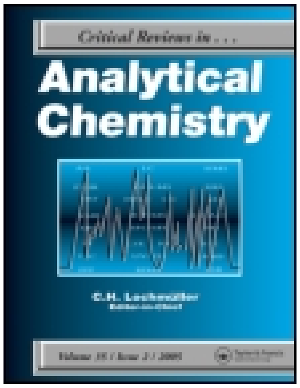

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Conductometric Studies on Cation-Crown Ether Complexes: A Review

Francis A. Christy [a] [b] & Pranav S. Shrivastav [a]
[a] Department of Chemistry, School of Sciences, Gujarat University, Navrangpura, Ahmedabad, India
[b] Department of Chemistry, St. Xavier's College, Navrangpura, Ahmedabad, India

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Conductometric Studies on Cation-Crown Ether Complexes: A Review

Francis A. Christy[1,2] **and Pranav S. Shrivastav**[1]
[1]*Department of Chemistry, School of Sciences, Gujarat University, Navrangpura, Ahmedabad, India*
[2]*Department of Chemistry, St. Xavier's College, Navrangpura, Ahmedabad, India*

Crown ethers have proved to be unique cyclic molecules for molecular recognition of suitable substrates by hydrogen bonds, ionic interactions, and/or hydrophobic interactions. The study of interactions involved in complexation of different cations with crown ethers in mixtures of solvents is important for a better understanding of the mechanism of biological transport, molecular recognition, and other analytical applications. This fundamental review summarizes different aspects of cation-crown ether complexes studied by conductometry in diverse solvent systems. A comprehensive literature summary is presented in tabular form for the complexation of cations with different crown ethers and their derivatives and other related crown ethers, highlighting their formation constant and thermodynamic parameters in diverse solvent media. Various factors that influence the stability and selectivity of cation-crown ether complexes have been discussed for thermodynamic consideration.
Supplemental materials are available for this article. Go to the publisher's online edition of **Critical Reviews in Analytical Chemistry** ***to view the free supplemental file.***

Keywords Crown ethers, conductometry, cations, solvent system, formation/stability constant, thermodynamic parameters

INTRODUCTION

Crown ethers are one of the most widely studied family of host compounds in the field of supramolecular chemistry, involving non-covalent interactions. Since the fortuitous discovery of macrocyclic polyethers by Pedersen in 1967 (Pedersen, 1967), there has been a huge interest in these compounds as complexing agents, primarily for metal ions and also for some neutral and anionic species. The complexation of potassium ion with DB18C6 in 1967 was the defining moment in the emergence of crown ether chemistry, especially for alkali and alkaline earth cations. Crown ethers are compounds with at least three or more oxygen atoms incorporated in a monocyclic carbon backbone. The name "crown" was coined due to their unique shape, which resembles a crown. A typical characteristic of crown ethers is the way in which they interact with various ionic species via ether oxygen atoms. They exhibit strong affinity and high selectivity for alkali and alkaline earth metal ions because of a hydrophilic cavity consisting of heteroatoms, demarcated by a lipophilic envelope of ethylene units (Lamb et al., 1979; Popov and Lehn, 1979; Lifson et al., 1987; Potvin and Lehn, 1987; Dietrich et al., 1991). "Host-guest" chemistry of crown ethers (wherein the crown plays the "host" and the "guest" is the incoming species) can be a key to identify the movement of essential elements in the body and can play the part of very complicated biological reactions (Stolwojk et al., 1987), such as enzyme functions, which can be applied to develop new pharmaceuticals.

Crown ethers have found applications in many areas based on their ability to selectively recognize cations of different ionic size. The ammonium ion is of special significance as it plays a fundamental role in biological processes. In analytical chemistry, crown ethers' selective cation binding properties are exploited in separation and transport processes for the recovery or the removal of cations, from very dilute solutions (trace enrichment of radionuclides) and in the design of ion-selective electrodes. They have also been used as stationary phase in chromatographic techniques. Owing to their ability to dissolve salts in organic media, by reducing the cation/anion interaction (i.e., by shielding the cation and activating the anion), they have been used in many syntheses, as catalysts in phase-transfer catalysis, or enzyme mimics. They also have medical applications as diagnostic or therapeutic agents (Lamb et al., 1979; Popov and Lehn, 1979; Potvin and Lehn, 1987; Lindoy, 1989; Gokel, 1994; Arnaud-Neu et al., 2003).

Due to their wide range of applications, crown ethers have been modified to enhance their complexing ability for cations

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Address correspondence to Pranav S. Shrivastav, Dept. of Chemistry, School of Sciences, Gujarat University, Navrangpura, Ahmedabad-380009, Gujarat, India. E-mail: pranav_shrivastav@yahoo.com

of different sizes. Some of these modifications include the use of alkyl substituents, aromatic sub-cyclic units, nitrogen and/or sulfur atoms substituted for oxygen in the macrocyclic ring, and other changes that provide crowns with unique complexing properties. Enormous amounts of data have been reported on the equilibrium constants and thermodynamic functions of complex formation of crown ethers with alkali and alkaline-earth metal cations, transition metal ions, lanthanide ions, and small organic molecules (Izatt et al., 1992; Wagner-Czauderna et al., 1999). The interactions between these ligands and metal cations are generally non-covalent in nature (Pedersen, 1970; Pedersen and Frensdorff, 1972). The selectivity behavior of crown ethers for metal cations has often been explained based on the size-fit concept, i.e., a more stable complex is formed when the cation size matches the size of the crown ether cavity.

Many diverse physicochemical techniques such as nuclear magnetic resonance (NMR) spectrometry (Irandoust et al., 2010; Shamsipur et al., 2003), mass spectrometry (Malhotra et al., 1990; Katritzky et al., 1992), capillary electrophoresis (Katsuta et al., 2002), calorimetry (Buschmann et al., 2001, 2008), polarography (Rounaghi et al., 2002; Samec and Papoff, 1990), ion-selective electrodes (Yidiz et al., 2004; Erk et al., 1999), spectrophotometry (Buschmann et al., 1997; Semnani and Shamsipur, 1997), potentiometry (Zolgharnein et al., 2007; Kuzmina et al., 2009), and fluorescence (Yapar and Erk, 2001; Erk and Göçmen, 2000) have been used to study the complex formation between crown ethers and metal cations in solution. In addition to these techniques, conductometry offers a simple and an inexpensive experimental arrangement for such investigations. The advantage of conductometry is that the measurements can be carried out with high precision at very low concentration in solution systems. Conductance measurements of a solution of metal salt in the presence of a crown ether provide two valuable pieces of information: the stability of the cation-crown ether complex and transport phenomena of metal salt-crown ether complex in the solution. Also, it is one of the most reliable methods for obtaining the formation constants of cation-macrocyclic complexes (Takeda et al., 1991).

Owing to the vast amount of literature available for complexation of cations with crown ethers employing diverse analytical techniques, the scope of this review is limited to conductometric studies only. The literature was scanned for peer-reviewed research articles and review articles dealing with cation-crown ether complexes in the past four decades. The keywords selected for the search included "conductometry," "crown ether," "cation," and "complexation." The year-wise distribution (group of five years) of most relevant research publications (103) is presented in Figure 1. The majority of these papers (61%) have appeared in the *Journal of Inclusion Phenomena Macrocyclic Chemistry* (37%), the *Journal of Solution Chemistry* (13%), followed by the *Bulletin of the Chemical Society of Japan* with 11% contribution, while the remaining 39% are reported in 17 different journals as shown in Figure 2. In our effort to make the article useful to expert and student alike, it embraces the fundamentals of conductivity measurement, outlines a mathematical treatment for calculating formation constant, and includes a detailed discussion of the factors influencing cation-crown ether complexes in solution and their effect on thermodynamic parameters like enthalpy, entropy, and free energy.

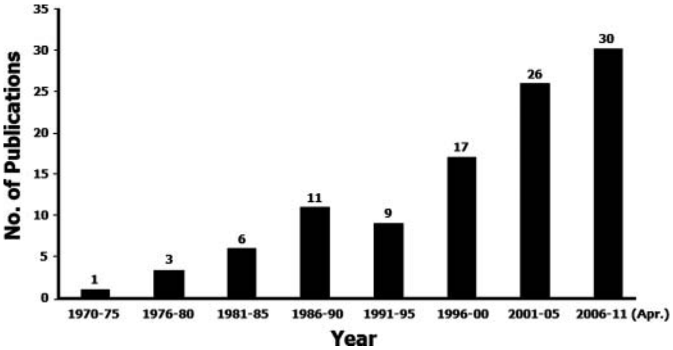

FIG. 1. Year-wise (group of five years) distribution of research publications on cation-crown ether complexes studied by conductometry in the past four decades.

FUNDAMENTALS OF CONDUCTIVITY MEASUREMENT

The principle of conductivity measurement is based on the Ohm's law, which explains the conductance in metals as well as in electrolytes. It states that the *current* (*I*, amperes) flowing

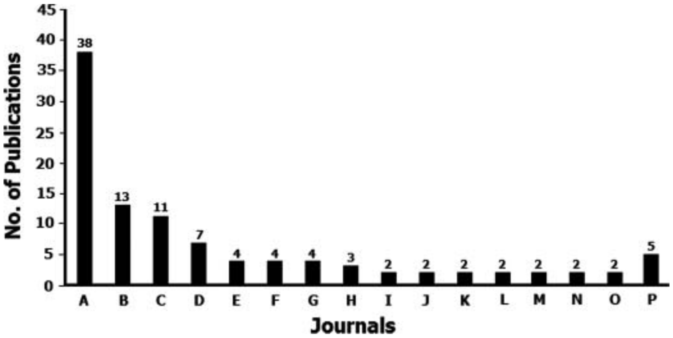

FIG. 2. Number of research publications in different journals in the past four decades. A, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*; B, *Journal of Solution Chemistry*; C, *Bulletin of the Chemical Society of Japan*; D, *Polish Journal of Chemistry*; E, *Journal of Chemical and Engineering Data*; F, *Journal of Molecular Liquids*; G, *Russian Journal of Inorganic Chemistry*; H, *Inorganica Chimica Acta*; I, *Journal of Chemical Society, Faraday Transactions*; J, *Indian Journal of Chemistry*; K, *Journal of Chemical Thermodynamics*; L, *Russian Journal of Coordination Chemistry*; M, *Analytica Chimica Acta*; N, *Journal of Coordination Chemistry*; O, *Journal of the Chinese Chemical Society*; P, one article each in *Talanta*, *Journal of Physical Chemistry, Russian Journal of General Chemistry, Polyhedron, and Bulletin of the Korean Chemical Society*.

through a conductor is equal to the *electromotive force* (E, volts) divided by the resistance of the circuit (R, ohms). Mathematically, it is expressed as

$$I = \frac{E}{R} \qquad [1]$$

For a conductor at a given temperature, the resistance is expressed as

$$\text{resistance} \propto \frac{\text{length}}{\text{crosssection}} \qquad [2]$$

It is measured in *ohms*. However, for a solution of electrolytes it is more convenient to use the reciprocal of the resistance, which is termed *conductance*.

$$\text{conductance} \propto \frac{\text{crosssection}}{\text{length}} \qquad [3]$$

Since conductance is the reciprocal of resistance, the unit of conductance is termed *ohm*$^{-1}$ or *mho*.

Ways of Expressing Conductance (Crockford and Knight, 1964)

Specific Conductance

As shown in Equation [3], the conductance of a solution is proportional to the cross section and inversely proportional to the length. If each of two electrodes is 1 cm^2 in area and if these are placed 1 cm apart, the conductance of 1 cm^3 of the solution is termed the specific conductance. It is denoted by κ.

Equivalent Conductance

This is defined as the conductance of a solution that contains 1 g equivalent of the electrolyte placed between electrodes 1 cm apart (the electrodes completely covering the opposite sides of the volume of the solution). Mathematically this can be written as

$$\Lambda = \frac{1000\kappa}{C} \qquad [4]$$

where κ is the specific conductance, Λ is the equivalent conductance, and C is the concentration in equivalents per liter.

Molar Conductance

This is defined as the conductance of a solution that contains 1 mole of the electrolyte placed between electrodes 1 cm apart. For the substances in which the equivalent and molar weights are same, the equivalent conductance and the molar conductance have the same value.

Determination of Equivalent Conductance (Crockford and Knight, 1964)

This can be determined by obtaining the specific conductance of the solution and applying Equation [4]. The specific conductance could be obtained by using a conductance cell with electrodes 1 cm^2 in area and 1 cm apart. An exact knowledge of the size of the electrodes and their distance apart is hard to obtain by actual measurement, but the combination of these magnitudes, known as the *cell constant*, is obtained by introducing into the cell a solution of the known specific conductance (usually 0.1 N potassium chloride). The conductance is then measured and the cell constant is calculated as

$$\kappa = \text{observed conductance} \times \text{distance between electrodes}/\text{area}$$

$$\kappa = \text{observed conductance} \times \textit{cell constant}$$

Conductance Measurement and Evaluation of Formation Constant K$_f$ (Takeda et al., 1991)

A solution in which ions are dissolved is capable of conducting an electric current. The extent of conductivity of such solution depends on, among other factors, the concentration, ionization, and solvation of the ions. The latter two factors change in the presence of a crown ether ligand. By measuring the change in conductivity of a metal salt solution to which crown ether is added, valuable information is obtained about the cation-crown ether interaction. Conductometry gives information about the stoichiometry of complexation and affinity of ligands for cations. A conductometric experiment is generally carried out by titrating a metal salt solution with a crown ether ligand in a suitable solvent system. Such a titration may give rise to two different conductometric effects. In the case in which the applied metal salt is fully dissociated in the applied solvent, complexation by a crown ether leads to a large cationic complex of metal ion and crown ether. This complex can have less mobility in solution than the uncomplexed metal cation, resulting in diminished capacity of charge transport and hence diminished conductivity of the solution. In the case when a crown ether is titrated to a metal salt solution in which the metal salt is not fully dissociated, the opposite conductometric effect is observed. Since the crown ether coordinates to the metal cation, leaving the anion undisturbed, enhanced dissociation of the metal salt results, and hence the conductivity of the solution is increased.

In some cases there is a negligible change in conductance in spite of an increase in the crown ether concentration; consequently, conductometric determination of the complex formation constant becomes impossible. Two factors are responsible for a negligible change in conductance in spite of an increase in the crown ether concentration: (a) when hardly any complexation occurs between crown compounds and cations, and (b) mobilities of a resulting cation-crown compound complex and the corresponding cation are equal at the same concentration. The first factor is responsible in the majority of cases. When conductance measurements are made at very low concentration in solvents of relatively high dielectric constants, corrections for viscosity changes and association between a cation, i.e., a cation-crown compound complex, an uncomplexed cation, and an anion are neglected.

The following mathematical treatment to calculate the formation constant is based on Evans et al. (1972) and Nedler and Mead (1965).

