

Articles

Conductance Study on the Characteristics of Solution Containing Crown Ethers and Univalent Cation Perchlorates

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The equivalent conductance of univalent cation (potassium, silver, thallium and ammonium) perchlorates in methanol containing 18-membered crown ethers, 18-crown-6 (18C6) and 1,10-dithia-18-crown-6 (DT18C6) were measured at different temperatures. The equivalent conductances of ammonium perchlorate were increased by increasing content of DT18C6 exceptionally, due to more favorable solvations than complexations. From the equivalent conductance changes, the formation constants for 1:1 complexes have been determined, and the values of enthalpy and entropy changes have been calculated. The complexations of 18C6 and DT18C6 with the univalent cations under investigation are all exothermic and the ΔS values are all negative and no considerable differences around 50 J/(k mol). The selectivity order of 18C6 is $K^+ > Tl^+ > Ag^+ > NH_4^+$, while that of DT18C6 is $Ag^+ > Tl^+ > NH_4^+ > K^+$. By sulfur substitutions in 18C6 result in significant decrease in stability, but the stability of Ag^+ -DT18C6 complex are 10^4 times larger than those of K^+ . This increase of stabilities for Ag^+ -DT18C6 complex are primary due to the result of favorable exothermic heat of reaction between the polarizable soft cation and soft sulfur centers. In NMR experiment, the stepwise additions of cation perchlorates into crown ether solutions induced two major spectral changes. First, the resonance all shift down field and the cation induced shifts were linear up to 1:1 cation/crown ratio, above which no further changes were observed. On the basis of these results, it could be concluded that 1:1 complex is formed. Second, the magnitudes of cation induced shifts were different each other in same ligand. By addition of silver ion to the solution of DT18C6, the largest shift of proton peak near the sulfur atom was observed. These effects are also arisen from the results of covalent bonding between "soft-soft" interactions.

Introduction

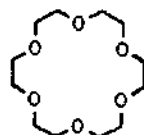
Numerous crown ethers containing mixture of oxygen, sulfur and nitrogen donor atoms have been synthesized.¹ The thermodynamic quantities associated with their complexation have been determined in a number of cases.^{2,3}

The solution chemistry of univalent cations was mainly developed only in the last twenty years.⁴ The lack of complex reactivities with simple ligands and the absence of spectroscopic and magnetic properties are the major explanations for this differed exploration of these species.

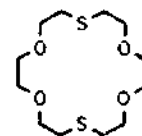
The selectivity shown by certain cyclic polyethers toward cations is well documented,^{5,6} but few studies involving sulfur derivatives have been reported.⁷ The partial substitution of sulfur for oxygen in several crown ethers produce drastic effects on ion-ligand interactions. In aqueous solution, little or no reaction occurs between the sulfur containing crown ethers and alkali or alkaline earth metal ions.⁸

The present study was undertaken in order to quantify the strength of complexation in a solution as a function of sulfur substitutions, temperature and the chemical properties of cation. In this paper the formation constants and the thermodynamic quantities for 1:1 complexes of 18C6 and DT18C6 with potassium, silver, thallium and ammonium ions in methanol at 15~35 °C have been determined conductometrically and on the basis of molar conductivity changes,

the solvation behaviors of the complexes in solutions are discussed. The stoichiometry, and the degree of binding contributions of donor atoms on complexation in solution by NMR are also discussed here and further detailed informations for various crown ether by NMR have been in the preceding paper.⁹



18-crown-6
(18C6)



1,10-dithia-18-crown-6
(DT18C6)

Experimental

Materials. DT18C6 was synthesized and purified by the method of Izatt.¹⁰ The identification and its purity were established by NMR and infrared spectroscopy. A sharp singlet at 3.55 and a pair of triplet at 2.75 and 3.64 ppm was observed, which were identical with the results of previous workers.¹⁰ The infrared spectra exhibited spectral characteristics which were nearly identical with those reported in the literature¹⁰: 2880, 1050 and 685 cm^{-1} . 18C6 was obtained from Aldrich and recrystallized from acetonitrile and prior to

Table 1. Equivalent Conductances of Methanolic Solutions Containing Cationic Perchlorates and 18C6 at 25.0°C

