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Electrochemical Studies on Ion Recognition of Alkali Metal Cations by 18-crown-6 in Methanol

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Electrochemical studies of alkali metal cations (Na^+, K^+, Rb^+, Cs^+) were performed in methanolic solutions of 18-crown-6 and tetrabutylammonium salts at dropping mercury electrodes (DME) and thin mercury film electrodes (TMFE). All the cations investigated were reduced reversibly at DME in the absence and presence of 18-crown-6, and in the latter the limiting currents were decreased and the reduction potentials shifted to the negative direction. The reduction potentials of the metal ions (0.2 mM) in the presence of the crown (10 mM) were -2.14 (Na^+), -2.26 (K^+), -2.20 (Rb^+) and -2.14 (Cs^+) V vs. SCE, respectively. The measured potentials were rationalized with ion recognition of the cations by the crown. Electroreduction at TMFE were highly irreversible. A new representation method of ion recognition is presented. In aqueous solutions, electroreduction of the alkali metal ions were characterized by adsorption.

Introduction

Recognition at the molecular level is a fundamental characteristic of enzyme catalysis, metal ion transport and information storage in biochemical systems.[1-3] There is a great deal of interest in elucidating mechanisms of molecular recognition by modeling host molecules that are highly selective in their binding to guest molecules or ions and by determining the thermodynamic stability constants in solutions and the crystal structures of host-guest complexes.[4,5] A particular

class of host molecules studied extensively are the crown ethers. Extensive thermodynamic and kinetic data are compiled for cation-crown ether complexes by Izatt et al.[6] Recent studies include theoretical evaluations of thermodynamic and kinetic aspects of Na^+ and K^+-(18-crown-6)complexes.[7-9]

Although electrochemical methods can compensate for or excell other methods, e.g., spectroscopic, calorimetric and potentiometric methods, in certain aspects to determine the thermodynamic and kinetic parameters on the complexation not many electrochemical investigations were made to cha-
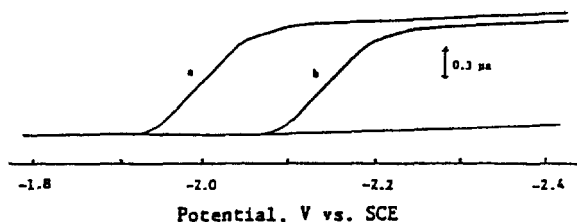
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Figure 1. Typical normal pulse polarograms obtained for 0.2 mM sodium ions in methanolic solution of 50 mM tetrabutylammonium iodide in the absence (a) and presence (b) of 18-crown-6 (10 mM).

Figure 2. Heyrovsky-Ilkovic plots for the data in Figure 1.

Figure 3. Half-wave potentials $vs.$ log [18-crown-6] plot for electroreduction of sodium ions in the presence of 18-crown-6.

racterize the host-guest interactions.[6] Some electrochemical studies were done by Koryta *et al.* for substituted crowns-monovalent cation complexes[10] and by Agostiano *et al.*[11] but not for the unsubstituted crowns. In addition, there are some conflicting results between the two reports; the shifts in half-wave potentials measured agreed in the two reports but the limiting currents disagreed each other. In the present report, we resolve the disagreement, describe the electroreduction of alkali metal ions-(18-crown-6) complexes for the first time and explore the recognition of the cations by the crown receptor.[13] Also, we introduce a new representation method of ion recognition through size-match (or other molecular variable in general), which could be useful for the ligand with limited availability.

Experimental

Tetrabutylammonium iodide (Southwestern analytical) was recrystalized from methanol/ether, and tetrabutylammonium perchlorate (Southwestern analytical) and 18-crown-6 (Aldrich) were used as received. Other chemicals were the best chemicals available commercially. All cations used were chloride salts. Most of the measurements were performed by normal pulse or direct-current polarography using Metrohm model E505 and E506. The auxillary electrode was a Pt-wire, and silver-silver chlorides or saturated calomel electrodes (SCE) with salt bridge were used as a reference electrode. Thin mercury films at glassy carbon electrodes were prepared by applying -0.5 V ($vs.$ SCE) for 5 min in 1 mM mercuric nitrate solutions.[12] The supporting electrolyte used was 0.05 M tetrabutylammonium ioide or perchlorate. Nitrogen of high purity passed a bubbler containing methanol was used for removing oxygen from the sample solution. All experiments were done at 25°C using three compartment cells to minimize the leakage of potassium ions from SCE, which can cause serious errors on electrochemical measurement of the system (vide infra). Quoted potentials were given with respect to SCE. In liquid ammonia solution, silver quasi reference electrode was used as a reference electrode.[13]