For a 1:1 metal-ligand binding, the equilibrium can be described as

$$\mathrm{M}^+ + L \Leftrightarrow \mathrm{ML}^+ \qquad [5]$$

where M$^+$, L, and ML$^+$ represent the free solvated cation, the free ligand, and the complex respectively. The thermodynamic equilibrium constant K_f for the association is given by

$$\mathrm{K_f} = \frac{\left[ML^+\right] f\left(ML^+\right)}{\left[M^+\right]\left[L\right] f\left(M^+\right) f\left(L\right)} \qquad [6]$$

where$[ML^+]$, $[M^+]$, [L], and f represent the equilibrium molar concentrations of the complex, the free cation, the free ligand, and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, where the ionic strength is less than 0.001 M, the activity coefficient of the uncharged ligand $f(L)$ can be reasonably assumed to be unity. The use of the Debye-Hückel limiting law of electrolytes leads to the conclusion that$f(ML^+) \cong f(M^+)$; thus, Equation [6] reduces to

$$K_{\mathrm{f}} = \frac{[ML^+]}{[M^+][L]} \qquad [7]$$

If α is the fraction of total metal cation that is uncomplexed with the ligand, then the following equations result:

$$[M^+] = \alpha\,[M]_t \qquad [8]$$

$$\left[ML^+\right] = (1-\alpha)\,[M]_t \qquad [9]$$

$$[L] = [L]_t - (1-\alpha)\,[M]_t \qquad [10]$$

where$[M]_t$, $[L]_t$, $\left[M^+\right]$, $\left[ML^+\right]$, and $[L]$ represent the concentration (in molarity) of total cation, total ligand, free uncomplexed cation, and the complex and free solvated ligands respectively.

The dilute conditions used make it possible to neglect ion aggregation and corrections for viscosity changes. The molar conductivities Λ can be calculated by using the following equation:

$$\Lambda = \frac{1000\kappa}{[M]_t} \qquad [11]$$

where κ is the conductivity of the test solution in Siemens.cm^{-1}. On the other hand, Λ can be related to α by the following equation,:

$$\Lambda = \alpha\Lambda_{M^+} + (1-\alpha)\Lambda_{ML} \qquad [12]$$

where Λ_{M^+} and Λ_{ML} represent the molar conductivities of the ligand free metal salt solution and the complexed cation solution at the same concentration, respectively. Rearranging Equation [12] gives an expression for α as

$$\alpha = \frac{\Lambda - \Lambda_{ML}}{\Lambda_{M^+} - \Lambda_{ML}} \qquad [13]$$

Substituting Equations [8] and [9] into Equation [7] gives the following equation:

$$K_{ML^+} = \frac{(1-\alpha)}{\alpha\,[L]} \qquad [14]$$

Substituting the value of α from Equation [13] in [14]:

$$K_{ML^+} = \frac{\Lambda_{M^+} - \Lambda}{\Lambda - \Lambda_{ML}\,[L]} \qquad [15]$$

Further, substitution of Equation [13] into Equation [10] gives

$$[L] = [L]_t - \left(\frac{\Lambda_{M^+} - \Lambda}{\Lambda_{M^+} - \Lambda_{ML}}\right)[M]_t \qquad [16]$$

Substitution of Equation [16] into Equation [15] gives the expression for K_{ML^+}:

$$K_{ML^+} = \frac{\Lambda_{M^+} - \Lambda}{\Lambda - \Lambda_{ML}\left\{[L]_t - \left(\frac{\Lambda_{M^+} - \Lambda}{\Lambda_{M^+} - \Lambda_{ML}}\right)[M]_t\right\}} \qquad [17]$$

The above equation can be simplified as

$$K_{ML^+} = \frac{a_1 a_2}{a_3 a_2 [L]_t - a_3 a_1 [M]_t} \qquad [18]$$

where $a_1 = \Lambda_{M^+} - \Lambda$, $a_2 = \Lambda_{M^+} - \Lambda_{ML}$, and $a_3 = \Lambda - \Lambda_{ML}$.

Here, Equation [18] can be rearranged to form a quadratic equation in terms of Λ as

$$a\Lambda^2 + b\Lambda + c = 0 \qquad [19]$$

where $a = K_{ML^+}[M]_t$, $b = (K_{ML^+}[L]_t + 1) - [M]_t K_{ML^+}(\Lambda + \Lambda_{ML})$, and $c = [M]_t K_{ML^+}\Lambda\Lambda_{ML} - a_2([L]_t K_{ML^+}\Lambda + \Lambda_{ML})$.

Thermodynamic Criteria for Complexation (Arnaud-Neu et al., 2003)

The two fundamental equations $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$ are useful in comparing the contributions of enthalpy and entropy towards the stability of different complexes. The enthalpy contribution can be obtained experimentally by calorimetric titration or through van't Hoff plots, although the latter tends to be less reliable, especially if ΔH is not satisfactorily constant over the temperature range investigated or the temperature range investigated is not sufficient. Complexation enthalpy changes are mainly related to: (i) cation-crown interactions, (ii) solvation of the metal ion, the crown, and the metal complexes formed in solution, (iii) repulsion between neighboring donor atoms, and (iv) steric deformation of the crown. Entropy changes are linked to: (i) change in the number of particles involved in the complexation process, and (ii) conformational changes of the crown ether accompanying the complexation. In general, there is an enthalpy-driven stabilization, but in some cases, as for highly solvated cations for which complete or partial desolvation is an important step of the complexation process, the stabilization may be entropy-driven. There is often an entropy-enthalpy compensation effect, typical of alkali and alkaline earth

TABLE 1
Size of cations and crown ethers

Cations	Ionic radius (Å)	Cations	Ionic radius (Å)	Crown ether	Radius (Å)
Li^+	0.74	Ca^{2+}	1.00	12C4	0.60–0.75
Na^+	1.02	Hg^{2+}	1.02	15C5	0.85–1.1
K^+	1.38	Sr^{2+}	1.18	16C5	0.9–0.95
Rb^+	1.49	Pb^{2+}	1.19	18C6	1.3–1.6
Cs^+	1.70	Ba^{2+}	1.35	21C7	> 1.75
Ag^+	1.15	$UO_2{}^{+2}$	1.80	24C8	> 2.0
Tl^+	1.50	Fe^{3+}	0.64	30C10	2.8–3.2
H_3O^+	1.70	Cr^{+3}	0.80		
$NH_4{}^+$	1.48	Au^{3+}	0.84		
Mn^{+2}	0.67	Er^{3+}	0.89		
Ni^{+2}	0.69	Y^{+3}	0.90		
Mg^{+2}	0.72	Eu^{3+}	0.95		
Cu^{+2}	0.73	La^{+3}	1.03		
Zn^{+2}	0.74	Ce^{3+}	1.08		
Co^{+2}	0.75	Sn^{4+}	0.72		
Cd^{2+}	0.95				

Ionic radii and crown ether cavity size are from Arnaud-Neu et al. (2003), Liu et al. (2003), Izatt et al. (1985), and Khopkar (2008).

TABLE 2
Solvent properties

Solvents	ε_r	$\mu .10^{30}$ (Cm)	DN	AN	Specific gravity at 20/4, (g/cm^3)
DCE	10.36	6.1	0.0	16.7	1.270
NM	35.87	12.0	2.7	20.5	1.137
NB	34.78	14.0	4.4	14.8	1.204
BN	25.2	0.0	11.9	8.2	1.000
ACN	35.94	13.1	14.1	19.3	0.782
Di	2.3	1.5	14.8	10.8	1.033
PC	65.1	16.7	15.1	18.3	1.200
AC	20.56	9.0	17.0	12.5	0.790
EtOAc	6.02	5.9	17.1	9.2	0.895
H_2O	78.36	6.2	18–33[a]	54.8	0.998
MeOH	32.66	9.6	19.0	41.3	0.794
THF	7.58	5.8	20.0	8.0	0.888
DMF	36.71	12.7	26.6	16.0	0.945
DMA	38.9	12.4	27.8	13.6	0.945
DMSO	46.45	13.5	29.8	19.3	1.101
EtOH	24.55	5.5	31.5	37.1	0.789

ε_r = relative permittivity (dielectric constant) of the solvents.
μ = dipole moments in Coulomb meter (Cm), measured in benzene, tetrachloromethane, 1,4-dioxane, or n-hexane at 20°. . 30°C (Reichardt, 2003).
DN = Gutmann donor number, defined as the negative enthalpy value for the 1:1 adduct formation between a given electron-pair donor solvent and the standard Lewis acid SbCl5, in dilute solution in the noncoordinating solvent 1,2-dichloroethane, for which a DN of zero is assigned.
AN measures the power of a given solvent to accept electron pairs as a Lewis acid and is a dimensionless number.
[a] Depends on how it is assessed, as water reacts with $SbCl_5$.
Values for different solvent properties are obtained from Arnaud-Neu et al. (2003), Gutmann (1978), and (Reichardt, 2003).

cations, in which an enthalpy gain is accompanied by an entropy loss, or vice versa.

Factors Governing Complexation and Selectivity of Crown Ethers (Arnaud-Neu et al., 2003)

The factors responsible for the stability of cation-crown complexes can be classified as (a) relative size of a cation and crown compound cavity, (b) cation charge, (c) cation type, (d) counter anion, (e) number of donor atoms, (f) type of donor atom, (g) electron density of crown cavity, (h) crown substituents, (i) crown ether-ring flexibility, and (j) physical properties of a solvent. The major contributing factor towards binding and selectivity is attributed to size compatibility of the cation and the crown ether cavity. The cations that match the cavity size of the macrocycle are located in its center and optimize the interactions with the oxygen heteroatoms. The dimensions of the cations and the majority of crown ethers covered in this article are listed in Table 1 (Arnaud-Neu et al., 2003; Liu et al., 2003; Izatt et al., 1985; Khopkar, 2008), while the solvent properties are summarized in Table 2 (Arnaud-Neu et al., 2003; Gutmann, 1978; Reichardt, 2003). The size effect is the biggest contributor towards the stability of small cations that completely enter the cavity; however, other factors are more important for larger cations. The size adequacy concept in combination with the flexibility of the crown due to the presence of substituents allows for accommodation of medium- and large-size cations at some expense of energy. For example, 12C4 or 15C5 has cavities too small to accommodate some cations like Rb^+ or Cs^+. In such cases, the complexation takes place outside the circular bi-dimensional cavity, and the cation completes its coordination sphere with a second crown molecule to form a "sandwich complex." On the other hand, very large crown ethers like 30C10 are able to wrap around a small cation like Na^+ completely, so as to optimize the cation interactions with the donor sites. Thus, selectivity profiles of rigid crown ethers present peak selectivities, whereas more flexible crowns lead to plateau selectivities with a general decrease of the extent of complexation (Lamb et al., 1979).

The cation-crown binding energy also depends on the number of oxygen heteroatoms present in the macrocyclic structure. This factor determines not only the size of the cavity but also the bond energies with the cation. Conformational changes of the crown as well as the size of the rings formed upon complexation are the additional factors responsible for the stability of complexes. The nature of the cations always plays an important role. The alkali and alkaline earth metal ions are considered as "hard" acids in the Pearson classification (Pearson, 1963), the bonding with the oxygen heteroatoms is essentially electrostatic in nature, and, therefore, the charge density of the cations is dominant. Metal ions like Ag^+, Pb^{2+}, and Tl^+ are potentially softer and should, in principle, lead to less stable complexes with oxygen donor sites. However, their high polarizability and the covalent character of the bonds can lead in some cases to highly stable complexes.

One of the most important factors that needs significant consideration is the "solvation effect," which involves solvation of the crown compound, the cation, and the complex. In sufficiently polar solvents, where the interactions with the counter ions are negligible, stability of the complex is related to the standard Gibbs free energies of solvation of the different species by the following equation:

$$-\mathrm{RT}\ln \mathrm{K} = \Delta_{\mathrm{bind}}\mathrm{G}^\circ + \Delta_{\mathrm{solv}}\mathrm{G}^\circ(\mathrm{MC}^{n+}) - \Delta_{\mathrm{solv}}\mathrm{G}^\circ(\mathrm{M}^{n+}) - \Delta_{\mathrm{solv}}\mathrm{G}^\circ(\mathrm{C}) - \Delta_{\mathrm{conf}}\mathrm{G}^\circ(\mathrm{C})$$

where the terms on the right refer to the free energy for cation-crown bonding, for solvation of the cation-crown complex, for cation solvation, for solvation of crown, and for crown conformational changes (Srivanavit et al., 1977). Solvation of the cation depends strongly on the ionic size and on the nature of the solvent. Some of the important solvent parameters that affect complexation include the relative permittivity (dielectric constant) of the solvents, their dipole moments, and, in particular, the Gutmann donor numbers, DN, which are a measure of the electron-donating properties of a solvent (Gutmann, 1978). The donor number is defined as the negative enthalpy value for the 1:1 adduct formation between a given electron-pair donor solvent and the standard Lewis acid $SbCl_5$, in dilute solution in the non-coordinating solvent 1,2-dichloroethane, for which a DN of zero is assigned. DN reflects the ability of the solvent to solvate cations and other Lewis acids (Reichardt, 1979; Chipperfield, 1999). DN values range from zero, for solvents like hexane or tetrachloromethane, to 61.0 for triethylamine. In general, it is observed that the smaller the values of DN, the more stable the cation-crown ether complex.

The present article summarizes a comprehensive literature review through April 2011 on the complexation of cation with different crown ethers and their derivatives, studied by conductometry. The salient features of these methods like cations studied, solvent(s) used, stability constants at different temperatures, and thermodynamic parameters are presented in Tables 3–9[1]. The discussion that follows has been segregated broadly into four parts, which deal with univalent, bivalent, and tetravalent cation and other bulky cation complexes with various crown ethers. The factors affecting complexation like the nature of the solvent (polarity, donicity, and solvating power), size of the cation, type of counter anion, size of the crown macrocycle, number of donor atoms, type of donor atom, effect of substituents on the crown ether, flexibility, and effect of temperature are discussed. To limit the length of the article, the results of selected references are critically evaluated, stressing the above-mentioned criteria.