$[L]_0/[M]_0$	λ_{eq}	$[L]_0/[M]_0$	λ_{eq}	$[L]_0/[M]_0$	λ_{eq}	$[L]_0/[M]_0$	λ_{eq}	$[L]_0/[M]_0$	λ_{eq}
Na ⁺		K ⁺		Ag ⁺		Tl ⁺		NH ₄ ⁺	
0	117.2	0.000	123.23	0.000	117.89	0.000	131.14	0.000	125.60
0.148	116.57	0.355	119.12	0.240	115.34	0.231	130.09	0.264	123.11
0.297	115.87	0.685	115.33	0.481	113.31	1.401	127.51	0.367	122.31
0.431	115.24	1.010	112.18	0.694	111.57	0.580	125.09	0.486	121.39
0.556	114.74	1.291	111.58	0.908	110.14	0.753	124.88	0.713	119.70
0.683	114.15	1.581	111.51	1.113	109.26	0.922	120.66	0.826	118.88
0.810	113.76			1.312	108.70	1.064	119.37	0.906	118.36
0.921	113.37			1.504	108.47	1.241	118.70	0.991	117.80
1.033	113.1			1.868	108.19	1.398	118.45	1.094	117.23
1.148	113.1			2.041	108.07	1.529	118.41	1.274	116.36
1.269	112.67			2.530	108.04	1.665	118.37	1.589	115.26
1.357	112.67			2.709	108.02	1.790	118.35	2.002	114.46
1.456	112.67							2.260	114.18
1.552	112.36							2.354	114.16
1.653	112.32								
1.733	112.32								
1.823	112.16								

use, dried at 70°C in a vacuum oven.

Ammonium and thallium perchlorates¹¹ were prepared by adding an equimolar perchloric acid solution to aqueous solution to chlorides, respectively. Potassium and silver perchlorates were recrystallized from water two times and dried at 120°C in a vacuum oven. Methanol was distilled twice and the middle 70% of the distillate was stored with 4 Å molecular sieve under vacuum condition before use.

Apparatus and Procedures. The conductance measurements were with a Solea Tacussel conductivity apparatus, Model CD810 which has a stated accuracy of 0.2% of reading in water bath thermostated at 15, 20, 25, 30 and 35 ± 0.02°C. Two conductivity cell were used with cell constant of 0.1678 and 0.7590 cm⁻¹, calibrated with standard KCl solutions.

Our method is a slight variation of a procedure described by Takeda *et al.*¹² The experimental procedures to obtain equivalent conductivity of univalent cation perchlorates solution containing crown ether is as follows. The accurate concentration of perchlorate solution (4–6 × 10⁻⁴ M, 25.0 ml) was placed in thermostated vessel and the conductivity of solution measured. The stock solution of crown ether was prepared by dissolving an accurately weighted amount of ligand (app. 3 × 10⁻³ M) in perchlorate solution which has same composition as titrant. Then a step by step increase of crown ether concentration was effected by a titration with a microburet from the solution of crown/salt mixture to the vessel, until the concentration of ligand was about three times as large as that of salt.

These types of procedures differ from that commonly encountered in conductance studies of electrolyte solutions.¹³ Ordinarily, the equivalent conductivities of solution are measured as a function of ionic concentration, but in this study the electrolyte concentration remains constant to correct the effect of ion-ion interaction to be absent.¹⁴ Hence, the solution systems could be regarded as a mixed electrolyte solution with a common anion at constant ionic strength.

Table 2. Equivalent Conductances of Methanolic Solutions Containing Cationic Perchlorates and DT18C6 at 25.0°C

$[L]_0/[M]_0$	λ_{eq}	$[L]_0/[M]_0$	λ_{eq}	$[L]_0/[M]_0$	λ_{eq}
Ag ⁺		Tl ⁺		NH ₄ ⁺	
0.000	109.59	0.000	133.92	0.000	123.38
0.293	107.05	0.302	133.44	0.273	123.86
0.715	105.71	0.606	132.96	0.785	123.94
0.907	104.92	1.137	132.08	1.429	124.02
1.671	104.62	1.379	131.84	1.609	124.06
2.316	104.53	1.609	131.60	1.797	124.14
2.598	104.49	1.805	131.28	2.162	124.17
2.965	104.40	2.197	130.76	2.265	124.21
		2.361	130.52	2.258	124.25
		2.826	130.20	2.672	124.29
		3.094	129.96		
		3.344	129.68		

All PMR spectra were recorded using Bruker AW80 spectrometer and the chemical shifts are reported in ppm or Herz down field of TMS. The concentration of crown were held constant (about 0.1 M) and the salt concentrations varied. To develop the S/N ratio, spectrum accumulations were performed about 40 times or above.

