J. Chem. Eng. Data **2003,** *48,* 203−207

Complexation of Macrocyclic Compounds with Metal Ions: 2. Mg(II), Ca(II), Sr(II), Ba(II), Cu(II), and Ag(I) in 20 Mass % Propylene Carbonate + Ethylene Carbonate

Rajesh A. Samant, Vijaykumar S. Ijeri, and Ashwini K. Srivastava*

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai 400 098, India

The conductance behavior of magnesium, calcium, strontium, barium, copper, and silver perchlorates and their complexes with seven crown ethers have been studied in 20 mass % propylene carbonate + ethylene carbonate. The conductance studies indicate 1:1 complex formation between the metal ion and crown ether. For the alkaline earth metal ions, the order of stability constants with all crown ethers is found to be Mg(II) > Ca(II) > Sr(II) > Ba(II). The limiting ionic conductivities of metal ions and the complexed metal ions are also reported. In addition, complexation studies of Cu(II) and Ag(I) were carried out by potentiometry and voltammetry to compare the results with those obtained by conductivity measurements, which were found to be in good agreement with each other.

Introduction

Propylene carbonate (PC) and ethylene carbonate (EC) are dipolar aprotic solvents with large dipole moments and relatively high permittivities.[1] Although PC has been receiving increasing attention as an electrochemical solvent,[2−5] less attention has been directed toward EC as a solvent,[6] probably because of its high freezing point (37 °C). The dipole moment of both PC (1.65×10^{-29} cm = 4.94 D) and EC (1.64×10^{-29} cm = 4.94 D) are similar, and they are miscible with each other.[1] However, only a few fundamental studies have been reported in the binary mixtures of these solvents.[7−10] 20 mass % PC + EC has a relative permittivity of 87.2 at 25 °C which is higher than that of pure PC (64.4 at 25 °C). This offers a special advantage over the low dielectric media where ionic association often creates undesirable complications.[2−4,11]

The purpose of the present investigation was to study the conductance behavior of alkaline earth metal perchlorates and their complexes with crown ethers, viz., 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6), dibenzo-24-crown-8 (DB24C8), and dicylohexano-24-crown-8 (DCH24C8) in 20 mass % PC + EC as a solvent. As a result of the present study, the limiting ionic conductivities of alkaline earth metals, and their complexes with crown ethers, the association constants of these metal perchlorates and the formation constants of their complexes with crown ethers in 20 mass % PC + EC have been determined. In addition, complexation studies of Cu(II) and Ag(I) were carried out by potentiometry and voltammetry to compare the results with those obtained by conductivity measurements, which were found to be in good agreement with each other.

Experimental Section

Solvent. The purification of PC[2,4] and EC[10] has been described earlier. Both of the solvents were stored in sealed containers to prevent contamination with carbon dioxide and water from air. Known masses of each solvent were mixed to form a (PC + EC) mixture with 20 mass % PC.

Crown Ethers. 15-crown-5 (Fluka), benzo-15-crown-5 (Aldrich), 18-crown-6 (Aldrich), dibenzo-18-crown-6 (Aldrich), dicyclohexano-18-crown-6 (Fluka, mixture of isomers), dibenzo-24-crown-8 (Aldrich), and dicyclohexano-24-crown-8 (Aldrich, mixture of isomers) were used without further purifications.

Anhydrous Metal Perchlorates. Magnesium perchlorate (BDH−India), a micro analytical reagent, was used without further purification. The metal perchlorates were prepared from their respective carbonates/oxides by the general methods described elsewhere.[12] The metal perchlorates, so prepared were recrystallized thrice with conductivity water and dried in a vacuum oven to get anhydrous perchlorates. (Perchlorate solutions should not be evaporated to complete dryness on a hot-plate or burner as they are explosive). Mercuric chloride (SDS−AR) was high purity material and was used without further treatment.

Mercury used for the preparation of the reference electrode was triple distilled under reduced pressure.