DISCUSSION

Crown Complexes with Monovalent Cations (H_3O^+, $NH_4{}^+$, Li^+, Na^+, K^+, Rb^+, Ag^+, Cs^+, and Tl^+)

Complex formation of hydronium ion (from $HClO_4$) with several crown ethers in DCM, ACN, and NB solutions has been studied by Amini and Shamsipur (1992). The stability constants of the resulting 1:1 complexes in ACN and NB were found to vary in the order 18C6 > DB30C10 > DC18C6 > DB18C6 > DB21C7 > DB24C8 > B15C5. However, in NB an unusual conductance behavior was observed for the complexation of 18C6 and DC18C6 with H_3O^+ ion. The unexpected increase in conductance from mole ratio (C_{crown}/C_{H3O+}) of 1 up to mole ratio of 2 was ascribed to the ion pairing of hydronium perchlorate, brought about by the addition of crown ether, and/or the formation of a second sandwich adduct with a 2:1 (crown/H_3O^+) stoichiometry in the solvent system used. This behavior may be rationalized by considering the following equilibria in NB solution:

$$\begin{aligned} H_3O^+, ClO_4^- &\leftrightarrow H_3O^+(\mathrm{crown})\,ClO_4^- \\ &\leftrightarrow H_3O^+(\mathrm{crown})_2\,ClO_4^- \end{aligned}$$

In contrast to ACN and NB, the complexation process in DCM resulted in the dissociation of the ion-pairs formed, which was evident from the large conductance values after addition of crown ethers to the hydronium perchlorate solutions. In ACN, the stability of hydronium ion complexes with smaller crown ether (15C5) was much weaker than with 18C6 as the cavity size of 15C5 is too small for the ionic size of H_3O^+ ion (3.4 Å). The stability of H_3O^+ complexes with larger crown ethers varies in the order DB30C10 > DB21C7 > DB24C8. It is well known that that large crown ethers such as 30C10 are flexible enough to wrap around the cations of proper size so as to encapsulate them in a three-dimensional structure, allowing the oxygen atoms in the ring to participate in bond formation (Shamsipur et al., 1980).

Among other cations, ammonium ions have special significance as they play a fundamental role in different biological processes, and the study of thermodynamics of its complexes with crown ethers has been of special interest (Lehninger, 1984; Frensdorff, 1971; Cram and Cram, 1974). There are at least five different factors that contribute towards the stability of ammonium and alkylammonium complexes with macrocyclic ligands. These include the cavity size of the crown ether, the number and type of donor atoms in the ring, the number and nature of alkyl groups, the number of N-H bonds in the cation available for H-bonding, and the solvation energies of the species in different solvent systems involved in the complexation reactions. Hasani and Shamsipur (1994) studied the interaction of $NH_4{}^+$ ions with several crown ethers in ACN solution. The stability constants of

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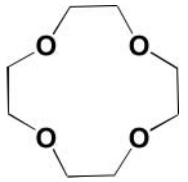
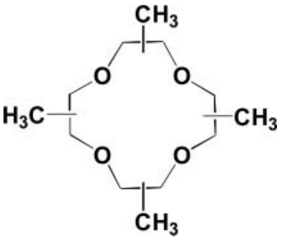
[1] Tables 8 and 9 are supplemental files available online.

TABLE 3
Cation complexes with 12C4 and its derivatives



12-crown-4

Cation	Solvent		logK			−ΔG[a]/ΔH[a]/ΔS[b]	References
			25°C				
Li^+	ACN		3.40			NA	Hopkins and Norman (1980)
	MeOH		< 0.0			NA	Zollinger et al. (1987)
	MeOH		1.32				D'Aprano et al. (1995)
	ACN		3.14				D'Aprano et al. (1995)
Na^+	ACN		3.32			NA	Hopkins and Norman (1980)
	MeOH		2.05, 1.73[c]			NA	Zollinger et al. (1987)
	MeOH		1.09				D'Aprano et al. (1995)
	ACN		4.42				
K^+	MeOH		1.73, 0.86[c]			NA	Zollinger et al. (1987)
	MeOH		1.41			NA	D'Aprano et al. (1995)
	ACN		2.23				
Rb^+	MeOH		1.65, 0.87[c]			NA	Zollinger et al. (1987)
Cs^+	MeOH		1.60, 0.74[c]			NA	Zollinger et al. (1987)
Tl^+	ACN		4.01			NA	Jabari et al. (1993)
	AC		3.12				
	DMF		[d]				
Ag^+	ACN		[d]			NA	Jabari et al. (1993)
	AC		[d]				
	DMF		[d]				
NH_4^+	NB		2.72			NA	Hasani and Shamsipur (1993)
	ACN		<2				
	DMF		<2				
		20°C	**25°C**	**30°C**	**35°C**		
$Ph(CH_3)_3N^+I^-$	H_2O	1.96	2.00	2.04	2.08	—/14.2/86	Marji et al. (1999)
$(C_2H_5)_4N^+Br^-$	H_2O	1.96	2.00	2.05	2.08	—/13.7/84	
$(C_2H_5)_3HN^+Cl^-$	H_2O	2.72	2.76	2.78	2.82	—/10.9/89.9	



Tetramethyl 12-crown-4

Cation	Solvent		logK			−ΔG[a]/ΔH[a]/ΔS[b]	References
			25°C				
Li^+	ACN		3.46			—/—/—/	Hopkins and Norman (1980)

[a] KJ/mol.

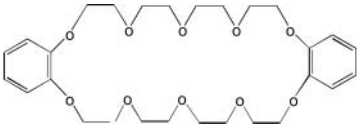
[b] J/mol.K.

[c] Indicates value of $\log K_2$, second formation constant.

[d] Complex not formed.

NA: not available.

TABLE 4
Cation complexes with DB30C10 and its derivatives



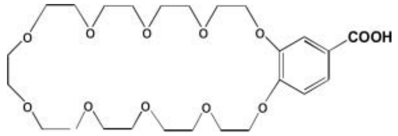
Dibenzo-30-crown-10

Cation	Solvent		logK			$-\Delta G^a/\Delta H^a/\Delta S^b$	References
			25°C				
Li^+	DCE		4.68			NA	Amini and Shamsipur (1991)
	NM		4.49			NA	
Na^+	DCE		5.25			NA	Amini and Shamsipur (1991)
	NM		4.66			NA	
	ACN		3.14			NA	
	AC		3.04			NA	
Na^+	NM		6.73			NA	Katsuta et al. (2005b)
K^+	DCE		5.96			NA	Amini and Shamsipur (1991)
	NM		5.37			NA	
	ACN		4.36			NA	
	AC		4.39			NA	
	DMF		3.13			NA	
K^+	NM		6.38			NA	Katsuta et al. (2005b)
Rb^+	DCE		5.60			NA	Amini and Shamsipur (1991)
	NM		5.26			NA	
	ACN		4.76			NA	
	AC		4.26			NA	
Rb^+	NM		5.55			NA	Katsuta et al. (2005b)
		15°C	**25°C**	**35°C**	**45°C**		
Rb^+	ACN	4.83	4.64	4.50	4.25	—/−33/−21	Shamsipur and Saeidi (2000)
Cs^+	DCE		4.92			NA	Amini and Shamsipur (1991)
	NM		4.56			NA	
	ACN		3.81			NA	
	AC		3.70			NA	
Cs^+	NM		4.34			NA	Katsuta et al. (2005b)
		15°C	**25°C**	**35°C**	**45°C**		
Cs^+	ACN	4.33	4.20	4.08	3.63	—/−38/−49	Shamsipur and Saeidi (2000)
Ag^+	DCE		5.27			NA	Amini and Shamsipur (1991)
	NM		4.79			NA	
	ACN		4.22			NA	
	AC		3.88			NA	
Ag^+	AC		3.53			NA	Jabari et al. (1993)
	DMF		<2			NA	
Tl^+	DCE		6.30			NA	Amini and Shamsipur (1991)
	NM		5.48			NA	
	ACN		5.15			NA	
	AC		5.03			NA	
Tl^+	ACN		5.66			NA	Jabari et al. (1993)
	AC		5.39			NA	
	DMF		—			NA	

(Continued on next page)

TABLE 4
Cation complexes with DB30C10 and its derivatives *(Continued)*

Cation	Solvent	logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	DMF-ACN (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**		
Tl^+	Pure DMF	2.74	2.48	2.19	<2	—/−46/−109	Khayatian et al. (2003)
	80:20	3.17	2.92	2.53	<2	—/−54/−127	
	60:40	3.58	3.35	2.90	2.39	—/−70/−173	
	40:60	4.06	3.81	3.30	2.75	—/−77/−189	
H_3O^+	ACN		4.54			NA	Amini and Shamsipur (1992)
	NB		> 6			NA	
NH_4^+	NB		> 6			NA	Hasani and Shamsipur (1993)
	ACN		5.13			NA	
	DMF		<2			NA	
		5°C	**15°C**	**25°C**	**35°C**		
NH_4^+	ACN	5.46	5.28	5.13	—	—/26.2/10.2	Hasani and Shamsipur (1994)



4′-Carboxy-benzo-30-crown-10

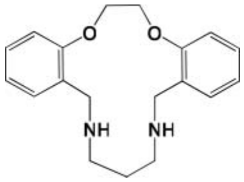
Cation	Solvent	logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
		5°C	**15°C**	**25°C**	**35°C**		
Na^+	ACN	4.42	4.25	4.01	3.82	—/−33.4/−35	Rouhollahi et al. (1999)
K^+	ACN	6.11	5.66	5.31	4.96	—/−67.2/−125	
Rb^+	ACN	5.79	5.38	5.06	4.78	—/−55.0/−87	
Cs^+	ACN	5.16	4.90	4.63	4.39	—/−42.3/−53	
Tl^+	ACN	6.34	5.90	5.52	5.06	—/−70.6/−132	

[a] KJ/mol.
[b] J/mol.K.
NA: not available.

the resulting 1:1 complexes at various temperatures varied in the order DC18C6 > 18C6 > DB30C10 > DB21C7 > DB24C8 > DB18C6 > 15C5 > B15C5.

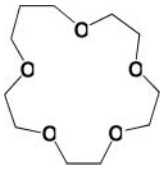
Compared to alkali and alkaline earth cations, NH_4^+ ions have two distinct features that can explain the observed stability trend. The first is the hydrogen bonding ability with the donor atoms of the macrocycles, and, second, it has a tetrahedral arrangement of hydrogen atoms about the central nitrogen atom, which can lead to special stereochemical arrangements. The preferred tetrahedral arrangement in NH_4^+ ion has also been shown by ab initio calculations (Pullman and Armbruster, 1975). The cavity size and the conformations of DB18C6 and 18C6 are most suitable for NH_4^+ ion to bind with three out of six available oxygen atoms to form a stable complex. Thus, one of the four NH_4^+ hydrogen atoms protrudes upward from the center of and perpendicular to the plane of the donor oxygen atoms in the ring. Further, due to the electron donating effect of cyclohexyl groups and electron withdrawing ability of the benzo groups, the stability of the NH_4^+-DC18C6A complex is much higher than that of the NH_4^+-DB18C6 complex. On the other hand, the cavity size of 15C5 is too small to accommodate the NH_4^+ ion, thus they form the weakest complex of all the crown ethers studied. Comparing the larger cavity size crown ethers (DB21C7, DB24C8, and DB30C10) it is apparent that NH_4^+ ion fits more comfortably into the cavity of DB21C7 through hydrogen bonding than that of DB24C8. However, DB30C10A, although having the largest cavity size in the series, forms a much more stable complex than DB21C7 or DB24C8 due to its high flexibility. DB30C10 can easily twist around the NH_4^+ ion to form a stable “wraparound” complex, wherein all 10 oxygen atoms can more or less play some part in bond formation. A conductance study of the interaction between substituted NH_4^+ ions with 12C4, 15C5, and 18C6 in aqueous solutions is reported at different temperatures (Marji et al., 1999). The stability of these complexes depends mainly on the number of hydrogen bonds between N-H and the ether oxygen atoms. The formation constants ($\log K_f$) of the 1:1 complexes at different temperatures varied in the order 18C6 > 15C5 > 12C4 for the same salt, while with the same crown ether the formation constants followed the order $(C_2H_5)_3NHCl > (C_2H_5)_4NBr > (CH_3)_3NPhI$.

TABLE 5
Cation complexes with other crown ethers



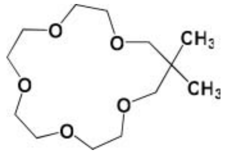
Dibenzo-diaza-15-crown-4

Cation	Solvent	logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
		20°C	**25°C**	**30°C**	**35°C**		
Ag^+	ACN	5.61	5.60	5.59	5.58	—/−3.45/41.5	Marji and Taha (2000)
Ni^{2+}	ACN	5.21	5.18	5.15	5.12	—/−10.4/64.3	
Fe^{+3}	ACN	4.94	4.93	4.92	4.90	—/−4.50/79.2	



16-crown-5

Cation	Solvent	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
		25°C		
Li^+	ACN	4.4	NA	Takeda et al. (1992)
	PC	3.2	NA	
	MeOH	—	NA	
Na^+	ACN	5.3	NA	
	PC	5.7	NA	
	MeOH	4.1	NA	
K^+	ACN	3.5	NA	
	PC	3.3	NA	
	MeOH	2.9	NA	
Rb^+	ACN	2.9	NA	
	PC	2.5	NA	
	MeOH	2.4	NA	
Cs^+	ACN	2.3	NA	
	PC	2.1	NA	
	MeOH	2.0	NA	
Tl^+	H_2O	0.73	NA	Takeda and Kimura (1991)
Sr^{+2}	H_2O	2.08	NA	
Ba^{+2}	H_2O	1.84	NA	



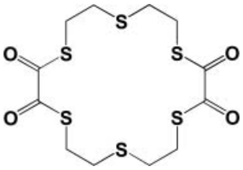
Dimethyl-16-crown-5

Cation	Solvent	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
		25°C		
Li^+	ACN	4.1	NA	Takeda et al. (1992)
	PC	3.13	NA	
Na^+	ACN	4.3	NA	
	PC	4.0	NA	

(Continued on next page)

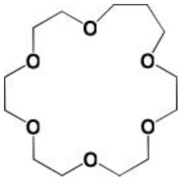
TABLE 5
Cation complexes with other crown ethers *(Continued)*

Cation	Solvent	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	MeOH	3.53	NA	
K^+	ACN	3.13	NA	
	PC	2.89	NA	
	MeOH	2.43	NA	
Rb^+	ACN	2.64	NA	
	PC	2.14	NA	
	MeOH	2.05	NA	
Cs^+	ACN	2.40	NA	
	PC	1.61	NA	
	MeOH	1.73	NA	



Hexathia-18-crown-6-tetraone

Cation	Solvent	**15°C**	**25°C**	**35°C**	**45°C**	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
Co^{+2}	ACN	5.12	4.86	4.63	4.40	27.7/ − 41.9/ − 47.6	Ganjali et al. (1998)
Ni^{+2}	ACN	5.25	4.98	4.79	4.53	28.4/ − 41/ − 43	
Cu^{+2}	ACN	5.35	5.12	4.87	4.66	29.2/ − 40.7/ − 39	
Zn^{+2}	ACN	5.04	4.76	4.52	4.25	27.1/ − 45.8/ − 62	
Cd^{+2}	ACN	6.12	5.67	5.27	4.85	32.3/ − 73.9/ − 139	
Pb^{+2}	ACN	> 7	6.87	6.13	5.44	39.2/ − 121/ − 290	
Hg^{+2}	ACN	> 8	7.5	6.58	6.31	43/−108/−240	