Results and Discussions

The typical normal pulse polarograms are shown in Figure 1 for the electroreduction of sodium ions in the methanolic solutions of 50 mM tetrabutylammonium iodide. The half-wave potential of the polarogram is shifted to more negative potentials in the presence of 18-crown-6 because of the com-
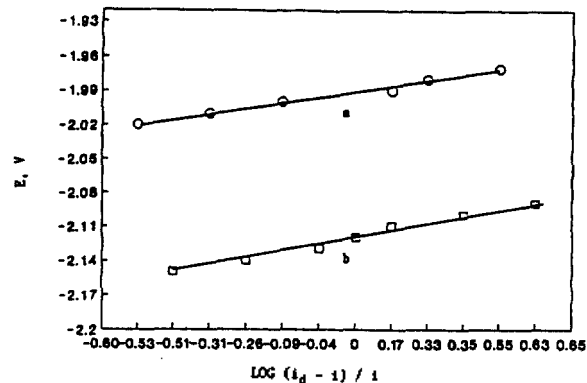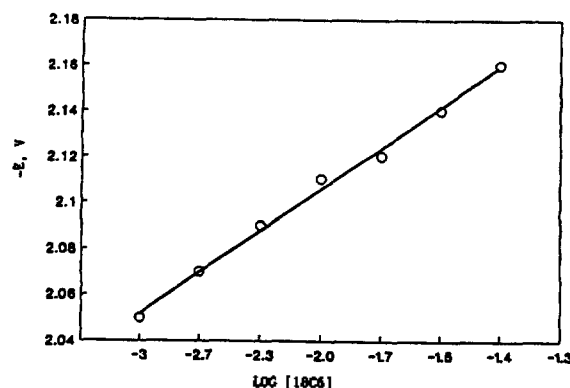
plex formation between the guest, Na^+, and the host, 18-crown-6. The limiting currents of sodium ion reduction were controlled by diffusion (from the square-root dependence on corrected mercury column height) in the absence of as well as in the presence of 18-crown-6 and the potential $vs.$ log $(i_d\text{-}i)/i$ plot showed a linear slope near 60 mV for both cases (Figure 2) under the present experimental conditions, indicating the fast charge transfer across the electrode/electrolyte interface resulting in the establishment of an equilibrium between the free and coordinated sodium ions in solution and sodium atoms dissolved in the amalgam. The voltammetric responses at thin mercury film electrodes were highly irreversible. Accordingly, the electrochemical responses can be assigned as follows

$$Na^+\text{-}(18\text{-crown-6}) + e = Na(amalgam) + 18\text{-crown-6}$$

The backward reaction is very slow. This is contrasted with the $Tl^+/Tl°$(amalgam) couple in the presence of excess cryptand, where Nernstian voltammograms are reported to be obserbed.[15]

The irreversible behavior is not unexpected since the metal ion will escape the cavity of the host in the electron transfer process. Thus at the surface of the electrode the equilibrium between the complexes and the free sodium ions with the hosts is disturbed as a consequence of the electroreduction of the free sodium ions and the complexes dissociate into the free sodium ions and the hosts.