Procedure for Conductometry. All conductivity measurements were made using a dip type cell (cell constant = 1.080 cm^{-1}) at 25 ± 0.05 °C. A Toshniwal digital conductivity meter type CLO 1.10A was used in the measurements. All reported conductivities refer to a frequency of 200 Hz; no significant change in conductivities was found on using another frequency (3 kHz). All molar conductivities have been calculated after correcting for the solvent conductance.

Step 1. Determination of the Limiting Molar Conductivity (Λ_0) and First Step Association Constant (K_A) of Metal Perchlorates. The conductivity of a measured volume of the solvent was determined, and then the increments of the metal perchlorate stock solutions (~2×10^{-2} M) were added to the cell using microliter syringe buret. The conductivity of the solution in the cell was measured after each transfer.

Step 2. Determination of the Formation Constant ($K_{ML^{n+}}$) of the Metal Ion and Crown Ether Complex. A solution (in 20 mass % PC + EC) of metal perchlorate

---

* To whom correspondence should be addressed. Fax: 91-022-6528547. E-mail: aks@mail.mu.ac.in; akschbu@yahoo.com.

10.1021/je0201774 CCC: $25.00

was placed in the cell and conductivity was measured. Step by step increments of the crown ether stock solution (~2 × 10^{-2} M) in 20 mass % PC + EC were effected by a rapid transfer using a microliter syringe buret until the total concentration of crown ether was approximately three times larger than that of metal perchlorate. The conductivity of the solution was measured after each transfer of crown ether solution.

Step 3. Determination of Λ_0 of $MLClO_4$. A solution of crown ether (~2 × 10^{-3} M) in 20 mass % PC + EC was placed in the cell, and the conductance of the solution was measured. Then, a step by step increase in the concentration of metal perchlorates was effected by a rapid transfer of the metal perchlorate solution (~2 × 10^{-2} M) in 20 mass % PC + EC to the cell until the concentration of metal perchlorate becomes approximately twice as large as that of the crown ether. The conductivity of the solution was measured after each transfer of metal perchlorate solution.

Procedure for Potentiometry. Cu(II) and Ag(I) Indicator Electrode. A platinum wire (1.5 cm long, 16 gauze) sealed into a Pyrex glass tube was cleaned by treating with hot aqua regia and then electroplated with copper[9]/silver[5] by electrolyzing 0.1 M copper(II) perchlorate solution/2% potassium argentocyanide, respectively, at a low current density using a platinum anode encased in a glass frit. The plated electrodes, which were usually prepared in batches of 5−6 electrodes at a time under the same conditions, were washed over 2 days by repeatedly suspending them in fresh conductivity water to leach out the last traces of the plating solution. The electrodes were stored in conductivity water until use. They were rinsed thoroughly with conductivity water and then with reagent-grade acetone followed by air-drying before placing into the experimental solution.

Reference Electrode. The preparation and use of the $Hg/HgCl_2(s)$ in 20 mass % PC + EC reference electrode are given in our earlier article.[9, 10]

An Equip−Tronics digital potentiometer (model EQ DGS) was used for the emf measurements. As a general procedure, the emfs were noted after every 2−3 min for all of the cells over a period of about 20 min; the reported potentials are averages of the last two readings which normally agreed to ±0.5 mV or better. The measured cell potentials were reproducible to ±2 mV.

Step 1. The emf of the cell given below was measured at different concentrations of copper and silver perchlorates.

$$M/MX_n//HgCl_2\ (s)\ \text{in 20 mass \% PC + EC}/Hg$$

where M = Cu or Ag and X = ClO_4^-.

Step 2. Stock solutions of silver/copper perchlorates and crown ethers were prepared in 20 mass % PC + EC. Experimental solutions were prepared by appropriate dilution of the stock solutions to the required concentrations. The emf of each solution was measured using the cell given below.

$$M/MX_n + \text{crown ether}//HgCl_2\ (s)\ \text{in 20 mass \% PC + EC}/Hg$$

Procedure for Voltammetry. The voltammetric system used for the studies was a Princeton Applied Research model EG&G 264A potentiostat with 303A electrode assembly and X−Y chart recorder RE0089. A three electrode cell comprising platinum working and counter electrodes and the $Hg/HgCl_2$ (s) in 20 wt % PC + EC reference electrode was used for differential pulse voltammetry of copper and silver solutions. Initially, voltammograms for the free metal ion (~10^{-3} M) were recorded, and then the crown ether solution was added in small increments until its total concentration was more than twice the concentration of the metal ion. After each addition, voltammograms were recorded at a scan rate of 5 mV/s and pulse amplitude of 50 mV. The supporting electrolyte used was 0.05 M tetraethylammonium perchlorate.

