambda = \kappa/[M]_t = \alpha\Lambda_{MXn} + (1-\alpha)\Lambda_{MLXn}. \tag{7}$$

The correction for the viscosity changes is neglected, as the crown ether concentration was kept low. Using Equations (3) and (7) one obtains

$$K_{ML^{n+}} = (\Lambda_{MXn} - \Lambda)/(\{\Lambda - \Lambda_{MLXn}\}[L]). \tag{8}$$

where $[L] = [L]_t - \{[[M]_t(\Lambda_{MXn} - \Lambda)]/(\Lambda_{MXn} - \Lambda_{MLXn})\}$. The Λ_{MLX_n} value is estimated from the Λ values at the point of large $[L]_t$ to $[M]_t$ ratio. Using the Λ_{MLXn} value, the $K_{ML^{n+}}$ value in Equation (8) is calculated.

Potentiometric study of crown ether complexation with silver nitrate

The stability constant ($K_{ML^{n+}}$) for Ag(I) with crown ether, using Equations (3) and (7), is given by

$$K_{ML^{n+}} = (\Lambda_{MXn} - \Lambda)/(\{\Lambda - \Lambda_{MLXn}\}[L]). \tag{9}$$

The determination of α is based on the measurement of the emf of the cell:

Ag/AgCl reference electrode//
Ag$^+$ + Ligand in surfactant media/Ag.
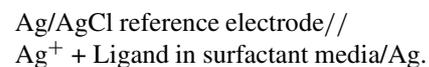
The conductance and potentiometric studies on AgNO$_3$ in all the surfactant media showed that it is completely dissociated and the silver electrode behaves linearly over the range

Table 1. Results of the emf measurements for the determination of $K_{ML^{n+}}$ of silver ion complexes with 15C5 in TX 100

Concentration $[M]t \times 10^3$ (M)	Concentration $[L]t \times 10^3$ (m)	E (mV)	ΔE (mV)	Log $(K_{ML^{n+}}/\text{mol dm}^{-3})$
1.000	0.000	170.3	–	–
1.000	0.530	170.0	0.3	1.35
1.000	2.120	169.0	1.3	1.39
2.000	0.000	180.0	–	–
2.000	1.060	179.4	0.6	1.36
2.000	4.240	177.9	2.1	1.31
2.000	2.120	178.8	1.2	1.37
2.000	6.360	177.0	3.0	1.30
			Average	1.35

1×10^{-1} M to $1 \times^{-7}$ M. So, the difference (ΔE) between the emf of the salt solution and that of the salt + crown ether solution can be taken to reflect the concentration ratios. The Nernst equation is used to give the following relation

$$\alpha = 10^{-\Delta E/59.16}. \qquad (10)$$

Using this value of α in Equation (10), $K_{ML^{n+}}$ is obtained. All calculations were done using Microsoft Excel.

Results and discussion

A representative set of the data obtained by potentiometry and conductometry are given in Tables 1 and 2, respectively. From Table 3, it is observed that the stability constants for the complexes of Ag(I) with the various crown ethers in the different media follow the order Tween 80 > Tween 20 > TritonX 100 > water > Brij 35. Studies on the structure of micelles indicate that the interior or core of the micelles is assumed to be fluid like and acts as a hydrophobic environment composed of flexible hydrocarbon chains. Crown ether molecules being hydrophobic themselves will prefer to remain solubilized within this nonaqueous core of the micelles. Thus the Ag(I)-crown ether complex formation in the presence of the nonionic surfactants can effectively be said to take place in a nonaqueous environment.

It has been noted in case of nonionic surfactants that the solubilizing power expressed as moles of solubilizate per mole of surfactant increases as the polyoxyethylene chain length increases [19]. Thus TX 100 ($E = 9$) would show the least solubilizing power due to its least polyoxyethlene chain length and Brij 35 ($E = 23$) would show the most. Hence it is seen that Benzo 15C5 which is completely insoluble in water solubilizes very easily in all the surfactants. Dibenzodiaza 15C4 which is another water insoluble crown ether does not solubilize in Tween 20 and Tween 80 but solubilizes with sufficient ease in Brij 35. However this compound is also found to dissolve in TX 100, which is less hydrophobic than Tween 20 or Tween 80. The reason for this is unclear. Finally Dibenzyl diaza 18C6, which is the bulkiest and hence the most hydrophobic of the above crown ethers is soluble in only Brij 35.