As shown in Figure 1, the limiting current of the complex was smaller than that of the free sodium ions, indicating

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Table 1. Half-Wave Potentials (V, vs. SCE) for Electroreduction of Alkali Metal Ions and Formation Constants for (18-crown-6)-alkali Metal Ions in 50 mM TBAP Methanol at 25℃

M^+	[18C6]	$E_{1/2}$	log K
Na^+	0	-2.00	4.44
	10	-2.14	
K^+	0	-1.99	6.55
	10	-2.26	
Rb^+	0	-1.99	5.55
	10	-2.20	
Cs^+	0	-1.97	4.88
	10	-2.14	

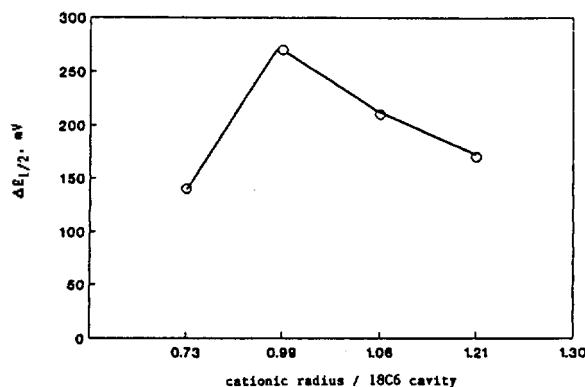**Figure 4.** Shift in half-wave potential vs. the ratio of the ionic radius to the 18-crown-6 cavity radius.

the smaller diffusion coefficient of the former.[13] The larger size of the complexed sodium ions is compatible with the smaller diffusion coefficient. Our result agrees with that of Koryta et al.[10] but disagrees with that of Agostiano et al.[11] We believe that the leakage of potassium ions from SCE were the source of error in reference 11 because we observed the significant leakage of the potassium ions from SCE when we used one compartment cell.[13]

The ratio for the host-guest interaction can be determined by Lingane's method from the concentration dependence of the half-wave potential measured in the presence of the host ligand.[14] Thus from the half-wave potentials vs. log [crown] (Figure 3), the ratio between sodium ion and the crown is determined to be one. Further, for the reversible amalgam-forming reduction of labile complexes of high stability the simple Lingane equation

$$E_{1/2}^{complex} - E_{1/2}^{Na^-} = -RT/F\ [\ln K + m\ \ln\ [Crown]\ ]$$

is applicable to determine the stability constant, where $E_{1/2}^{complex}$ and $E_{1/2}^{Na^+}$ are the half-wave potentials for $Na^+/Na(Hg)$ couple in the presence of a large excess of crown and in noncomplexing media, respectively, K is the stability constant of sodium ion-(18-crown-6) and [crown] is the total (analytical) concentration of crown. The analysis of the data for sodium ions yielded log $K = 4.44$; in good agreement with an earlier determination (4.36) using titration calorimetry.[14] The slopes of the Heyrovsky-Ilkovic plots were 60 mV with all the cations and cation-complexes investigated in this study, showing Nernstian behavior for the electroreduction.

The measured half-wave potentials and the results of the analysis for the alkali metal ions investigated are summarized in Table 1. The formation constants of alkali metal ions with 18-crown-6 are larger than the reported values with substituted crowns,[10,11] indicating that additional structural rearrangements are required to form the metal ion-crown complex with the later. The crown forms the most stable complex with potassium ion (log $K = 6.55$) with the potential shift observed 270 mV in methanolic solution. This compares the potential shift, 140 mV, observed for sodium ions in the present experimental conditions (0.2 mM metal ions and 10 mM 18-crown-6). The differentiation by 18-crown-6 in recognizing potassium ions over sodium ions may originate from the size-match selectivity[4]; the cavity radius of 18-crown-6 is 1.34~1.43 Å, while the ionic radii are 1.02 (Na^+), 1.38 (K^-), 1.52 (Rb^+) and 1.67 (Cs^+) A, respectively.[6] Thus the

size matching may allow the host to reorganize and desolvate for complexing act.[1]