Results and Discussions

The equivalent conductance for each $[L]_0/[M^+]_0$ value in methanol are given in Table 1 and 2, where $[L]_0$ and $[M^+]_0$ are the total concentration of crown ether and cation, respectively. To evaluate the effect of adding crown ethers to the solution of cation perchlorates, the conductances at a constant salt concentration were monitored, while increasing the concentrations of crown ethers. Since the concentration of

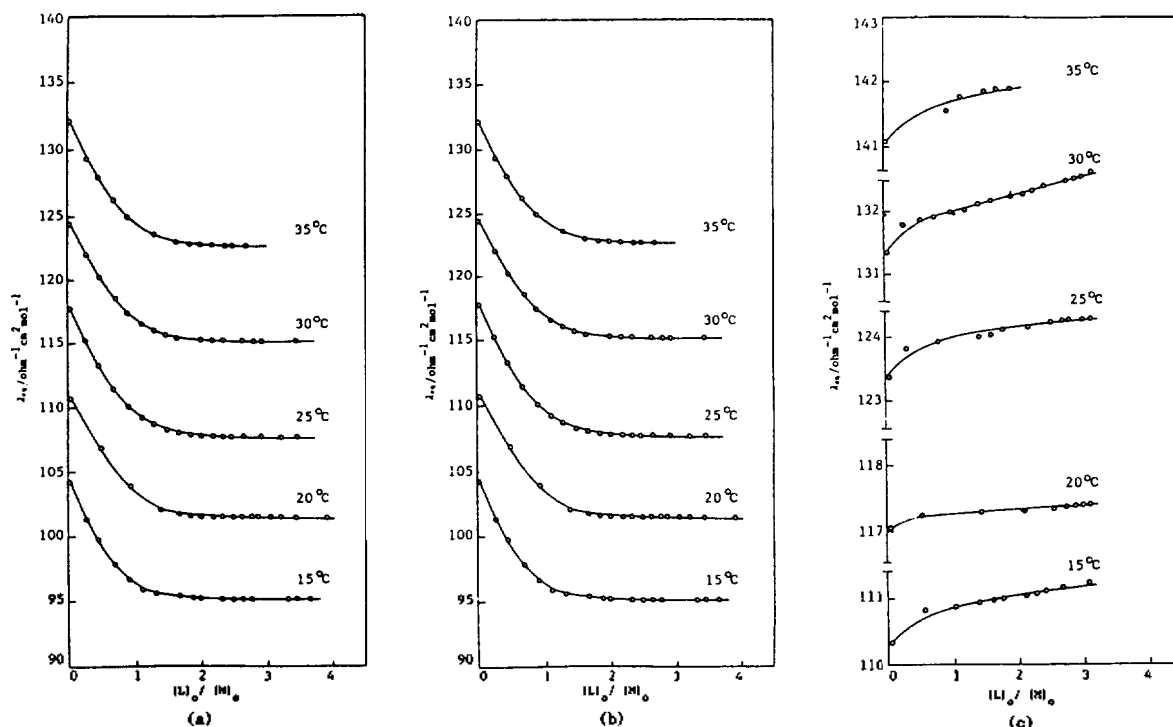
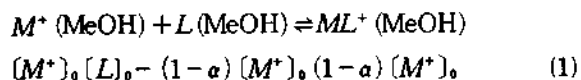


Figure 1. Plots for equivalent conductances vs. mole ratio of (a) 18C6 to silver perchlorates, (b) DT18C6 to silver perchlorates and (c) DT18C6 to ammonium perchlorates in methanol.

the solutes were kept low, the correction for viscosity changes were neglected.¹⁵