Table 2. Results of the conductivity measurements for the determination of $K_{ML^{n+}}$ of silver ion complexes with 15C5 in TX 100 by step 2

$[Lt]/[Mt]$	Λ Log (S cm^2 mol^{-1})	$(K_{ML^{n+}})$
0.125	124.95	1.41
0.250	124.75	1.35
0.375	124.57	1.29
0.500	124.38	1.32
0.625	124.21	1.34
0.750	124.05	1.31
0.875	123.92	1.29
1.000	123.81	1.32
1.125	123.72	–
1.250	123.48	–
1.500	123.51	–
1.750	123.54	–
2.000	123.53	–
2.250	123.53	–
2.500	123.53	–
2.750	123.54	–
3.000	123.56	–
	Average	1.34

It has been shown from previous studies of crown ether complexation in various solvents that the metal-complex stabilities are more in organic solvents as compared to that in water [20, 21]. This trend is also reflected in binary mixtures with water [2, 3, 16–18]. This enhancement of stability is primarily an enthalpic effect. The enthalpic stabilization is explained by the expending of less energy in the cation desolvation step in the solvent of lower dielectric constant.

The amphiphilic nature of nonionic surfactants is expressed in terms of the balance between the hydrophobic and hydrophilic portions of the molecule. This is estimated by the HLB values [22]. The lower the HLB value, the more lipophilic is the compound and vice versa. Hence TX 100 (HLB $\sim$ 18) is found to be the least lipohilic among the above surfactants. Tween 20 (HLB = 16.7) is slightly

Table 3. Comparison of the results obtained by the potentiometric and conductometric techniques for the determination of stability constants of Ag(I) metal ions with various crown ethers in different surfactant media

Crown ether	Water (Lit. val.)	TX 100		Tween 20		Tween 80		Brij 35	
		Cond.	Pot.	Cond.	Pot.	Cond.	Pot.	Cond.	Pot.
		Log ($K_{ML^{n+}}$)							
15C5	0.94	1.33	1.35	1.45	1.49	1.66	1.66	0.82	0.84
18C6	1.60	2.03	2.09	2.45	2.42	2.84	2.74	0.93	0.95
Cyclam	–	–	8.87	–	9.09	–	9.29	–	1.20
Diaza-15C5	5.85	–	6.02	–	6.28	–	6.61	–	1.83
Benzo-15C5	*	1.21	1.20	1.43	1.41	1.55	1.52	0.56	0.60
Dibenzo-diaza15C4	*	–	4.14	*	*	*	*	–	1.33
Dibenzyl-diaza18C6	*	–	*	*	*	*	*	–	1.14

– Not studied.

* Insoluble.

more lipophilic followed by Tween 80 (HLB = 15.0), and finally Brij 35 (HLB = 9.7), which is the most lipophilic of the above set of surfactants. This explains the above trend in results wherein the Ag(I)-crown ether complex stability constants are found to be less in water which has the highest dielectric constant, more in TX 100, higher in Tween 20 and highest in Tween 80 which may be assumed to have a higher dielectric constant than either TX 100 or Tween 20.

Brij 35, although is the most lipophilic surfactant is a major exception to this rule as the stability constants in this surfactant media are lower than in water. This anomaly can be explained on the basis of the fact that nonionic micelles being composed of polyethylene oxide residues are themselves very favorable for complexation with a cation [23]. The polar oxygen centers interact in a concerted manner through the orientation of the head groups of the surfactant to offer a relatively large electron density for stronger complex formation. The higher the alkyl hydrocarbon chain length of the surfactant, the higher is the electron donor capacity of the molecule due to an inductive effect. This fact further supports complex formation, or rather the solvation of the cation by the surfactant molecule. Recent investigations have shown that such a binding takes place by the formation of spiral type structures with inwardly directed oxygen atoms that coordinate with the cation by ion dipole interactions [24]. Such binding is however weak. 'Brij 35 (E = 25) being strongly lipophilic with a long polyoxyethylene chain probably complexes with the silver metal ion in a similar fashion thus hindering the cation from entering the crown ether cavity and creating less stable Ag(I)-crown ether complexes in this medium. This phenomenon is however not visible in other surfactants used in the present work due to their lower lipohilic characters.