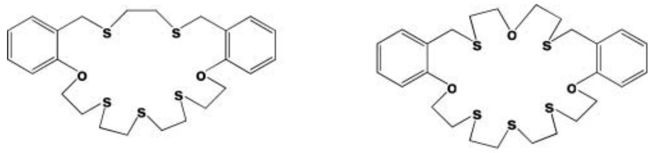
19-crown-6

Cation	Solvent	**25°C**	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
Li^+	H_2O	0.76	NA	Takeda et al. (1999)
	ACN	3.73	NA	Takeda et al. (2000)
	PC	2.29	NA	
	MeOH	—	NA	
	DMF	—	NA	
	DMSO	1.72	NA	
Na^+	H_2O	0.93	NA	Takeda et al. (1999)
	ACN	4.31	NA	Takeda et al. (2000)
	PC	4.49	NA	
	MeOH	2.83	NA	
	DMF	—	NA	
	DMSO	—	NA	
K^+	H_2O	1.27	NA	Takeda et al. (1999)
	ACN	4.62	NA	Takeda et al. (2000)
	PC	4.49	NA	
	MeOH	4.21	NA	

(Continued on next page)

TABLE 5
Cation complexes with other crown ethers *(Continued)*

Cation	Solvent	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	DMF	2.60	NA	
	DMSO	2.01	NA	
Rb$^+$	H_2O	1.33	NA	Takeda et al. (1999)
	ACN	4.06	NA	Takeda et al. (2000)
	PC	3.72	NA	
	MeOH	3.76	NA	
	DMF	2.25	NA	
	DMSO	1.73	NA	
Cs$^+$	H_2O	0.71	NA	Takeda et al. (1999)
	ACN	3.29	NA	Takeda et al. (2000)
	PC	2.92	NA	
	MeOH	3.00	NA	
	DMF	1.89	NA	
	DMSO	1.54	NA	
Ag$^+$	H_2O	0.93	NA	Takeda et al. (1999)
Tl$^+$	H_2O	1.08	NA	
Ca^{+2}	H_2O	1.26	NA	
Sr^{+2}	H_2O	1.83	NA	
Ba^{+2}	H_2O	1.95	NA	
Cd^{+2}	H_2O	1.54	NA	
Pb^{+2}	H_2O	2.38	NA	



I II

Oxathiadibenzocrown ethers

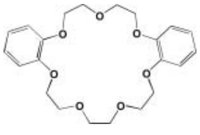
Cation	Solvent	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
		25°C		
Cu^{+2}-I	ACN	4.8	25.3/−48.9/−79.2	Ashram et al. (2010)
Zn^{+2}-I	ACN	3.5	24.7/−33.5/−29.7	
Cd^{+2}-I	ACN	3.0	16.8/85.3/342.2	
Pb^{+2}-I	ACN	5.0	29.3/−145.9/−391.4	
Cu^{+2}-II	ACN	4.2	23.8/−6.3/58.8	
Pb^{+2}-II	ACN	5.0	29.2/−120.9/−307.4	

[a] KJ/mol.
[b] J/mol.K.
NA: not available.

The thermodynamic data indicated that the complexes formed with different substituted ammonium ions were enthalpy destabilized but entropy stabilized. The reason for positive values for enthalpy ΔH was attributed to the strong competition of the solvent with crown molecules for the substituted ammonium cations. The higher $logK_f$ values for triethylammonium ion-crown ether complexes can be due to the tetrahedral arrangement around the central nitrogen atom such that the H$^+$ is directed towards the cavity of the crown ether.

To study the influence of other factors such as the size of macrocyclic cavity, steric effect of the alkyl group attached to the –NH_3^+ group, and Gutmann donicity of the solvents on the stability of ammonium ion-crown ether complexes, Sadeghi and Valavi (2003) investigated complex formation of ammonium and four *n*-alkylammonium perchlorate salts with DB18C6, DB21C7, and DB24C8 in ACN, NB, and NM solvents and their binary mixtures. All the investigated cations had a –NH_3^+ group that is expected to form a complex with crown ethers. In NB, the

TABLE 6
Cation complexes with DB21C7



Dibenzo-21-crown-7

Cation	Solvents	logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
			25°C				
Na^+	NM		6.04			NA	Katsuta et al. (2005a)
	ACN		2.96				
	PC		3.15				
		15°C	**25°C**	**35°C**	**45°C**		
Na^+	ACN	3.20	3.14	3.08	3.03	—/−10.0/26	Shamsipur et al. (2006)
K^+	NM		5.70			NA	Katsuta et al. (2005a)
	ACN		4.64				
	PC		4.53				
		15°C	**25°C**	**35°C**	**45°C**		
K^+	ACN	4.53	4.35	4.22	4.10	—/−24.7/01	Shamsipur et al. (2006)
Rb^+	NM		5.40			NA	Katsuta et al. (2005a)
	ACN		4.70				
	PC		4.58				
		15°C	**25°C**	**35°C**	**45°C**		
Rb^+	ACN	4.64	4.48	4.39	4.20	—/−24.9/03	Shamsipur et al. (2006)
Cs^+	NM		4.65			NA	Katsuta et al. (2005a)
	ACN		4.23				
	PC		3.97				
		15°C	**25°C**	**35°C**	**45°C**		
Cs^+	ACN	4.53	4.35	4.22	4.10	—/−24.7/01	Shamsipur et al. (2006)
Ag^+	AC		3.15			NA	Jabari et al. (1993)
	DMF		<2				
Tl^+	ACN		5.28			NA	Jabari et al. (1993)
	AC		5.07				
	DMF		—				
	DMF-ACN (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**		
Tl^+	Pure DMF	2.70	2.42	<2	<2	—/−7.8/−18.9	Khayatian et al. (2003)
	80:20	2.83	2.55	2.13	<2	—/−59/−151	
	60:40	3.18	2.84	2.65	2.38	—/−45/−97	
	40:60	3.54	3.29	3.05	2.69	—/−48/−101	
H_3O^+	ACN		4.20			NA	Amini and Shamsipur (1992)
	NB		> 5				
NH_4^+	NB		> 6			NA	Hasani and Shamsipur (1993)
	ACN		4.16				
	DMF		<2				
		25°C	**35°C**	**45°C**	**55°C**		
NH_4^+	ACN	4.16	4.07	3.97	3.83	—/−20.3/11.7	Hasani and Shamsipur (1994)
	ACN-DMSO (mole%)	**15°C**	**25°C**	**35°C**	**45°C**		
NH_4^+	Pure ACN	4.3	4.1	4.0	3.9	—/−22.9/2.3	Khayatian and Karoonian (2008)
	90:10	3.5	3.1	2.77	2.4	—/−63.7/−154.1	

(Continued on next page)

TABLE 6
Cation complexes with DB21C7 *(Conitnued)*

Cation	Solvents		logK			$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	80:20	<2	<2	<2	<2	—/—/—	
	NB-ACN (mole%)						
NH_4^+	Pure NB		>6			NA	Sadeghi and Valavi (2003)
	75:25		5.38			NA	
	50:50		5.03			NA	
	25:75		4.65			NA	
	Pure ACN		4.16			NA	
	NM-ACN (mole%)						
	Pure NM		5.88			NA	
	75:25		5.34			NA	
	50:50		4.74			NA	
	25:75		4.39			NA	
	Pure ACN		4.16			NA	
$MeNH_3^+$	Pure NB		5.58			29.4/−13.9/52.0	
	75:25		5.01			NA	
	50:50		4.58			NA	
	25:75		4.07			NA	
	Pure ACN		3.61			NA	
	NM-ACN (mole%)						
	Pure NM		4.68			26.6/−11.1/52.0	
	75:25		4.41			NA	
	50:50		4.19			NA	
	25:75		3.76			NA	
	Pure ACN		3.61			20.8/−18.5/7.72	
	NB-ACN (mole%)						
$EtNH_3^+$	Pure NB		5.22			30.6/−12.7/53.35	
	75:25		4.96			NA	
	50:50		4.30			NA	
	25:75		3.90			NA	
	Pure ACN		3.43			20.1/−18.2/6.34	
	NM-ACN (mole%)						
	Pure NM		4.65			26.4/−10.3/54.0	
	75:25		4.32			NA	
	50:50		4.05			NA	
	25:75		3.62			NA	
	Pure ACN		3.43			NA	
$PrNH_3^+$	NB-ACN (mole%)						
	Pure NB		5.19			27.9/−12.0/53.4	
	75:25		4.67			NA	
	50:50		4.21			NA	
	25:75		3.80			NA	
	Pure ACN		3.37			19.0/−20.5/−5.03	
	NM-ACN (mole%)						
	Pure NM		4.63			27.2/−10.6/55.7	
	75:25		4.31			NA	
	50:50		4.01			NA	
	25:75		3.61			NA	
	Pure ACN		3.37			NA	

(Continued on next page)

TABLE 6
Cation complexes with DB21C7 *(Conitnued)*

Cation	Solvents	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
$BuNH_3^+$	NB-ACN (mole%)			
	Pure NB	4.89	28.6/−13.9/49.3	
	75:25	4.64	NA	
	50:50	4.24	NA	
	25:75	3.86	NA	
	Pure ACN	3.40	19.4/−14.6/16.1	
	NM-ACN (mole%)			
	Pure NM	4.68	25.4/−11.3/47.3	
	75:25	4.41	NA	
	50:50	4.06	NA	
	25:75	3.64	NA	
	Pure ACN	3.40	NA	

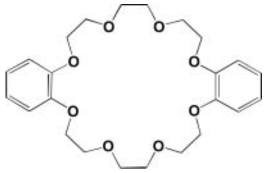
[a] KJ/mol.
[b] J/mol.K.
NA: not available.

trend in *log K_f* values was $NH_4^+ > CH_3NH_3^+ > C_2H_5\ NH_3^+ > C_3H_7NH_3^+ > C_4H_9NH_3^+$. Similar behavior was also seen in other solvents as well. With the increase in the size of the alkyl group, the steric factor comes into play, which results in the loss of complex stability. The methyl group has a destabilizing effect on the binding ability of the $CH_3NH_3^+$ cation because it causes elongation of the N…O distance, which might be responsible for a weaker complex than the NH_4^+ complex. Further, the *log K_f* value for the binding of NH_4^+ and other *n*-alkylammonium cations with 21C7 was considerably higher than that for 18C6 or 24C8. The size of 18C6 (diameter cavity 2.6 Å) is too small to produce a good fit for the NH_4^+ ion (ion diameter 2.9 Å), thus giving a weaker complex. When the cavity becomes large, i.e., in 24C8 (diameter cavity 4 Å), the cation cannot be sufficiently close to the oxygen atom and the *log K_f* value is decreased. In this study, all three solvents had nearly the same dielectric constant but with different donicities. In strong solvating solvents like ACN, the complex formation is poor due to a highly ordered and tightly bound solvating shell in the NH_4^+ ion, whereas in solvents with low donicity, such as NB and NM, a more stable complex was formed. Although the donor ability of NB is greater than that of NM, the stability constant of the crown ether-alkylammonium ion complex in NM was lower than that in NB. This behavior may be attributed to the fact that the NM molecules form a molecular complex with crown ether. In addition, in NB, the existence of the benzo group in the solvent may decrease the N…O interaction, so the stability constant of the complex increases. A similar study with alkyl ammonium ions was done by Hasani and coworkers (2003), wherein they used some aza-substituted crown ethers in binary ACN-DMSO mixtures. The formation constants of the 1:1 complexes, determined from the molar conductance-mole ratio plots, were found to vary in the order DBDA15C4 > DA18C6 > A18C6 > DBzDA18C6. In all cases, the substitution of alkyl groups on the ammonium ion decreased the stability of the resulting crown complexes in the following sequence: $NH_4^+ > CH_3NH_3^+ > C_2H_5\ NH_3^+ > (C_2H_5)_2\ NH_2^+ > (C_2H_5)_3NH^+$. It was observed that the solvating ability of the solvent, as expressed by the Gutmann donor number (Gutmann, 1978), plays an important role in this study. DMSO is a solvent of high solvating ability (DN = 29.8) that can compete strongly with macrocyclic ligands for the cations. Thus, addition of ACN, which has a low donicity (DN = 14.1) compared to DMSO, increased the extent of interaction between the donor atoms of the macrocycles and the cations. The molar conductance of both the solvated cations and complexes decreased in the order ACN > 80 wt.% ACN > 60% wt.% ACN > 40 wt.% ACN > 20 wt.% ACN > DMSO. This is due to both the higher viscosity and higher solvating ability of DMSO than ACN.

Solvent properties are considered as one of the major factors influencing the formation constants of cation-crown ether complexes. The complexation reactions between B15C5, B18C6, and DB18C6 with alkali and Ag^+ cation have been studied in a typical solvent, NM (Inerowicz et al., 2000). The formation constant of 1:1 and 1:2 complexes formed was determined and found to decrease with increasing cation size. In general the stability order was Li^+, $Ag^+ > Na^+ > K^+ > Rb^+ > Cs^+$ for all the crown ethers. NM is a peculiar solvent with a relative permittivity, $\varepsilon = 35.9$ and a very low Gutmann donor number (2.7). Thus, the solvent molecules compete poorly for position in the first coordination sphere of a metal cation due to its weak coordinating properties. This results in fairly high formation constants of the investigated complexes in the solvent.