The variation of conductance under these condition can be explained by assuming that crown ether forms 1:1 complexes with univalent cation in methanol. Thus complexation is given by the equation



where M^+ , L and α are the univalent cation, crown ether and the fraction of free ion, respectively. The concentration stability constant, K in equilibrium is defined by:

$$K = \frac{[ML^+]_e}{[M^+]_e [L]_e} = \frac{\alpha [L]_e}{(1-\alpha)} \quad (2)$$

The subscripts, o and e denote the stoichiometric and equilibrium concentrations of the species. The equivalent conductivities are given by:

$$\lambda_{MClO_4} = \frac{x_{MClO_4}}{[M^+]_e} = \frac{x_{MClO_4}}{\alpha [M^+]_o} \quad (3)$$

$$\lambda_{MLClO_4} = \frac{x_{MLClO_4}}{[ML^+]_e} = \frac{x_{MLClO_4}}{(1-\alpha) [M^+]_o} \quad (4)$$

where x_{MClO_4} and x_{MLClO_4} are the observed specific conductivity of cation perchlorate and its complex with crown ether, respectively. From the eq. (3) and (4), following equation can be obtained.

$$\lambda_{eq} = \alpha \lambda_{MClO_4} + (1-\alpha) \lambda_{MLClO_4} \quad (5)$$

As a consequence of eq. (3), eq. (2) can be transformed into:

$$K = \frac{\lambda_{MClO_4} - \lambda_{eq}}{(\lambda_{eq} - \lambda_{MLClO_4}) [L]_e} \quad (6)$$

where

$$[L]_e = \frac{[M^+]_e (\lambda_{MClO_4} - \lambda_{eq})}{\lambda_{MClO_4} - \lambda_{MLClO_4}}$$

The λ_{MLClO_4} value is estimated from the λ_{eq} value at point of large $[L]_o/[M^+]_o$ and calculated by nonlinear least square analysis.^{14,16}

In Figure 1, the equivalent conductances are plotted vs. mole ratio of crown ether to salt. The slope of each curve changes sharply near the point $[L]_o/[M^+]_o = 1$, indicating the crown forms 1:1 complex with cation stoichiometrically. But the equivalent conductance of ammonium perchlorate increases as the concentration of DT18C6 increases in Figure 1-(c). This is marked contrast with silver, and thallium perchlorate present.

Since the dissociation of perchlorate salts used in this experiments is complete in methanol,¹⁷ the changes are not due to ion pairing. Hopkins *et al.*¹⁸ observed the similar results of conductance changes in acetonitrile containing 12-crown-4 and lithium iodide, and also found the infrared spectral bands at 410 and 335 cm^{-1} , attributed to the vibration of lithium ion against acetonitrile and 12-crown-4 respectively. An identical behaviors was reported by Popov¹⁹ in the study of alkali metal crytates, where the vibrational frequency of lithium-cryptate was found lower than that of lithium-acetonitrile.

Thus it may be concluded that the methanol solvent molecules are attached to ammonium ion more tightly to make large and stable solvation shell than DT18C6 do, that is in contrast with the results for K^+ -18C6, Ag^+ -DT18C6 or Ag^+ -DT18C6 systems.

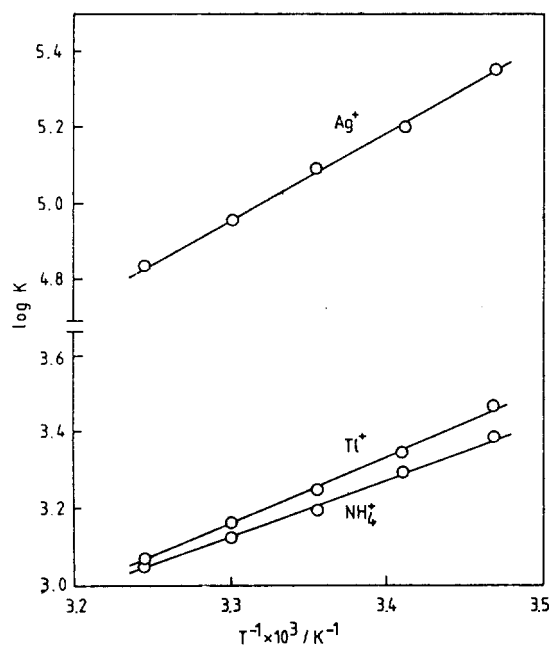


Figure 2. Vant'hoff plots of $\log K$ as a function of $1000/T$ for 1:1 reaction of univalent cation perchlorates with DT18C6 in methanol.