The well-known ion-in-hole concept is applicable in these media also. Silver ion which has a radius of 1.2 Å forms more stable complex with 18C6 (radius = 1.34–1.43 Å) among the oxygen containing macrocycles, the order being 18C6 > 15C5 (radius = 0.8–0.92 Å) > B15C5. Another

important observation to be noted from the above results is that the Ag(I) complexes with oxa crown ethers are less stable as compared to the Ag(I)-aza crown ether complexes. This can be explained on the basis of 'Hard and soft Acid-Base' (HSAB) concept [16, 18, 25]. The transition metal ion, silver, coming under the configuration of soft acids, would from stronger coordination bonds with nitrogen containing polyethers, which configure as softer bases compared to oxygen. Hence we see that, highest values of stability are obtained with cyclam which has 4 nitrogen atoms, followed by Diaza15C5 with 2 nitrogen atoms and Dibenzo-diaza15C4 which also has 2 nitrogen atoms but is smaller than Diaza15C5.

Conductometric experiments were performed only for the oxa-crown ethers and not the aza-crown ethers because the data obtained from the latter cannot be used for the calculation of stability constants as these crown ethers cause a change in the pH of the solution and give a V-shaped curve [16, 18].

The Nernstian response of silver indicator electrode in aqueous and in 1% TritonX-100 media is given in Figure 1. In both the media, the Nernstian slopes are found to be close to 59 mV, within the working range of the silver ion concentrations used in this study. However, the change in potential has been observed in surfactant media as has been reported in the literature [26, 27]. The linear Nernstian response was obtained in the working range of silver ion concentrations. Figure 2 is representative of the curves obtained by conductometry. It is observed that the Λ values decrease with an increase in $[L]t/[M]t$ ratio. This trend is explained on the basis of the fact that the silver ion when complexed with crown ethers becomes bulkier and therefore less mobile as a consequence of which its conductivity decreases [16, 18]. The curve shows a breakpoint at $[L]t/[M]t \approx 1$ which indicates the formation of 1:1 complexes between the crown ethers and the silver ions.

The close agreement between the results obtained by potentiometry and conductometry for the oxa-crown ethers is
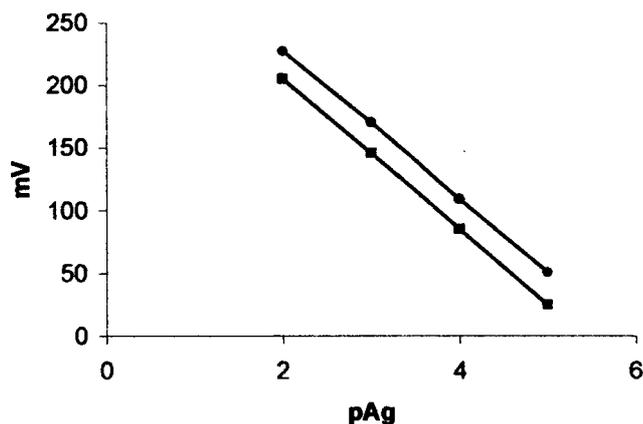
Figure 1. Plot of emf vs. silver-ion concentration in: ●, aqueous medium; ♦, 1% TritonX 100.
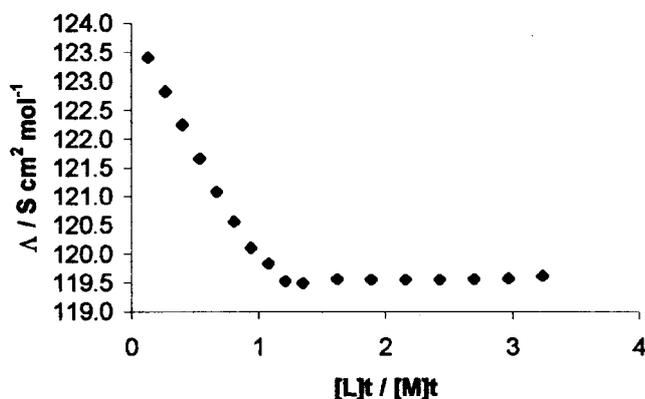
Figure 2. Plot of Λ vs. $[L]t/[M]t$ for $AgNO_3$ and 18C6 in 1% TX 100.

remarkable and gives an accurate indication of the stabilities of the complexes.

Conclusion

Macrocyclic compounds, as well as surfactants have been known to function as 'phase transfer catalysts' [28–30] and also both have been utilized in drug delivery systems [31, 32] and chromatographic separations of compounds of pharmaceutical interest [33, 34]. We hope that such complexation studies in surfactant media would provide useful guidelines to those involved in different applications of macrocyclic-surfactant systems, not limited to the above examples but also to other diverse fields like in photographic emulsions, inks, separations [35–37], spectroscopy [38, 39, 13], design of chemical sensors [26, 27] etc.

Acknowledgement

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