Table 1. Conductivity Data of $Cu(ClO_4)_2$ and $Cu(ClO_4)_2$−15C5 in 20 Mass % PC + EC by Steps 1, 2, and 3 (parts a, b, and c, Respectively)

(a) Conductivity Data of $Cu(ClO_4)_2$ in 20 Mass % PC + EC by Step 1

concentration C × 10^3 (M)	Λ_C S cm^2 mol^{-1}
0.318	50.91
0.634	49.54
1.258	47.61
2.024	46.94
3.072	44.99
4.521	43.62
7.261	41.10
9.808	39.09
13.310	36.97
19.363	34.99
22.821	34.02

(b) Conductivity Data of $Cu(ClO_4)_2$−15C5 in 20 Mass % PC + EC by Step 2

ratio $[L]_t/[M]_t$	Λ S cm^2 mol^{-1}
0.173	46.68
0.346	46.35
0.519	46.03
0.691	45.73
0.864	45.45
1.037	44.30
1.296	44.91
1.712	44.92
2.160	44.93
2.792	44.93

(c) Conductivity Data of $Cu(ClO_4)_2$−15C5 in 20 Mass % PC + EC by Step 3

concentration $[M]_t$ × 10^3 (M)	Λ S cm^2 mol^{-1}
0.107	56.98
0.265	56.54
0.422	56.14
0.629	55.84
0.833	55.52
1.132	55.04
1.474	54.69
1.854	54.09
2.315	53.51
3.185	52.87

Theory

Conductometry. The conductivity data (Table 1) of the metal perchlorates in 20 mass % PC + EC were treated by Fuoss and Edelson method as done earlier.[13−15] The method consists of evaluating limiting equivalent conductance, Λ_0, and the first step association constant, K_A, of an electrolyte of the type MX_2 in 20 wt % PC + EC based on the following equilibrium:

$$M^{2+} + ClO_4^- \overset{K_A}{\rightleftharpoons} MClO_4^+ \qquad (1)$$

where M = Mg, Ca, Sr, Ba, and Cu. The equations for determining K_A, stability constants ($K_{ML}{}^{n+}$) and limiting

Table 2. Summary of the Values of Λ_0, $\lambda^0{}_{M^{2+}}$, and K_A for Divalent Metal Perchlorates Obtained from Fuoss and Edelson Plots in 20 Mass % PC + EC

M $(ClO_4)_2$	Λ_0	$\lambda^0{}_{M^{2+}}$	K_A
$Mg(ClO_4)_2$	52.3	2.9	45.76
$Ca(ClO_4)_2$	57.9	8.6	5.22
$Sr(ClO_4)_2$	65.0	15.6	6.63
$Ba(ClO_4)_2$	61.2	11.8	16.52
$Cu(ClO_4)_2$	52.5	3.1	17.25

molar conductivity of the complexes have been discussed in detail before.[14,15] The limiting ionic conductance ($\lambda^0{}_{ML^{n+}}$) of the metal−crown ether complex is obtained by using $\lambda^0{}_{ClO_4^-} = 24.7$ S cm^2 mol^{-1} in 20 mass % PC + EC.[8]

Potentiometry. The theory of potentiometric determination of stability constants has been discussed before.[14,15]