The effect of substituent on the crown ether molecule and the role of solvent was investigated by studying the complexation of 4′-nitrobenzo-15-crown-5 with NH_4^+, Li^+, Na^+, and K^+ cations in ACN-MeOH binary solutions (Rounaghi and Razavipanah,

TABLE 7
Cation complexes with DB24C8 and its derivatives



Dibenzo-24-crown-8

Cation	Solvents	logK					−ΔG^a^/ΔH^a^/ΔS^b^	References
			25°C					
Na^+	PC		4.1				—/−37/−46	Takeda and Yano (1980)
	MeOH-H_2O (70:30, wt.%)		1.54				—/−32.4/−79.1	
Na^+	ACN		4.1					Takeda (1983)
		15°C	**20°C**	**25°C**	**30°C**	**35°C**		
Na^+	ACN	3.56	3.45	3.36	3.34	3.11	—/−34/−48	Tawarah and Mizyed (1989)
Na^+	NM			7.75			NA	Katsuta et al. (2004)
K^+	PC			3.7			—/−34.5/−44.4	Takeda and Yano (1980)
	MeOH			3.5			—/−35.3/−49.4	
	MeOH-H_2O (70:30, wt.%)			2.42			—/−35.7/−73.6	
K^+	ACN			3.8			NA	Takeda (1983)
		15°C	**20°C**	**25°C**	**30°C**	**35°C**		
K^+	ACN	4.03	3.87	3.86	3.81	3.67	—/−24/−8	Tawarah and Mizyed (1989)
	DMF-MeOH (mole%)	**15°C**	**25°C**	**35°C**	**45°C**	**55°C**		
K^+	Pure DMF	1.93	1.83	1.76	1.74	1.57	—10.46/−8.368/6.987	Rounaghi et al. (1999)
	61.1:38.9	2.30	2.24	2.13	2.10	2.04	12.67/−11.88/2.678	
	34.3:65.7	2.75	2.62	2.56	2.50	2.41	15.14/−14.97/0.543	
	14.9:85.1	3.56	3.43	3.27	3.17	3.11	19.54/−21.21/−5.61	
	Pure MeOH	3.75	3.70	3.47	3.32	3.19	20.71/27.36/−22.30	
K^+	NM		5.42					Katsuta et al. (2004)
	ACN-NM (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**			
K^+	Pure ACN	3.66	3.55	3.14	2.75		19/−53/−113	Taghdiri et al. (2007)
	80:20	4.04	3.88	3.75	3.63		22/−24/−6	
	60:40	4.09	3.99	3.85	3.65		23/−25/−10	
	40:60	4.38	4.23	4.12	1.00		24/−22/8	
Rb^+	PC		3.5				—/−32.9/−42.3	Takeda and Yano (1980)
	MeOH		3.8				—/−39.4/−57.7	
	MeOH-H_2O (70:30, wt.%)		2.55				—/−36.5/−73.6	
Rb^+	ACN		3.8				NA	Takeda (1983)
		15°C	**20°C**	**25°C**	**30°C**	**35°C**		
Rb^+	ACN	4.43	4.24	4.19	3.91	3.74	—/−58/−116	Tawarah and Mizyed (1989)
		15°C	**25°C**	**35°C**	**45°C**			
Rb^+	ACN	4.11	3.98	3.83	3.72		—/23/−2	Shamsipur and Saeidi (2000)
Rb^+	NM		4.92					Katsuta et al. (2004)
	ACN-NM (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**			
Rb^+	Pure ACN	3.67	3.56	3.26	2.94		20/−43/−79	Taghdiri et al. (2007)
	80:20	3.92	3.83	3.63	3.50		22/−26/−13	
	60:40	4.04	3.89	3.78	3.63		22/−23/−4	
	40:60	4.18	4.04	3.93	3.83		23/−20/−9	
Cs^+	PC		3.46				—/−32.3/−42.3	Takeda and Yano (1980)

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TABLE 7
Cation complexes with DB24C8 and its derivatives *(Continued)*

Cation	Solvents		logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	MeOH		3.84				—/−36.8/−49.0	
	MeOH-H_2O (70:30, wt.%)		2.48				—/−37.4/−77.8	
Cs^+	ACN		4.9				NA	Takeda (1983)
		15°C	**20°C**	**25°C**	**30°C**	**35°C**		
Cs^+	ACN	4.11	4.03	3.94	3.81	3.72	—/−34/−39	Tawarah and Mizyed (1989)
		15°C	**25°C**	**35°C**	**45°C**			
Cs^+	ACN	4.24	4.08	4.05	3.73		—/−27/−13	Shamsipur and Saeidi (2000)
Cs^+	NM		4.36					Katsuta et al. (2004)
	ACN-NM (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**			
Cs^+	Pure ACN	3.77	3.49	3.37	3.14		20/−37/−55	Taghdiri et al. (2007)
	80:20	3.76	3.62	3.40	3.14		30/−38/−26	
	60:40	4.04	3.87	3.77	3.61		23/−24/−3	
	40:60	4.14	3.99	3.85	3.70		24/−26/−4	
Ag^+	AC		4.20				NA	Jabari et al. (1993)
	DMF		<2					
	DMSO-H_2O (90:10, v/v)		1.75				NA	Ijeri and Srivastava (2003)
	PC-EC (20:80, mass%)		5.02				NA	Samant et al. (2003)
Tl^+	ACN		5.13				NA	Jabari et al. (1993)
	AC		4.90					
	DMF		—					
	DMF-ACN (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**			
Tl^+	Pure DMF	<2	<2	<2	<2		NA	Khayatian et al. (2003)
	80:20	2.36	2.17	2.27	<2		—/−6/−13.7	
	60:40	3.07	2.65	2.27	<2		—/−68/−177	
	40:60	3.22	2.89	2.70	2.39		—/−47/−101	
	ACN-NM (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**			
Tl^+	Pure ACN	4.76	4.63	4.49	4.35		25/−24/3	Taghdiri et al. (2007)
	80:20	4.74	4.60	4.42	4.30		26/−26/−0.2	
	60:40	4.95	4.79	4.74	4.53		25/−23/7	
	40:60	5.00	4.92	4.86	4.74		20/−15/20	
H_3O^+	ACN		4.00				NA	Amini and Shamsipur (1992)
	NB		> 5					
$NH_4{}^+$	NB		> 6				NA	Hasani and Shamsipur (1993)
	ACN		3.91					
	DMF		<2					
		5°C	**15°C**	**25°C**	**35°C**			
$NH_4{}^+$	ACN	4.15	3.98	3.91	3.75		—/21.3/2.8	Hasani and Shamsipur (1994)
	NB-ACN (mole%)		**25°C**					
$NH_4{}^+$	Pure NB		> 6				NA	Sadeghi and Valavi (2003)
	75:25		5.14				NA	
	50:50		4.75				NA	
	25:75		4.29				NA	
	Pure ACN		3.71				NA	
	NM-ACN (mole%)						NA	
	Pure NM		5.66				NA	
	75:25		4.40				NA	

(Continued on next page)

TABLE 7
Cation complexes with DB24C8 and its derivatives *(Continued)*

Cation	Solvents	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	50:50	4.74	NA	
	25:75	3.91	NA	
	Pure ACN	3.71	NA	
	NB-ACN (mole%)			
$MeNH_3^+$	Pure NB	5.00	29.1/−29.5/−1.34	
	75:25	4.23	NA	
	50:50	3.82	NA	
	25:75	3.27	NA	
	Pure ACN	2.77	15.7/−13.9/6.04	
	NM-ACN (mole%)			
	Pure NM	4.30	24.6/−18.3/21.2	
	75:25	3.88	NA	
	50:50	3.45	NA	
	25:75	3.11	NA	
	Pure ACN	2.77		
	NB-ACN (mole%)			
$EtNH_3^+$	Pure NB	4.97	28.0/−29.2/−4.03	
	75:25	4.18	NA	
	50:50	3.44	NA	
	25:75	3.06	NA	
	Pure ACN	2.80	16.0/−12.9/10.4	
	NM-ACN (mole%)			
	Pure NM	4.06	23.3/−13.8/31.2	
	75:25	3.73	NA	
	50:50	3.39	NA	
	25:75	3.09	NA	
	Pure ACN	2.08		
$PrNH_3^+$	NB-ACN (mole%)			
	Pure NB	4.67	27.1/−28.7/−5.37	
	75:25	4.14	NA	
	50:50	3.38	NA	
	25:75	2.95	NA	
	Pure ACN	2.76	16.0/−14.0/6.71	
	NM-ACN (mole%)			
	Pure NM	4.02	23.1/−18.5/15.4	
	75:25	3.68	NA	
	50:50	3.30	NA	
	25:75	3.07	NA	
	Pure ACN	2.76		
$BuNH_3^+$	NB-ACN (mole%)			
	Pure NB	4.64	26.7/−26.9/−0.671	
	75:25	4.12	NA	
	50:50	3.45	NA	
	25:75	2.92	NA	
	Pure ACN	2.72	15.8/−16.2/−1.34	
	NM-ACN (mole%)			
	Pure NM	4.12	23.4/−14.1/31.2	
	75:25	3.76	NA	
	50:50	3.48	NA	

(Continued on next page)

TABLE 7
Cation complexes with DB24C8 and its derivatives *(Continued)*

Cation	Solvents		logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	25:75		2.91				NA	
	Pure ACN		2.72					
Mg^{+2}	MeOH		2.71				NA	Chen et al. (1987)
Mg^{+2}	PC-EC (20:80, mass%)		4.83				NA	Samant et al. (2003)
	ACN-DMF (mole%)	**15°C**	**25°C**	**35°C**	**45°C**	**55°C**		
Mg^{+2}	90:10	2.20	2.2	2.29	2.37	2.54	12.55/14.64/92.05	Rounaghi et al. (2004)
	80:20	2.46	2.61	2.64	2.70	2.73	14.65/12.55/87.86	
	60:40	2.0	2.29	2.3	2.3	2.4	12.97/20.92/104.6	
	40:20	2.84	2.64	2.0	2.0	2.0	14.65/−33.47/−62.76	
	20:80	2.74	2.56	2.57	2.48	2.63	14.65/−12.55/12.55	
	Pure DMF	2.26	2.15	1.89	1.80	1.5	12.55/−33.47/−71.13	
Ca^{+2}	Pure ACN	3.21	3.44	3.47	3.56	3.71	20.92/20.92/92.05	
	80:20	3.0	2.86	2.6	2.93	2.85	16.74/−4.18/54.39	
	60:40	2.73	2.8	2.8	2.67	2.7	16.74/−2.5154.39	
	40:60	<1	<1	<1	<1	<1	NA	
	20:80	2.54	2.57	2.6	2.61	2.8	14.64/6.28/71.13	
	Pure DMF	2.76	2.3	2.62	2.2	2.2	12.97/−33.47/−66.94	
			25°C					
Ca^{+2}	MeOH		2.40				NA	Chen et al. (1987)
Ca^{+2}	PC-EC (20:80, mass%)		4.01				NA	Samant et al. (2003)
Mn^{+2}	$DMSO-H_2O$ (90:10, v/v)		1.85				NA	Ijeri and Srivastava (2003)
Co^{+2}	MeOH		2.71				NA	Chen et al. (1987)
Co^{+2}	$DMSO-H_2O$ (90:10, v/v)		1.54				NA	Ijeri and Srivastava (2003)
Ni^{+2}	MeOH		c				NA	Chen et al. (1987)
Ni^{+2}	$DMSO-H_2O$ (90:10, v/v)		1.55				NA	Ijeri and Srivastava (2003)
Cu^{+2}	MeOH		2.02				NA	Chen et al. (1987)
Cu^{+2}	$DMSO-H_2O$ (90:10, v/v)		1.74				NA	Ijeri and Srivastava (2003)
Cu^{+2}	PC-EC (20:80, mass%)		4.35				NA	Samant et al. (2003)
Zn^{+2}	MeOH		c				NA	Chen et al. (1987)
Zn^{+2}	$DMSO-H_2O$ (90:10, v/v)		1.57				NA	Ijeri and Srivastava (2003)
Sr^{+2}	PC-EC (20:80, mass%)		4.07				NA	Samant et al. (2003)
	ACN-DMF (mole%)	**15°C**	**25°C**	**35°C**	**45°C**	**55°C**		
Sr^{+2}	90:10	3.01	2.77	2.80	2.91	2.95	16.74/13.39/−121.34	Rounaghi et al. (2004)
	80:20	2.4	3.01	2.67	2.88	2.89	17.15/21.76/129.70	
	60:40	2.70	2.76	2.79	2.81	2.83	16.74/8.37/83.68	
	40:20	2.21	2.31	2.66	2.72	2.88	12.97/30.96/146.44	
	20:80	2.19	2.50	2.52	2.52	2.55	16.7/16.74/112.97	
	Pure DMF	2.46	2.51	2.90	2.80	2.93	14.64/22.18/100.42	
Ba^{+2}	Pure ACN	4.03	4.10	4.15	4.26	4.4	23.43/12.55/121.34	Rounaghi et al. (2004)
	80:20	3.3	3.34	3.38	3.28	3.33	17.57/2.09/66.94	
	60:40	2.97	3.08	3.03	3.12	3.09	16.74/6.28/75.31	
	40:60	2.5	2.87	3.09	3.06	3.05	16.74/20.92/129.79	
	20:80	2.69	2.84	2.87	2.89	3.03	16.74/13.39/100.41	
	Pure DMF	2.2	2.56	1.8	2.2	1.9	14.64/−12.55/8.37	
			25°C					
Ba^{+2}	PC-EC (20:80, mass%)		3.73				NA	Samant et al. (2003)
Pb^{+2}	MeOH		2.33				NA	Chen et al. (1987)
Pb^{+2}	$DMSO-H_2O$ (90:10, v/v)		2.97				NA	Ijeri and Srivastava (2003)

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TABLE 7

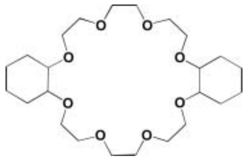
Cation complexes with DB24C8 and its derivatives *(Continued)*

Cation	Solvents	logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
$UO_2{}^{+2}$	EtOAc-ACN (mole%)	**15°C**	**25°C**	**35°C**	**45°C**		
	Pure EtOAc	e	e	e	e		Rounaghi et al. (2010)
	60:40	3.71	3.83	3.69	3.56	22/−80/d	
	40:60	3.41	3.35	3.23	3.27	19/−35/d	
	20:80	3.72	3.61	3.49	3.56	21/−11/d	
	Pure ACN	3.54	3.50	3.42	3.32	20/−13/23	
	DMF-ACN (mole%)	**15°C**	**25°C**	**35°C**	**45°C**		
	Pure DMF	2.54	2.70	3.20	2.80	15/d/d	
	70:30	2.80	2.74	2.80	2.70	16/−4/38	
	40:60	2.70	2.70	2.66	2.65	15/−3/43	
	20:80	2.83	2.78	2.71	2.74	16/−6/34	
	Pure ACN	3.54	3.50	3.42	3.32	20/−13/23	
	MeOH-ACN (mole%)	**15°C**	**25°C**	**35°C**	**45°C**		
	90:10	2.67	2.70	2.66	2.66	15/d/46	
	80:20	2.85	2.83	2.68	2.54	16/−18/d	
	60:40	2.82	2.81	2.54	2.83	16/d/d	
	30:70	2.82	2.83	2.78	2.75	16/d/d	
	Pure ACN	3.54	3.50	3.42	3.32	20/−13/23	
	EtOH-ACN (mole%)	**15°C**	**25°C**	**35°C**	**45°C**		
	90:10	2.68	2.82	2.68	2.79	16/d/d	
	70:30	2.36	2.33	2.55	2.58	13/d/d	
	50:50	2.55	2.49	2.25	2.82	14/d/d	
	30:70	2.70	3.02	2.88	2.71	17/d/d	
	Pure ACN	3.54	3.50	3.42	3.32	20/−13/23	
	PrOH-ACN (mole%)	**15°C**	**25°C**	**35°C**	**45°C**		
	Pure PrOH	2.53	2.06	2.70	2.70	NA	
	70:30	2.70	2.80	2.83	2.63	16/d/d	
	40:60	2.86	2.49	2.83	2.54	14/d/d	
	20:80	3.05	2.76	2.77	2.77	16/d/d	
	Pure ACN	3.54	3.50	3.42	3.32	20/−13/23	
Cr^{+3}	DMSO-H_2O (90:10, v/v)			3.16		NA	Ijeri and Srivastava (2003)
Fe^{+3}	DMSO-H_2O (90:10, v/v)			3.45		NA	Ijeri and Srivastava (2003)
	MeOH-DMF (mole%)	**15°C**	**25°C**	**35°C**	**45°C**		
Y^{+3}	Pure MeOH	2.82	2.85	2.91	2.95	16.26/7.83/8079	Rounaghi et al. (2009)
	85:15	d	d	d	d	NA	
	64.5:34.6	2.70	2.79	2.84	2.90	15.91/11.37/91.49	
	38.7 :61.3	2.78	2.84	2.90	2.92	16.18/7.60/79.75	
	Pure DMF	2.59	2.79	2.86	2.90	15.93/17.06/110.64	
	EtOH-DMF	**15°C**	**25°C**	**35°C**	**45°C**		
	Pure EtOH	2.79	2.95	2.99	2.95	16.85/ d /69.15	
	79.8:20.2	2.96	2.73	2.92	d	15.56/18.96/ d	
	56.8:43.2	2.73	2.83	2.91	d	16.13/15.19/105.04	
	30.5:69.5	2.89	2.92	2.95	2.99	16.65/5.80/72.295	
	Pure DMF	2.59	2.79	2.86	2.90	15.93/17.06/110.64	
	ACN-DMF	**15°C**	**25°C**	**35°C**	**45°C**		
	Pure ACN	3.07	d	d	3.10	NA	