Table 3. $\log K$, ΔH and ΔS Values for 1:1 Reactions of Univalent Cation Perchlorates with 18C6 and DT18C6 in Methanol

	18C6			DT18C6		
	$\log K^a$	$-\Delta H$ kJ/mol	$-\Delta S$ J/(k mol)	$\log K^a$	$-\Delta H$ kJ/mol	$-\Delta S$ J/(k mol)
Na ⁺	4.30	38.9	48.5	1 ^c	—	—
	4.36 ^b	35.1 ^b	34.4 ^b			
K ⁺	6.32	54.5	67.0	<i>f</i>	<i>f</i>	<i>f</i>
	6.20 ^b	56.1 ^c	72.2 ^c			
Ag ⁺	4.60	40.9	57.5	5.10	42.6	45.3
	3.83 ^d	40.7 ^d				
Tl ⁺	5.10	42.9	46.5	3.25	33.1	48.4
NH ₄ ⁺	4.10	39.2	52.8	3.21	26.6	27.6
	3.88 ^e	48.5 ^e				

^aValues at 25.0°C. ^bReference 20, conductometry. ^cReference 7, calorimetry. ^dReference 3, calorimetry. ^eReference 21, calorimetry.

^fThe changes of equivalent conductivity were observed but insignificant to calculate $\log K$, ΔH or ΔS .

The K values can be calculated by eq. (6) at each temperature and the $\log K$ vs. $1/T$ plot show a linear relationship in Figure 2. ΔH and ΔS values given in Table 3 together with $\log K$ at 25°C available literature values. The ΔS values in this study are all negative and no considerable difference around 50 J/(k mol). The ΔS is mainly made up of two contributions², the ligand-ring flexibility changes and the structural changes of solution²² on complexation. The uncomplexed DT18C6 or 18C6 may be more flexible than complexed each one.

Takeda¹² determined the thermodynamic parameters for the formations of alkali metal ion with dibenzo-24-crown-8 and dibenzo-30-crown-10 in methanol. In each cases, the ΔS values of 24- and 30-membered ring is around 70 and 90 J/(k mol) respectively for whole cations under investigation.

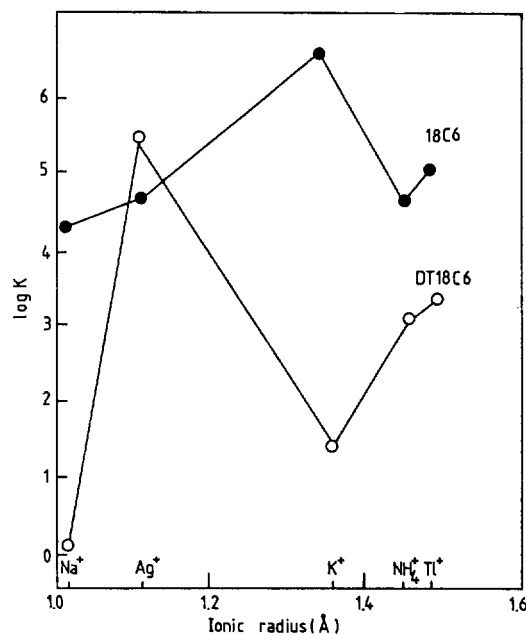


Figure 3. Plots of $\log K$ vs. cation radius in methanol at 25.0°C.

The ΔS sequence for the ring size in methanol are 30- > 24- > 18-membered, attributed to the ring flexibility on complexations.

Figure 3 shows that the selectivity order of 18C6 is $K^+ > Tl^+ > Ag^+ > NH_4^+$, while that of DT18C6 is $Ag^+ > Tl^+ > NH_4^+ > K^+$. Among the cations the size of K^+ is most closely correspond to that of 18 membered cavity.³ By sulfur substitutions the stability of complexes with silver are enhanced and those of potassium and thallium are reduced markedly. The replacement of two oxygen by sulfur atoms in 18C6 results in significant decrease in $\log K$.