Voltammetry. The determination of stability of complexes by voltammetry is based on the fact that on complexation the half wave potential is shifted to more negative potentials.[16] The relation between the shift in half wave potential and the stability constant is as follows:

$$\Delta E_{1/2} = (E_{1/2})s - (E_{1/2})c = (0.05916/n) \log B_p + (0.05916\, p/n) \log C_x \quad (2)$$

where $(E_{1/2})s$ and $(E_{1/2})c$ are the half wave potentials of the free and complexed cations, respectively. B_p is the stability constant, C_x the total ligand concentration, and "p" is the metal-to-ligand ratio. The half wave potential obtained by sampled DC polarography can be correlated to the peak potential (Ep) as obtained by differential pulse polarography by the following equation:

$$E_{1/2} = \mathrm{Ep} + \Delta E/2 \quad (3)$$

As the shift in peak potentials can be measured more accurately than the half wave potentials, eq 2 can be replaced by

$$\Delta \mathrm{Ep} = (\mathrm{Ep})s - (\mathrm{Ep})c = (0.05916/n) \log B_p + (0.05916\, p/n) \log C_x \quad (4)$$

Equation 4 indicates that if plots of ΔEp vs log C_x are made the intercept will give the value of (0.05916/n) log B_p and the slope will be (0.05916 p/n). These plots were used to calculate the stability constants and the value of p was found to be between 0.8 and 1.3 in all cases, which indicates 1:1 complexation.

Results and Discussion

A representative set of conductometric data for Cu^{2+} by steps 1−3 is given in Table 1. The values of limiting molar conductance, Λ_o, $\lambda^0{}_{M^{2+}}$, and K_A for $M(ClO_4)_2$ in 20 mass % PC + EC are summarized in Table 2. The order of limiting ionic conductivity for the alkaline earth metal ions is found to be Sr(II) > Ba(II) > Ca(II) > Mg(II). The lowest value of limiting ionic conductivity, and the highest value of K_A for $Mg(ClO_4)_2$, indicates that the Mg^{2+} ions are much more solvated than any other alkaline earth metal ions in 20 mass % PC + EC. The trend in the $\lambda^0{}_{M^{2+}}$ values obtained in the present work is similar to the trend reported in PC.[5]

Figures 1 and 2 are representative of the results of the studies on the metal ion complexation with 15C5, B15C5, 18C6, DB18C6, DCH18C6, DB24C8, and DCH24C8 by the conductometric method. It was observed that the Λ_C value decreases with an increase in $[L]_t/[M]_t$ for the complexes of Ca(II), Sr(II), and Ba(II) with 18-membered crown ethers and DB24C8. Also, Ca(II) and Sr(II) complexes with DCH24C8 showed the same trend. However, the reverse trend, i.e., increase in Λ_C value with the increase in $[L]_t/[M]_t$, is observed for all Mg^{2+}−crown ether complexes. The complexes of Ca(II), Sr(II), and Ba(II) with 15-membered crown ethers also showed this trend. The same pattern is observed in the case of Ba(II) complexes with DCH24C8. All Cu(II) and Ag(I) complexes showed a decrease in Λ_C values with increase in $[L]_t/[M]_t$.

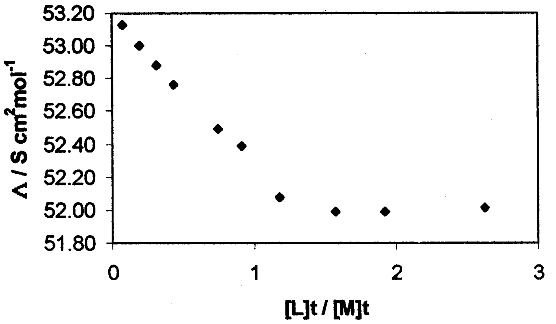

Figure 1. Plot of Λ vs $[L]_t/[M]_t$ for the DB18C6−$Ca(ClO_4)_2$ system.

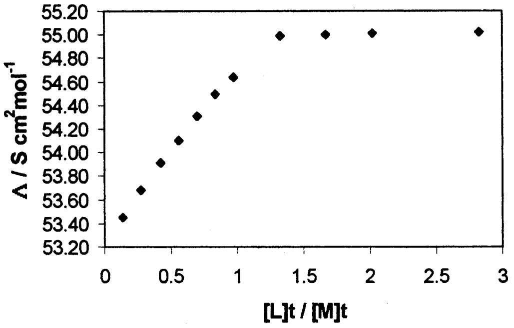

Figure 2. Plot of Λ vs $[L]_t/[M]_t$ for the 15C5−$Ca(ClO_4)_2$ system.