(Continued on next page)

TABLE 7
Cation complexes with DB24C8 and its derivatives *(Continued)*

Cation	Solvents	logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	81.6:18.4	2.95	2.85	2.75	d	16.26/−16.98/ d	
	59.6:40.4	2.93	2.90	2.87	2.85	16.55/−4.842/39.26	
	33.0:67.0	2.90	2.79	d	2.67	15.93/−12.33/17.02	
	Pure DMF	2.59	2.79	2.86	2.90	15.93/17.06/110.64	
	THF-DMF	**15°C**	**25°C**	**35°C**	**45°C**		
	Pure THF	e	e	e	2.95	NA	
	73.9:26.1	e	e	e	e	NA	
	48.5:51.5	3.08	d	d	d	NA	
	23.9:76.1	2.95	3.11	3.11	3.02	17.77/ d / d	
	Pure DMF	2.59	2.79	2.86	2.90	15.93/17.06/110.64	



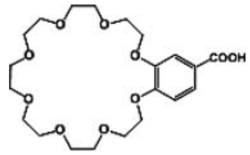
Dicyclohexano-24-crown-8

Cation	Solvents	logK				$-\Delta G^a/\Delta H^a/\Delta S^b$	References
	ACN-NM (wt.%)	**15°C**	**25°C**	**35°C**	**45°C**		
K^+	Pure ACN	4.52	4.42	4.37	4.26	−25/−14/36	Rofouei et al. (2008)
	80:20	4.69	4.63	4.51	4.41	−26/−17/32	
	60:40	4.68	4.66	4.55	4.43	−26/−15/38	
	40:60	4.92	4.78	4.70	4.52	−27/−22/22	
Rb^+	Pure ACN	4.31	4.13	4.09	4.04	−23/−17/22	
	80:20	4.59	4.53	4.38	4.27	−25/−19/21	
	60:40	4.55	4.43	4.32	4.19	−25/−21/15	
	40:60	4.65	4.57	4.45	4.39	−26/−16/34	
Cs^+	Pure ACN	4.35	4.25	4.08	3.98	−24/−22/5	
	80:20	4.57	4.34	4.25	4.14	−25/−24/2	
	60:40	4.67	4.59	4.43	4.38	−26/−18/27	
	40:60	5.06	5.07	4.90	5.07	−29/−3/87	
Tl^+	Pure ACN	5.66	5.47	5.42	5.21	−31/−25/23	
	80:20	5.89	5.78	5.62	5.54	−32/−21/39	
	60:40	5.88	5.78	5.65	5.53	−33/−21/41	
	40:60	5.93	5.84	5.77	5.64	−33/−17/55	
			25°C				
Ag^+	DMSO-H_2O (90:10, v/v)		1.80			NA	Ijeri and Srivastava (2003)
Ag^+	PC-EC (20:80, mass%)		4.49			NA	Samant et al. (2003)
Mg^{+2}	PC-EC (20:80, mass%)		4.46			NA	Samant et al. (2003)
Ca^{+2}	PC-EC (20:80, mass%)		3.88			NA	Samant et al. (2003)
Mn^{+2}	DMSO-H_2O (90:10, v/v)		1.98			NA	Ijeri and Srivastava (2003)
Co^{+2}	DMSO-H_2O (90:10, v/v)		1.64			NA	Ijeri and Srivastava (2003)
Ni^{+2}	DMSO-H_2O (90:10,v/v)		1.61			NA	Ijeri and Srivastava (2003)
Cu^{+2}	DMSO-H_2O(90:10, v/v)		1.76			NA	Ijeri and Srivastava (2003)
Cu^{+2}	PC-EC (20:80, mass%)		3.97			NA	Samant et al. (2003
Zn^{+2}	DMSO-H_2O (90:10, v/v)		1.63			NA	Ijeri and Srivastava (2003)
Pb^{+2}	DMSO-H_2O (90:10, v/v)		3.14			NA	Ijeri and Srivastava (2003)
Sr^{+2}	PC-EC (20:80, mass%)		3.87			NA	Samant et al. (2003)
Ba^{+2}	PC-EC (20:80, mass%)		3.50			NA	Samant et al. (2003)
Cr^{+3}	DMSO-H_2O (90:10,v/v)		3.23			NA	Ijeri and Srivastava (2003)

(Continued on next page)

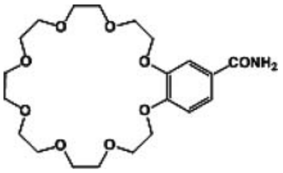
TABLE 7
Cation complexes with DB24C8 and its derivatives *(Continued)*

Cation	Solvents	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
Fe^{+3}	DMSO-H_2 O(90:10, v/v)	3.63	NA	Ijeri and Srivastava (2003)



4-Carboxy-benzo-24-crown-8

Cation	Solvents	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
		25°C		
Li^+	NM	4.00	NA	Ganjali et al. (1996)
	ACN	<2	NA	
	DMF	<2	NA	
Na^+	NM	4.51	NA	
	ACN	3.71	NA	
	DMF	<2	NA	
K^+	NM	> 6	NA	
	ACN	4.81	NA	
	DMF	2.35	NA	
Rb^+	NM	> 6	NA	
	ACN	4.28	NA	
	DMF	2.26	NA	
Cs^+	NM	> 6	NA	
	ACN	4.16	NA	
	DMF	<2	NA	



4′-Amido-benzo-24-crown-8

Cation	Solvents	logK	$-\Delta G^a/\Delta H^a/\Delta S^b$	References
		25°C		
Li^+	NM	4.53	NA	Ganjali et al. (1996)
	ACN	<3		
	DMF	<2		
Na^+	NM	5.22	NA	
	ACN	4.50		
	DMF	<2		
K^+	NM	> 6	NA	
	ACN	5.07		
	DMF	3.08		
Rb^+	NM	> 6	NA	
	ACN	4.71		
	DMF	2.96		
Cs^+	NM	6.23	NA	
	ACN	4.53		
	DMF	<2		

[a] KJ/mol.

[b] J/mol.K.

[c] No or very small change in conductance.

[d] High uncertainity

[e] The data cannot be fitted in equations

NA not available.

2008). The order of stability of complexes formed in pure MeOH depended on the size compatibility; Na^+ with an ionic size of (0.98 Å) and 4′-nitrobenzo-15-crown-5 with a similar cavity diameter (0.86–1.1 Å) formed the most stable complex. The stability order was $Na^+ > Li^+ > NH_4^+ > K^+$. But some reversal in stability was observed with the changes in composition of mixed solvent systems. In 50-50 mole% of ACN-MeOH binary mixture, the stability sequence was $K^+ > Li^+ > Na^+ > NH_4^+$. But in the case of 25-75 mole% ACN-MeOH, the sequence was $NH_4^+ > Na^+ > Li^+ > K^+$. The values of thermodynamic parameters for the formation of these complexes were obtained from temperature dependence of the stability constants using the van't Hoff plot. The results showed that the complexes were both enthalpy and entropy stabilized. The strength of alkali ion interaction with crown ethers is known to depend on the basicity of the ether oxygen (Ungaro et al., 1976). The electron withdrawing character of the $–NO_2$ group decreases the basicity of the two aromatic oxygen atoms and thus the stability of the complexes was lower than that of 15C5 and B15C5.

Rounaghi et al. (2007b) have studied the complexation reactions between Li^+, Na^+, and K^+ cations with DB18C6 in ACN-MeOH and THF-$CHCl_3$ binary mixtures at different temperatures. Addition of DB18C6 to Na^+ cation in ACN-MeOH (75 mol% of ACN) at different temperatures results in a decrease in molar conductivity, which indicates that the complex is less mobile than the free solvated cation. However, in the case of Li^+ ions under the same conditions, there was an increase in the molar conductivity on addition of DB18C6. The nature and charge on the cation affects the shape of the conductivity plots. Li^+ ions are small and are easily solvated by the solvent molecules; upon complexation, the crown ether replaces the solvation sheath around the cation and as a result the species becomes less bulky and more mobile than the corresponding free solvated cation. An interesting observation was noted in the case of K^+ ion upon addition of crown ether, the molar conductivity initially decreased until the mole ratio (C_{crown}/C_{K+}) reached 1 and then started to increase. This behavior can be explained according to the following equilibria:

$$(K^+, ClO_4^-) + DB18C6 \leftrightarrow K^+, DB18C6, ClO_4^-$$
$$K^+, DB18C6, ClO_4^- + DB18C6 \leftrightarrow K^+, (DB18C6)_2 + ClO_4^-$$

Addition of DB18C6 to K^+ ion solution results in the formation of relatively stable 1:1 complex, which is present as an ion-pair, then further addition causes formation of a sandwich-type complex with a 1:2 stoichiometry. This decreases the space for diffusion and interaction of the ClO_4^- ion with the K^+ cation and results in the dissociation of the ion-pair, and thus the conductivity increases. Similar behavior has been reported for the complexation of Li^+, K^+, and Rb^+ by 18C6 (Takeda et al., 1980) and also for Tl^+ complex with DC18C6 (Rounaghi et al., 2001) and 18C6 (Rounaghi et al., 2003) in ACN-MeOH binary solution.

The complex formation between Na^+, K^+, Rb^+, Cs^+, and Tl^+ and DCH18C6 in ACN-H_2O binary systems at different temperatures has been investigated by Soorgi et al. (2008). DCH18C6 formed 1:1 complexes with these metal ions and the selectivity order of the complexes in 25.3 and 50.4 mol% ACN was $Tl^+ > K^+ > Rb^+ > Cs^+ > Na^+$. Nonlinear behavior was found between the formation constants and the composition of the mixed solvent systems. The ACN molecules added to water were assumed to occupy cavities in the water network structure. Davis and Douhéret (1986) inferred the presence of three structurally different regions over the ACN-H_2O mixture composition range. Also, Catalan et al. (2003) showed that acidity, basicity, and polarity for ACN-H_2O binary mixture do not change linearly with the solvent composition. From the values of thermodynamic properties it was evident that in most of the cases the complexes were enthalpy stabilized and entropy destabilized.

Shamsipur and coworkers (2006) studied the thermodynamics of DB21C7 complexes with Na^+, K^+, Rb^+, and Cs^+ ions in ACN at different temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio plots at 15°, 25°, 35°, and 45°C. The stability order of DB21C7 complexes was $Rb^+ > K^+ > Cs^+ > Na^+$. The observed trend can be justified based on size compatibility of cations and the crown ether cavity. In fact, the ionic size of Rb^+ ion (3.02 Å) is appropriate for the cavity size of DB21C7 (3.4 Å), while the sizes of K^+ and Na^+ are too small for the cavity. On the other hand, the ionic size of Cs^+ ion is relatively so large that it can only partially penetrate inside the cavity, resulting in a weaker complex. The thermodynamic data for complexation of alkali cations revealed that the complexes were both enthalpy and entropy stabilized. It was interesting to note that the large negative ΔH values for Rb^+ and K^+ complexes, in comparison with the Cs^+ and Na^+ complexes, reflect much better fitting of these two cations inside the cavity and consequent overlapping of the donor and acceptor partners. In contrast, the ΔS values of Rb^+-DB21C7 and K^+-DB21C7 were much less positive than those for Na^+ and Cs^+ complexes. This is most probably due to the conformational change of the crown ether from a rather flexible structure in the free state to a rigid conformation in the stable metal ion complex form, which results in the decrease in entropy of the system.

Thermodynamic study of DCH24C8 complexes with K^+, Rb^+, Cs^+, and Tl^+ ions in binary ACN-NM mixtures has also been studied by conductometry (Rofouei et al., 2008). The stability constants of the resulting 1:1 complexes at 25°C in all solvent mixtures varied in the order $Tl^+ > K^+ > Rb^+ \sim Cs^+$. Since DCH24C8 is too large for the size of the metal ions, the "cation-in-the-hole" model (Izatt et al., 1985) has a limited usefulness in predicting its relative binding capacity with the cations. DCH24C8 is flexible enough that it can wrap itself around a metal ion of proper size so that all donating oxygen atoms of the ring can participate in bond formation. Evidence for the existence of such tri-dimensional structures both in solid (Hašek et al., 1979) and in solution (Farhadi and Shamsipur,

1999) state has been reported. The increased stability of Tl^+-DCH24C8 complex is probably due to the increased polarizability of Tl^+ ion, despite its less suitable size for the complexation with DCH24C8. Further, it was found that the stability of the resulting complexes increased with increasing NM content in the solvent mixture, due to its low donicity (DN = 2.7) compared to ACN (DN = 14.1). The thermodynamic data revealed that the complex formation process was both enthalpy and entropy stabilized. The complex formation of Ag^+, Tl^+, and alkali metal ions with DB30C10 has been studied in DCE, NM, ACN, AC, and DMF by Amini and Shamsipur (1991). The stability constants of the 1:1 complexes formed followed the sequence $Tl^+ > Rb^+ \sim K^+ > Ag^+ > Cs^+ > Na^+ > Li^+$. Further, the stability of the complexes with DB30C10 in different solvents decreases in the order DCE > NM > ACN > AC > DMF, which can be correlated to the solvating power of the solvents, as expressed by the Gutmann donor number (Gutmann, 1978).The data obtained in this study support the existence of a "wraparound" structure for the complexes due to the large size of the crown ether.