When the electrochemical responses are Nernstian, as are shown in this study, the ability of the host in recognizing the guests can be evaluated directly from the shift in half-wave potential observed. To see the size-match selectivity (or other molecular variable in general) the potential shifts measured for the alkali metal ions are plotted as a function of the ratio of the ionic radius to the 18-crown-6 cavity radius in Figure 4. The results reveal the perceiving capability of 18-crown-6 in identifying the guest ions through size matching, maximizing the potential shift with potassium ion. The size-match selectivity has been demonstrated by the plot of log K versus the ratio of the ionic cation radius to the host cavity radius.[4,6] The new method of potential shift representation is quick, because it does not require long time of data analysis (often true with potentiometric titration method[16]), and easy, because the shift in half-wave potential can be measured directly from the experimental voltammograms, but clear, because the error involved in the measurement of potentials is not large (usually several mV). However, it should be noted that the method of using the potential shifts in ion recognition by hosts can be applied for the Nernstian signals of amalgam-forming electrode reactions. The present method would be useful for the ligand with limited availability, which is often the case of newly prepared compounds.

In aqueous solutions of tetrabutylammonium salts, electroreductions of the alkali metal ions were characterized by adsorption with half-wave potentials of -2.15 V versus SCE and the reduction potentials were nearly unchanged in the presence of 18-crown-6. In liquid ammonia solutions, the alkali metal cations were reduced reversibly at DME but little change was observed in the reversibility and half-wave potentials in the presence of 18-crown-6, conforming to the small formation constant in the medium.[6]

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Molecular Dynamics Study on the Structural Phase Transition of Crystalline Silver Iodide

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The β to α phase transition in silver iodide is studied with the (N, V, E) and (N, P, T) molecular dynamics (MD) method. In experiments, the phase transition temperature is 420 K. Upon heating of β form, the iodine ions undergo hcp to bcc transformation and silver ions become mobile. MD simulations for the β and α phases are carried out at several temperatures and the radial distribution functions (rdf) are obtained at those temperatures in the (N, V, E) ensemble. But the phase transition is not found in our calculation. Next the phase transition is studied with the (N, P, T) MD and we find some evidences of phase transition. At 3 Kbars and 2 Kbars the phase transition temperature is about 300 K. For 3.55 Kbars, the phase transition is higher (420 K) than the low pressure case. The phase transition temperature is somewhat dependent on the pressure in our calculations.

Introduction

In the last several years, many theoretical and experimental works have been done for the study of crystalline silver iodide, which, in the high temperature α phase, may be considered as the model of the superionic conductor. Superionic conductors are a class of systems in which pheomena observed in fluids and solids come together in an interesting manner.[1-3] Silver iodide shows a number of structural transitions as a function of pressure and temperature.[4,5] At 420 K, β phase undergoes a transition into superionic α phase.

Computer simulation is one of most powerful techniques of studying liquids and highly anharmonic solids. Historically, Monte Carlo method was the first simulation technique applied to determine the equilibrium properties of fluids, such as their pair distribution functions and the thermodynamic properties.[6] This approach consists of using a canonical ensemble in which a given number of particles N are confined to fixed volume V at temperature T. Usually the particles interact with an assumed potential $\phi(r_{ij})$, where r_{ij} is the distance between particles i and j and periodic boundary conditions are used to simulate an infinite system. Other ensembles, such as the isothermal-isobaric one in which N, T, and P are fixed but the volume V fluctuates, have also

been used.[7] For molecular systems, the first Monte carlo calculation was that of Barker and Watts who used the canonical (N, V, T) ensemble to study a model of liquid water.[8] Subsequent workers have employed the (N, V, T) approach and also the (N, P, T) ensemble to test a variety of potential models for molecular systems and such calculations are now routine. In the other simulation technique, called molecular dynamics (MD),[9] the Newtonian equations of motion are integrated numerically for the systems of N particles, confined to a fixed volume V. It was Anderson[10] who first proposed how one might carry out MD calculations under conditions of constant temperature, constant pressure, or constant temperature and pressure rather than the more usual constant energy and volume. Note that in the method of Anderson only changes in the volume of the cell were possible but not in its shape. Thus crystal structure transitions are inhibited in Anderson's method because of the suppression of the essential fluctuations, namely those in the shape of MD cell. The next important development was the work of Parrinello and Rahman[11,12] who introduced a Lagrangian that allowed for the possibility that the MD cell might changes its shape. An alternative procedure rescales the coordinates of each atom at each time step. The atomic coordinate and the characteristic distance for repeating boundary conditions are re-