The decrease in value of Λ_C with an increase in $[L]_t/[M]_t$ can be explained on the basis of the much larger size of the complexed ion compared to that of the simple uncomplexed ion, although the increase in Λ_C with the increase in $[L]_t/[M]_t$ shows that the conductivity of the complexed ion is larger than that of the simple uncomplexed ion. Generally, such phenomenon can be explained as follows:

In a solvent of low donicity, a stable complex is formed even between a small metal ion and small crown ether, which has a poor binding ability. On account of strong solvation of the small metal ions and the less solvated complex with the small crown ether, the conductivity of the less solvated complex is larger than that of the strongly solvated uncomplexed ion. Hence, the conductivity of Mg(II) complexed with all crown ethers is larger than that of the simple uncomplexed Mg(II) ion.

In either case, a clear break point at $[L]_t/[M]_t \approx 1$ is observed for all metal ion−crown ether complexes studied. This indicates 1:1 complexation for all of the systems studied. A summary of the results, i.e., stability constants and limiting ionic conductivities of the complexes, obtained from the complexation studies are given in Tables 3 and 4.

With the perchlorate anion being common for all of the systems studied, the values of $\lambda^0{}_{ML^{n+}}$ for particular crown ether show the following order for alkaline earth metal cations: Sr(II) > Ba(II) > Ca(II) > Mg(II)

Many formation constant values have been reported by using diverse experimental methods. The enhancement of complex stability by a close correspondence between the ionic crystal radius and the radius of cavity formed by the polyether ring has been noted.[17−19] A full participation of

Table 3. Stability Constants (log $K_{ML}{}^{n+}$) for the Metal Ion−Crown Ether Complexes by Conductometry[a]

	log $K_{ML}{}^{n+}$						
metal ion	15C5	B15C5	18C6	DB18C6	DCH 18C6	DB24C8	DCH 24C8
Mg	4.74	4.41	4.61	4.40	4.21	4.83	4.46
Ca	4.10	3.79	4.07	3.78	3.81	4.01	3.88
Sr	4.04	3.71	3.89	3.71	3.50	4.07	3.87
Ba	3.81	3.35	3.51	3.48	3.17	3.73	3.50
Cu	4.20	3.78	4.17	3.86	3.99	4.35	3.97
Ag	4.52	4.13	4.92	4.55	4.93	5.02	4.49

[a] In all cases the standard deviation was less than 0.06 ($5 \leq n \leq 9$).

Table 4. Limiting Ionic Conductivities ($\lambda^0{}_{ML}{}^{n+}$) for the Metal Ion−Crown Ether Complexes by Conductometry

	$\lambda^0{}_{ML}{}^{n+}$/S cm^2 mol^{-1}						
metal ion	15C5	B15C5	18C6	DB18C6	DCH 18C6	DB24C8	DCH 24C8
Mg	2.5	7.5	5.7	7.2	8.2	3.5	6.0
Ca	7.6	12.7	10.6	12.0	13.1	8.5	11.1
Sr	16.8	19.0	18.3	18.8	19.5	17.5	18.7
Ba	12.6	15.8	13.9	15.4	16.2	13.4	14.6
Cu	8.5	10.7	10.0	10.6	11.1	9.1	10.4
Ag	0.4	2.3	1.5	2.1	2.8	0.9	1.0

Table 5. Potentiometric Data Obtained for Cu(II)−15C5 System

$[M]_t \times 10^3$ (M)	$[L]_t \times 10^3$ (M)	ΔE (mV)
0.1140	0.0953	07
0.1140	0.2383	16
0.2281	0.1906	09
0.2281	0.4766	22
1.5962	2.8592	40