Conductance study of complex formation of Tl^+ and Ag^+ ions with several crown ethers in ACN, AC, and DMF solvents has been reported by Jabbari et al. (1993). The stability constants of the 1:1 complexes were found to decrease in the order DA18C6 > DCH18C6 > DB30C10 > 18C6 > DB21C7 > DB24C8 > DB18C6 > B15C5 > 12C4 for Tl^+ complexes and DA18C6 > DCH18C6 > 18C6 > DB18C6 > DB24C8 > DB30C10 ∼B15C5 > DB21C7 for Ag^+ complexes. There was an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents, as expressed by the Gutmann donor number (Gutmann, 1978). Comparing the 18-crowns used in the study, where the ring frame remains the same, the stabilities of the resulting complexes with both Tl^+ and Ag^+ ions vary in the order DA18C6 > DCH18C6 > 18C6 > DB18C6. The substitution of two oxygen atoms by two nitrogen atoms in the 18C6 ring increases the stability of the complexes significantly. These results are quite predictable as both Tl^+ and Ag^+ ions are soft acids and would interact more strongly with nitrogen atoms of the ring as soft bases. Also, the presence of two cyclohexyl groups on 18C6 can pump electrons into the ring and thus increase the basicity of the donating oxygen atoms. Introduction of two electron-withdrawing benzo groups reduces the donicity of oxygen atoms in the ring and hence reduces the cation-crown interactions.

Crown Complexes with Bivalent Cations (Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and UO_2^{2+})

Complexation reactions between alkaline earth cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) with DB24C6 were investigated in ACN-DMF binary mixtures at different temperatures by Rounaghi and coworkers (2004). In all solvent mixtures, DB24C8 formed 1:1 complexes with these cations. It was found that stability of complexes in these solvent systems was affected by the nature and composition of the solvent. The stability constants increased with increasing mol% of ACN, which has lower donicity than DMF. The general selectivity order found ($Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$) was in accordance with the size-fit concept: cavity ring size (> 4 Å) and relative size of metal cations. However, in the case of Mg^{2+} and Sr^{2+} anomalous behavior for the stability constants ($log\ K_f$) was observed with increase in the mole fraction of ACN. In 40 mol% ACN, the selectivity was reversed, that is, the Mg^{2+}-DB24C8 complex was more stable than the Sr^{2+}-DB24C8 complex. This behavior may be related to hetero-selective solvation of cations and also due to solvent-solvent interactions in the binary mixtures. The thermodynamic parameters of complex formation evaluated using the van't Hoff plots showed that the complexation reactions were enthalpy destabilized but entropy stabilized and were also influenced by the nature and composition of the mixed solvents. The influence of solvent on the complex formation between these cations and B15C5 in some pure and binary solvent mixtures has been studied by Rounaghi and coworkers (2010d). The conductance data showed that the stoichiometry of the complexes in most cases was 1:1, but in the case of Ca^{2+} cation 1:2 [ML_2] was observed in THF, which shows that the stoichiometry of the complexes can be changed by the nature of the medium. Moreover, the complexation equilibria at different temperatures were quite complex for Ca^{2+}, which may be due to changes in solvation of the cation, macrocycle, or even the complex with temperature. In ACN-H_2O binary mixtures, with the increase in concentration of water, there was a decrease in the stability of Ca^{2+}-B15C5 complex. This may be due to relatively higher Gutmann donor number of H_2O, which can lead to higher solvation of the cation or possibly the macrocycle. Contrary to this observation, the changes in the stability constants of Mg^{2+}-B15C5 and Sr^{2+}-B15C5 were not monotonic. This behavior may be due to interaction between ACN and H_2O molecules via hydrogen bonding in their binary mixtures, which results in changes in their structure and therefore the solvation behavior. In MeOH (DN = 20) and THF (DN = 20) solvent mixture, the stability of Mg^{2+}-B15C5 complex was found to increase with increase in MeOH concentration. This behavior may be due to the formation of hydrogen bonding between NO_3^- anion (from $MgNO_3$) and MeOH molecules because the anions are usually solvated in protic and amphiprotic solvents via hydrogen bonding. Therefore, the competition between this counter ion with B15C5 for Mg^{2+} is decreased as the concentration of MeOH increases in MeOH-THF binary mixed solvents. Additionally, the dielectric constant for MeOH (32.6) and THF (7.3) are quite different, thus MeOH can decrease the electrostatic interactions between the NO_3^- anion and Mg^{2+} cation, resulting in higher stability of Mg^{2+} complexes. The selectivity order of B15C5 for the three cations in binary ACN-H_2O mixtures was $Mg^{2+} > Ca^{2+} > Sr^{2+}$. Since Mg^{2+} ion has a small ionic size compared to Ca^{2+} and Sr^{2+}, it can attain a more convenient fit condition with B15C5. Although Ca^{2+} cation has a smaller size than Sr^{2+} cation, the stability of the Sr^{2+}-B15C5 complex is greater than the stability of the Ca^{2+}-B15C5 complex. This may be related to the strong solvation of Ca^{2+} cation compared to Sr^{2+} in these binary solutions. The values of thermodynamics parameters (ΔH and ΔS) and their sign vary significantly with the nature and composition of the mixed solvents. These variations can be attributed to solvation-desolvation of the species involved in the complexation reactions and also the conformational changes of the macrocyclic ligand. Complexation of alkaline earth cations with 18C6 (Ansarifard and Rounaghi, 2005) and DCH18C6 (Rounaghi and Moffazzeli, 2005) have also been reported in H_2O-MeOH and H_2O-EtOH binary mixtures. The stability constants with 18C6 varied in the order $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ in these binary solvent mixtures. However, as reported previously (Rounaghi et al., 2010b), the thermodynamic parameters were quite sensitive to the nature and composition of the mixed solvents. Similar results were obtained with DCH18C6 as well, however, the complexation reactions were enthalpy stabilized but entropy destabilized in most of the cases. A conductance study of 1:1 19C6 complexes with various divalent ions and some monovalent ions has also been reported in water at 25°C (Takeda et al., 1999). The stability order of the complexes formed is $Pb^{2+} > Ba^{2+} > Sr^{2+} > Cd^{2+} > Ca^{2+}$. The ionic sizes of Ca^{2+} and Cd^{2+} are almost the same, while the Gibbs energy of hydration is smaller for Cd^{2+} (-1801 kJ/mol) than for Ca^{2+} (-1593 kJ/mol). Thus, 18C6 is expected to form a more stable complex with Ca^{2+} in water than with Cd^{2+}, but the opposite holds for 19C6. In a similar manner, Pb^{2+} and Sr^{2+} are nearly equal in size and also have almost the same hydration energies, Sr^{2+} (-1447 kJ/mol) and Pb^{2+} (-1497 kJ/mol). But still, Pb^{2+} forms a stronger complex with 19C6 than Sr^{2+} in water. This could be related to increased flexibility of 19C6 over 18C6 due to an additional methylene group in the ring.

Crown ethers that are designed for chelating transition and heavy metal ions are mixed crown ethers containing different types of soft chelating atoms. Ashram and coworkers (2010) studied the complexation and thermodynamics of two oxathiadibenzocrown ethers (dibenzo-O_2S_5-macrocycle-I and dibenzo-O_3S_4-macrocycle-II) with Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} ions in acetonitrile. All the complexes formed had 1:1 stoichiometry. The study revealed that variation of the heteroatoms in the crown ether cavity altered the selectivity and that the soft cation Pb^{2+} forms the most stable complexes with both the macrocycles. The stability order for complexes with I followed the sequence $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ and $Pb^{2+} > Cu^{2+}$ with II. However, there was no change in the molar conductance when II was added to Zn^{2+} and Cd^{2+} solutions, which suggests either no complex formation or similar mobility of metal ions and their complexes. The complexes of Pb^{2+} with I and II had the largest negative enthalpy changes, negative entropy changes, and negative free energy changes. This observation can be explained based on the two concepts of the size fit and hard and soft acid base (HSAB) conjecture. To accommodate a Pb^{2+} ion, the crown ether cavity attains a certain conformation such that the repulsion between adjacent C-O and C-S dipoles is minimum and the interaction of these dipoles with the cation is maximum. The soft nature and size of the Pb^{2+} ion allows it to have the strongest interaction with the C-S dipoles. A similar study of some transition and heavy metal complexes with 1,10-DA18C6 in binary ACN-DMSO mixture has been reported at different temperatures (Ghasemi and Shamsipur, 1996). The formation constants ($\log K_f$) of the resulting 1:1 complexes were determined and found to vary in the order $Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. The sequence of the first transition series complexes with DA18C6 follows the Irving-Williams order (Irving and Williams, 1953), which generally holds for the equilibrium constants of transition metals. Pb^{2+} ion with an ionic size of 2.38 Å forms the most stable complex with DA18C6 (cavity size 2.6–3.2 Å) mainly because of the best fitting conditions. Further, there was a linear relationship between the formation constants and increasing weight percent of ACN in the mixed solvent systems due to relatively low solvent donicity of ACN compared to DMSO. Additionally, the lower dielectric constant of ACN (38.0) than DMSO (45.0) contributed towards electrostatic bond formation with increasing percentage of ACN in the mixed solvent system. The $T\Delta S$ versus ΔH plots of all the thermodynamic data obtained showed a fairly good linear correlation, indicating the existence of enthalpy-entropy compensation in the complexation reactions. Ganjali and coworkers (1998) have studied the interaction between Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} ions with HT18C6TO in DMSO at different temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data and found to vary in the order $Hg^{2+} > Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. This is based on the size of the cations relative to the macrocycle cavity and the hard-soft acid-base character of the cations and the donating sites of the macrocycle. The first-row transition metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are all small for the cavity of HT18C6TO and have a borderline character according to the HSAB principle of Pearson (1963). Thus, their HT18C6TO complexes are considerably weaker than those with the heavy metal ions studied and follow the Irving-Williams order (Irving and Williams, 1953), which generally holds for the equilibrium constants of transition metals (Ghasemi and Shamsipur, 1996). On the other hand, both Hg^{2+} and Pb^{2+} ions, with the same ionic radius, have the best size to fit suitably inside the cavity of the thiacrown ether used. The stronger Hg^{2+}-HT18C6TO complex compared to Pb^{2+}-HT18C6TO may be attributed to the much softer acid character. It is important to note that although the Cd^{2+} ion possesses a softer acid character than Pb^{2+}, the stability of its complex is lower than that of the Pb^{2+}-HT18C6TO complex. This can be related to poor fitting conditions of the Cd^{2+} ion inside the HT18C6TO cavity. The thermodynamic study revealed that all the complexes were enthalpy stabilized but entropy destabilized. The main reason for the negative entropy was related to the decrease in the conformational entropy of HT18C6TO brought about upon complexation from a rather flexible free state to a structured rigid complex.

Relatively few studies have been reported to date for the complexation of uranyl ions (UO_2^{2+}) with crown ethers. Fard and coworkers (2009) studied complex formation between 18C6 and DA18C6 with UO_2^{2+} in some binary mixed aqueous and nonaqueous solvents. The complexation reaction between UO_2^{2+} cation and 18C6 was studied in ACN-MeOH, NM-MeOH, and PC-MeOH, while UO_2^{2+}-DA18C6 complexation was investigated in ACN-MeOH, ACN-EtOH, ACN-EtOAc, MeOH-H_2O, EtOH-H_2O, ACN-H_2O, DMF-MeOH, DMF-EtOH, and DMF-EtOAc binary solutions at 25°C. The stability order of UO_2^{2+}-DA18C6 complex in pure solvents was H_2O > MeOH > EtOH, which can be due to high solvation of DA18C6 in alcoholic solvents compared to H_2O. In the case of the UO_2^{2+}-18C6 complex the stability sequence in pure organic solvents was EtOH > ACN ∼ NM > PC ∼ MeOH. The conductance data showed 1:1 complex stoichiometry with both the crown ethers in most of the binary solvent mixtures, however, 1:2 [UO_2^{2+}: $(\text{crown})_2$] was also found in some of the cases. From the values of stability constants it was evident that the nature and the composition of the solvent systems played a significant role in the complex stability and also the stoichiometry of the complexes formed with both the crown ethers. Addition of DA18C6 to UO_2^{2+} cations in MeOH-H_2O, EtOH-H_2O, ACN-H_2O, and DMF-MeOH solvent systems resulted in a decrease in molar conductivity, while an increase in molar conductivity was observed in ACN-EtOH, ACN-EtOAc, and DMF-EtOAc as well as for UO_2^{2+}-18C6 complexation in ACN-MeOH, NM-MeOH, and PC-MeOH binary solutions. This behavior can be explained on the basis of the solvation effect. The UO_2^{2+} ions must have been weakly solvated in MeOH-H_2O and EtOH-H_2O solvent systems, thus upon complexation the species becomes bulkier and results in a decrease in molar conductivity. On the other hand, due to a high degree of solvation in ACN-MeOH and subsequent complex formation by replacing the solvent sheath around the UO_2^{2+} ions, the moving entity becomes less bulky and more mobile. Spectroscopic study of UO_2^{2+}-crown ether complexes in nonaqueous solvents has shown that the crown ethers with six oxygen donor atoms form inclusion complexes with the UO_2^{2+} ion in the center of the cavity, but aza crowns coordinate externally to the UO_2^{2+} ions (Kelly et al., 2004). In the case of 18C6, a complex with high coordination symmetry is formed. The crystal structures of UO_2^{2+} complexes with DA18C6 have revealed that linear uranyl moiety is included in the macrocycle with hexagonal-bipyramidal coordination geometry (Thuery et al., 1995). Thermodynamic study of complex formation between DB18C6 and UO_2^{2+} cations in EtOAc-DMF, EtOAc-AN, EtOAc-THF, and EtOAc-PC at different temperatures has also been reported (Rounaghi and Kakhki, 2009). The results demonstrate that the thermodynamics of the complexation reaction between UO_2^{2+} cation and DB18C6 is affected strongly by the nature and composition of the mixed solvents. Very recently in another report (Rounaghi et al., 2011), UO_2^{2+} cation along with Ce^{3+}, Y^{3+}, and Sr^{2+} have been studied with DB18C6 in ACN-Di mixed solvent systems with similar results.