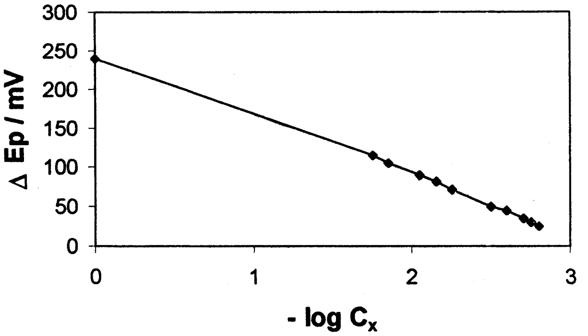

Figure 3. Plot of ΔEp vs − log C_x for the B15C5−$AgClO_4$ system.

all macrocycle donor atoms with the complexed cation is expected to give the highest possible stability to the resulting complex. Thus, it is found that Mg(II) (ionic radius = 0.66 Å) forms a more stable complex with 15C5 (cavity radius = 0.85−0.92 Å) than the other alkaline earth metal ions, as they are larger. However, in 20 wt % PC + EC, it is also observed that the Mg(II) complex with DB24C8 (cavity radius = 2.0−2.2 Å) is as stable as the Mg^{2+}−15C5 complex. Similarly, Sr(II) (1.12 Å) gives an equally stable complex with DB24C8 and 15C5 inspite of the large differences in their cavity radii. Also, Cu(II) (0.77 Å), which is a closer match to 15C5 than Mg(II), happens to form less stable complex than Mg(II).

From these studies, the "ion-in-hole" model does not seem to be universally applicable in predicting relative binding capabilities of metal cations with polyethers. For example, as the number of ring atoms increases, the flexibility of the macrocycle increases, and it becomes more difficult to define the cavity diameter. These large polyethers are capable of wrapping around the cation to form a three-dimensional cavity with all oxygen atoms coordinated to the cation. So, it is found that small ions such as Mg(II), form equally stable complexes with 15C5 as well as DB24C8.

Table 6. Summary of the Stability Constants (log $K_{ML}{}^{n+}$) of Copper−Crown Ether Complexes by Different Methods

crown ether	conductometric method	potentiometric method	voltammetric method
15C5	4.20	4.17	4.19
B15C5	3.78	3.81	3.79
18C6	4.17	4.16	4.18
DB18C6	3.86	3.90	3.84
DCH18C6	3.99	4.00	3.99
DB24C8	4.35	4.36	4.36
DCH24C8	3.97	3.91	3.94

[a] In all cases the standard deviation was less than 0.06 ($5 \leq n \leq 9$).

Table 7. Summary of the Stability Constants (log $K_{ML}{}^{n+}$) of Silver−Crown Ether Complexes by Different Methods[a]

crown ether	conductometric method	potentiometric method	voltammetric method
15C5	4.52	4.65	4.59
B15C5	4.13	4.12	4.06
18C6	4.92	4.89	4.94
DB18C6	4.55	4.53	4.55
DCH18C6	4.93	4.94	4.92
DB24C8	5.02	5.01	5.16
DCH24C8	4.49	4.48	4.43

[a] In all cases the standard deviation was less than 0.06 ($5 \leq n \leq 9$).

In general, the results in Table 3 show a specific trend in the stability constant values. The values of stability constants for any particular crown ether are found to be in the order of Mg(II) > Ca(II) > Sr(II) > Ba(II). The similar order of the stability constants has been obtained with 18C6 complexes in PC.[5]

Table 5 gives a representative set of data for Cu(II)−15C5 complexation by potentiometry, and Figure 3 shows the plot of ΔEp vs −log C_x for the B15C5−$AgClO_4$ system obtained by voltammetry. From Tables 6 and 7, it is seen that the stability constants obtained by the three methods are nearly same, which shows the reliability of the results.

Literature Cited

(1) Lee, W. H. Cyclic Carbonates. In *The Chemistry of Non-Aqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1976; Vol. 4.

(2) Mukherjee, L. M. Non-Aqueous Solvent Chemistry-Some Recent Studies. *Crit. Rev. Anal. Chem.* **1975**, *4*, 325−327.