Crown Complexes with Trivalent Cations (Cr^{3+}, Fe^{3+}, Y^{3+}, La^{3+}, Ce^{3+}, Eu^{3+}, Er^{3+}, and Au^{3+})

The stability constants for the complexes of Cr^{3+} and Fe^{3+} ions along with several other bivalent transition metal ions in DMSO:H_2O (90:10, v/v) with 15C5, B15C5, 18C6, Db18C6, DC18C6, DB24C8, and DCH24C8 has been studied (Ijeri and Srivastava, 2003). The choice of this specific composition of binary solvent mixture was taken to prevent the hydrolysis of Cr^{3+} and Fe^{3+} salts and to ensure the solubility of the benzo and dibenzo crown ethers. In general, the stability constant values for Cr^{3+} and Fe^{3+} with different crown ethers were higher than those of several divalent ions (except Pb^{2+}) studied. Trivalent and divalent ions have a high charge-to-radius ratio because of which they are highly solvated. Upon complexation, the crown ether molecule replaces the solvent sheath around the metal ion, and as a result the moving entity becomes less bulky and more mobile. Among different crown ethers, Cr^{3+} and Fe^{3+} ions formed more stable complexes with DB24C8 and DCH24C8, even though there is no match between the ionic size and cavity diameter. The reason for this behavior could be due to the flexibility of the larger crown ethers, which can wrap around the smaller ion, giving rise to stable and stronger complexes. The effect of counter anions (nitrate and perchlorate) on the complexation of Fe^{3+} and other divalent ions, Cu^{2+}, Cd^{2+}, and Hg^{2+}, with PhA15C5 has been studied in ACN-H_2O by Marji and Fraihat (1999). The formation constants were determined at different temperatures and binary solvent mixtures. It was found that the stability constants of PhA15C5 with metal nitrate salts in 95% ACN-H_2O follow the sequence $Hg^{2+} > Cu^{2+} > Fe^{3+} > Cd^{2+}$. Replacing nitrate by perchlorate resulted in higher stability constant values while retaining the same trend. This behavior can be explained based on the size of these counter anions. Since the perchlorate ion has a larger radius (2.36 Å) than the nitrate ion (1.89 Å), it is possible to stabilize its electron density more than that of the nitrate ion. Thus, the nitrate ion becomes more nucleophilic and as a result the metal-crown interaction is weakened. Further, the solvent properties also influenced the stability of these transition metal-PhA15C5 complexes. The formation constants for a given complex increased with increasing weight percent of acetonitrile because of its low donicity value. In another report, Marji and Taha (2000) have studied effect of size of the macrocycle and the hard and soft acid base (HSAB) character of metal ions, which can influence the stability of the complex. The thermodynamic stabilities of Fe^{3+}, Ni^{2+}, and Ag^{+} with two diaza-crown ethers (DBzDA18C6 and DBDA15C4) of different cavity size were determined conductometrically in ACN at different temperatures. The formation constants of 1:1 complexes with these diaza-crown ethers followed the order $Ag^{+} > Ni^{2+} > Fe^{3+}$ in accordance with Pearson's principle of HSAB character. The ionic size of Ag^{+} (2.3 Å) fits suitably in the cavity of DBzDA18C6 (2.3–3.2 Å), while Fe^{3+} forms the least stable complexes with both the crown ethers, as it is relatively hard compared to Ag^{+} and Ni^{2+} ions. Further, the $\log K_f$ values of Fe^{3+} with $DBA_2$15C4 were higher than those with the DBzDA18C6 complex, which could be due to good size fit of Fe^{3+} (1.3 Å) with the cavity of DBDA15C4 (∼1.4 Å).

The complexation reaction of DB24C8 with the Y^{3+} ion was studied in some binary mixtures of MeOH, EtOH, ACN, and THF with DMF at different temperatures using the conductometric method (Rounaghi et al., 2009b). The stability order of 1:1 Y^{3+}-DB24C8 complex in pure nonaqueous solvents was ACN > EtOH > MeOH > DMF, which is consistent with the inverse order of their solvating abilities as expressed by the Gutmann donor number (Gutmann, 1978). The stability of the Y^{3+}-DB24C8 complex in binary mixed solutions followed the sequence ACN-DMF > EtOH-DMF > MeOH-DMF, which can be attributed to the inherent solvating ability of the pure solvents that form the mixture. However, a nonlinear relationship was found for the stability constants of Y^{3+}-DB24C8 in ACN-DMF binary system with increasing mol% of ACN. Somewhat similar observations were found for other binary mixtures as well. This behavior can be due to some kind of solvent-solvent interactions between these solvents, thereby changing the structure of these mixtures and their solvating ability for the cation, DB24C8, and possibly the resulting complex. Studies have been reported to investigate such interactions in some binary solvent systems (Krestov et al., 1994). In a typical mixture such as ACN-DMF, there is a mutual destruction of dipolar structures of these aprotic solvents with the release of free dipoles (Rounaghi et al., 2007d). As a result, the strong dipolar interaction between ACN and DMF molecules is predictable. The experimental values obtained for enthalpy and entropy suggest that in most of these binary systems, the Y^{3+}-DB24C8 complex was enthalpy destabilized and entropy stabilized, thus the contribution of entropy was the principal driving force for complexation. However, in the typical case of ACN-DMF the complex formation was stabilized from both the enthalpy and entropy.

Very recently, the complexation reaction between Y^{3+}, La^{3+}, Eu^{3+}, and Er^{3+} cations with DCH18C6 has been studied in ACN-DMF and ACN-MeOH binary systems at different temperatures (Kazemi, 2010). The conductometric data showed 1:1 stoichiometry in both solvent systems in different mole ratios. In pure solvents, the stability constants of the complexes follow the order ACN > MeOH > DMF. This can be explained by the Gutmann donor number concept (Gutmann, 1978); DMF, which has a higher donicity (DN = 26.6) than ACN (DN = 14.1) and MeOH (DN = 20), competes more with the crown ether for the metal cations and hence results in weaker complexes. The selectivity pattern of DCH18C6 for these cations showed that in addition to the ionic size of lanthanides, chemical and physical properties of the mixed solvent systems played a significant role by changing the solvating capacity of the metal cations, crown ether molecules, and even the resulting complexes. In pure MeOH, the selectivity order for these cations was $Y^{3+} > La^{3+} > Er^{3+} > Eu^{3+}$, which is in agreement with the results of a previous report (Ohyoshi and Kohata, 1989). The selectivity sequence of DCH18C6 for these cations in ACN-MeOH binary system (25 and 50 mol% MeOH) was $Y^{3+} > Er^{3+} > Eu^{3+} > La^{3+}$, while in 75 mol% MeOH it changed to $Eu^{3+} > Er^{3+} > Y^{3+} > La^{3+}$. The results for thermodynamic parameters for complexation in ACN-MeOH and ACN-DMF were influenced by the nature and the composition of the binary systems. Recently, Rounaghi et al. (2011) have studied complex formation of Ce^{3+}, Y^{3+}, $UO_2{}^{2+}$, and Sr^{2+} ions with DB18C6 in ACN-Di and Ce^{3+}, Fe^{3+}, Y^{3+}, Cd^{2+}, Au^{3+}, and Sn^{4+} ions with 4′-NB15C5 in ACN, MeOH, and NB solvent systems (Rounaghi et al., 2010c). In ACN-Di solvent system, the molar conductivity initially decreased by addition of DB18C6 to a solution containing Ce^{3+}/Y^{3+} ion ($NO_3{}^{-}$ salts). However, in pure ACN there was a decrease up to 1:1 mole ratio (due to ion-pair formation) and then an increase in molar conductivity upon further addition of DB18C6. This behavior may be due to the formation of 1:2 (ML_2) complex with a sandwich structure, which decreases the space for diffusion and interaction of $NO_3{}^{-}$ with Ce^{3+}/Y^{3+}, resulting in dissociation of the ion pair giving rise to increase in the molar conductivity of the solution. The selectivity of 4′-NB15C5 for Au^{3+} was the least of the trivalent ions, $Cd^{2+}$and Sn^{4+} ions in MeOH, however, in ACN the stability order was $Y^{3+} > Au^{3+} > Fe^{3+} > Cd^{2+}$. The complex stoichiometry of Au^{3+} with 4′-NB15C5 in ACN, MeOH, and NB was 1:1 (M:L).

Crown Complexes with Tetravalent Cation (Sn^{4+})

So far only one tetravalent cation, Sn^{4+}, has been studied for complex formation with 4′-NB15C5 along with Fe^{3+}, Y^{3+}, Ce^{3+}, Au^{3+}, and Cd^{2+} ions (Rounaghi et al., 2010c). The study was intended to evaluate the effect of different nonaqueous solvents (ACN, MeOH, and NB) on the stoichiometry and selectively of the complexes formed with these cations at different temperatures. The stoichiometry observed in MeOH and ACN was uniformly 1:1 (M:L) for all the cations, except for Sn^{4+}, which showed a 2:1 (M:L) ratio in ACN. Addition of 4′-NB15C5 to Sn^{4+} solution in ACN at different temperatures showed a gradual increase in the molar conductivity up to 1:1 mole ratio and then increased rapidly. The initial increase in conductivity can be due to the mobility of the solvated complex, which is very close to the mobility of the free solvated Sn^{4+} ion. The sharp increase in molar conductivity thereafter may be attributed to the formation of $M{:}L_2$ sandwich complex, which is less solvated than the M:L complex formed initially. This behavior can be described by the following equilibria:

$$4' - \mathrm{NB15C5} + \mathrm{Sn}^{4+} \leftrightarrow (4' - \mathrm{NB15C5} \cdot \mathrm{Sn}^{4+})$$

$$(4' - \mathrm{NB15C5} \cdot \mathrm{Sn}^{4+}) + 4' - \mathrm{NB15C5}$$
$$\leftrightarrow [(4' - \mathrm{NB15C5})_2 \cdot \mathrm{Sn}^{4+}]$$

Crown Complexes with Anilinium (An^+) Ion, Pyridinium (Py^+) Ion, and Their Derivatives

Shamsipur and Ganjali (1997) studied the complexation reactions between the protonated salts of aniline (An^+), *o*-hydroxy aniline (HAn^+), *o*-amino aniline (AAn^+), and 2,3-benzo aniline (BAn^+) with 18C6 and DA18C6 by conductometry in ACN, DMF, and their mixtures at 25°C. It was found that the molar conductance of each protonated amine nitrate solution in the solvents used decreases in the order ACN > ACN + DMF > DMF, mainly due to the large difference in the viscosity of the two solvents. From the $logK_f$ values it was evident that the nature of the solvent has a very fundamental influence on the stability of the resulting 1:1 complexes between the protonated amines and the macrocyclic ligands. Since in the complexation process, the ligand must compete with solvent molecules for the cations, variation of the solvent properties is expected to change the apparent binding abilities of the complexes. The binding ability of the solvents was in agreement with the Gutmann DN value, so the stability of the protonated amine-macrocycle complexes followed the sequence ACN > ACN-DMF > DMF. It was also observed that, in the aromatic anilinium series studied, increasing the bulkiness of the organic substituent in the *ortho* position results in a loss of complex stability. In all the solvent systems studied, the stability order for 1:1 complexes was $An^+ > AAn^+ > HAn^+ > BAn^+$. Comparing the two macrocycles, complexes with DB18C6 were more stable due to the stronger N^+-H. . .N hydrogen bonding than the N^+-H. . .O bonding in 18C6.

Based on a similar concept, a thermodynamic study of some pyridinium ion derivatives (Py^+, $MePy^+$, $DMePy^+$, and $TMePy^+$) with 18C6, A18C6 and DA18C6 has been reported in ACN at different temperatures (Ganjali et al., 2000). The major factor responsible for the stability of the protonated pyridinium complexes was the steric hindrance due to the presence of methyl groups in the *ortho* position of the Py^+ ions. In general, the 1:1 formation constants ($logK_f$) with all three macrocycles at different temperatures followed the order $Py^+ > MePy^+ > DMePy^+ > TMePy^+$. Further, in all the cases, the complexes were enthalpy stabilized and entropy destabilized.

CONCLUDING REMARKS

This review presents an extensive compilation of literature reports on the conductometric studies of cation-crown ether complexes. Conductometry, although a simple and cost effective technique compared to other sophisticated techniques like NMR, polarography, calorimetry, ion-selective electrodes, fluorescence, and spectrophotometry, has amply demonstrated its utility in the investigation of cation-macrocyclic crown ether interactions in solutions. Conductometric titrations with crown ethers have proved to be very useful in determining the stability constants, selectivity, and also the thermodynamic parameters of the crown ether complexes with various cations in nonaqueous and aqueous/nonaqueous media. Studies on complexation reactions of crown ethers with cations in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent systems. Conductance measurements of crown-complexable electrolytes in the presence of crown compounds also provide valuable information on ion-solvent and ion-ion interactions of the complexes in solutions. It is worth noting that even after more than four decades since it was first discovered in 1967, crown ether chemistry is still being explored despite the emergence of new supramolecular entities like calixarenes, resorcinarenes, thiacalixarenes, calixpyrroles, and others. This can be attributed to their unique and unparalled behavior, especially towards alkali and alkaline earth cations and their wide range of application areas. One major limitation associated with other supramolecular entities for cation complexation in solution is their limited solubility in water-miscible solvents. However, with the knowledge acquired from the solution chemistry of cation-crown complexes, we believe that the scope and future prospect of conductometric studies with other supramolecules like calixarenes and thiacalixarenes are also a promising preposition.

ABBREVIATIONS

AAn^+	*o*-Amino anilinium ion
AB24C8	4′-Amido-benzo-24-crown-8
AC	Acetone
ACN	Acetonitrile
A18C6	Aza-18-crown-6
An^+	Anilinium ion
BAn^+	2,3-Benzo anilinium ion
B15C5	Benzo-15-crown-5
B18C6	Benzo-18-crown-6
BN	Benzonitrile
15C5	15-Crown-5
16C5	16-Crown-5
18C6	18-Crown-6
19C6	19-Crown-6
24C8	24-Crown-8
30C10	30-Crown-10
CB24C8	4-Carboxy-benzo-24-crown-8
CB30C10	4’-Carboxy-benzo-30-crown-10
DA15C5	Diaza-15-crown-5
DA18C6	Diaza-18-crown-6
DB18C6	Dibenzo-18-crown-6
DB21C7	Dibenzo- 21-crown-7
DB24C8	Dibenzo 24-crown-8
DB30C10	Dibenzo 30-crown-10
DBDA15C4	Dibenzo-diaza-15-crown-4
DBPY18C6	Dibenzo-pyridino-18-crown-6
DBzDA18C6	Dibenzyldiaza-18-crown-6
DCH18C6	Dicyclohexyl-18-crown-6
DCH24C8	Dicyclohexano-24-crown-8
DDzDA18C6	Didecyldiaza-18-crown-6
DCE	1,2-Dichloroethane
Di	Dioxane
DMA	Dimethylacetamide

DM16C5	Dimethyl-16-crown-5
$DMePy^+$	2,4-Dimethyl pyridinium ion
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DT18C6	Dithia-18-crown-6
DTbDCH18C6	Di-*tert*-butyl-dicyclohexano-18-crown-6
EC	Ethylene carbonate
EtOAc	Ethyl acetate
EtOH	Ethanol
HAn^+	*o*-Hydroxy anilinium ion
HA18C6	Hexaaza-18-crown-6
HT18C6TO	Hexathia-18-crown-6-tetraone
MeOH	Methanol
$MePy^+$	2-Methyl pyridinium ion
NB	Nitrobenzene
4’-NB15C5	4′-Nitrobenzo-15-crown-5
NM	Nitromethane
PC	Propylene carbonate
PhA15C5	Phenylaza-15-crown-5
PrOH	Propanol
Py^+	Pyridinium ion
$TMePy^+$	2,4,6-Trimethyl pyridinium ion
THF	Tetrahydrofuran
TM12C4	Tetramethyl 12-crown-4

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