(3) Izutsu, K.; Kolthoff, I. M.; Fujinaga, T.; Hattori, M.; Chantooni, M. K., Jr. Acid−Base equilibria of Some Acids in Propylene Carbonate *Anal. Chem.* **1977**, *49*, 503−508.
(4) Srivastava, A. K.; Mukherjee, L. M. Some potentiometric studies in Propylene Carbonate: Application of hydrogen and quinhydrone electrode and evaluation of proton medium effect from ferrocene assumption. *J. Electroanal. Chem.* **1984**, *160*, 209−216.
(5) Srivastava, A. K.; Tiwari, B. Behaviour of alkaline earth metals and silver perchlorates and their complexes with some crown ethers in propylene carbonate. *J. Electroanal. Chem.* **1992**, *325*, 301−311.
(6) Petrella, G.; Sacco, A. Viscosity and Conductance Studies in Ethylene Carbonate at 40 °C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2070−2076.
(7) Fong, R.; Sacken, U. V.; Dhan, J. R. Studies of lithium intercalation into carbons using nonaqueous electrochemical cells. *J. Electrochem. Soc.* **1990**, *137*, 2009−2016.
(8) Srivastava, A. K.; Samant, R. A. Ionic Conductivity in Binary Solvent Mixtures. 1. Propylene Carbonate (20 Mass %) + Ethylene Carbonate at 25 °C. *J. Chem. Eng. Data* **1994**, *39*, 358−360.
(9) Samant, R. A.; Ijeri, V. S.; Srivastava, A. K. Electrochemical Behaviour of some Copper (II) salts in 20 wt % Propylene Carbonate + Ethylene Carbonate: Standard Potential of the Cu^{2+}/Cu system at 25 °C. *J. Electroanal. Chem.* Accepted for publication.
(10) Srivastava, A. K.; Samant, R. A. Some conductance and potentiometric studies in 20 mass % propylene carbonate + ethylene carbonate: application of hydrogen and quinhydrone electrodes. *J. Electroanal. Chem.* **1995**, *380*, 29−33.
(11) Fuoss, R. M. Conductance−concentration function for the paired ion model. *J. Phys. Chem.* **1978**, *82*, 2427−2440.
(12) Popov, A. I.; Geske, D. H. Silver−silver chloride Reference Electrode in Acetonitrile. Polarography. *J. Am. Chem. Soc.* **1957**, *79*, 2074−2079.
(13) Fuoss, R. M.; Edelson, D. Bolaform Electrolytes. I. Di-(β-trimethylammonium Ethyl) Succinate Dibromide and Related Compounds. *J. Am. Chem. Soc.* **1951**, *73*, 269−273.
(14) Ijeri, V. S.; Srivastava, A. K. The Complexation Behaviour of Crown Ethers with Some Divalent Transition Metal and Silver Ions in 40%(v/v) Ethanol + Water Medium. *Eur. J. Inorg. Chem.* **2001**, 943−947.
(15) Ijeri, V. S.; Srivastava, A. K. Complexation of Macrocyclic Compounds with Metal Ions: 1. Cd(II), Pb(II), Co(II), Mn(II), and Ag(I) in 40 vol % Ethanol + Water Medium. *J. Chem. Eng. Data* **2002**, *47*, 346−350.
(16) Irving, H. The stability of metal complexes and their measurements polarographically. In *Advances in Polarography*; Langmuir, I. N., Ed.; Pergamon Press: New York, 1960; Vol. I.
(17) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. The Synthesis of Ion Binding of Synthetic Multidentate Macrocyclic Compounds. *Chem. Rev.* **1974**, *74*, 351−384.
(18) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. Thermodynamic and Kinetic Data for Cation-Macrocycle Interaction. *Chem. Rev.* **1985**, *85*, 271−339.
(19) Frensdorff, H. K. Stability Constants of Cyclic Polyether Complexes with Univalent Cations. *J. Am. Chem. Soc.* **1971**, *93*, 600−606.

Received for review September 13, 2002. Accepted October 30, 2002.

JE0201774