The decrease of stabilities for group IA ions (hard acid) by sulfur (soft base) substitution are due to the results of weak "hard acid-soft base" interactions²⁵ and the decrease of cavity size. But the stability of Ag^+ -DT18C6 complex are 10^4 times larger than those of K^+ . The increase of stability for Ag^+ -DT18C6 is primarily due to the result of favorable exothermic heat of reaction and this result is consistent with the following facts.

From the extensive thermodynamic studies for univalent cations in various solvents, Parker^{11,23} revealed that silver ion is better solvated by sulfur donor solvent than would be expected. Indeed, the systems studies here can be viewed as cationic solution of mixed solvent with common anion. Potassium cation with its closed electronic shell and moderate size ($r_c = 1.33 \text{ \AA}$)²⁴ is expect to respond almost exclusively to electrostatic solvation or complexation effect, whereas silver cation as a transition metal of d^{10} electronic configuration is expected to be capable of experiencing a variety of covalent interactions¹¹, because of its small size ($r_c = 1.26 \text{ \AA}$) and poorly shielded electrostatic interactions with all solvents or ligands than potassium ion. Furthermore, these results are also thought to arise from influence of oxygen as hard, and sulfur as soft acid centers in Pearson's view²⁵.

The stepwise addition of diamagnetic cations into the crown ether solutions of constant concentration were accomplished and the results of series of NMR spectral changes are shown in Figure 4. In Figure 4-(a) and (b) 18C6

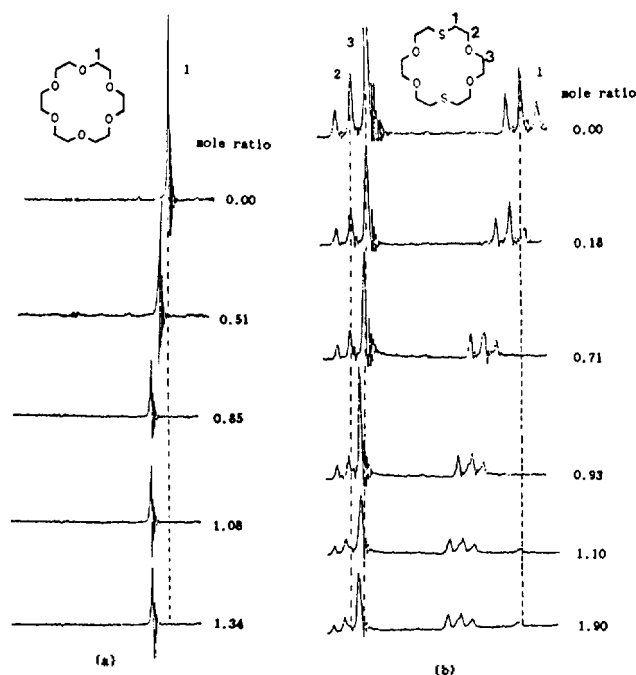


Figure 4. Proton NMR spectra of (a) 18C6 at various $\text{KClO}_4/18\text{C6}$ mole ratio in acetonitrile, and (b) DT18C6 at various $\text{AgClO}_4/\text{DT18C6}$ mole ratio in Acetone- d_6 .

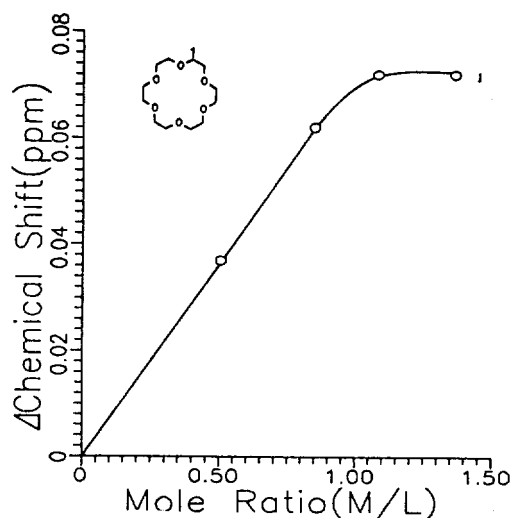


Figure 5. The plot of cation induced shifts of proton signals of 18C6 by incremental addition of potassium perchlorate.

shows the simple singlet at about 3.5 ppm because of high symmetry, but the spectra of DT18C6 consist of two triplet at about 2.7 and 3.6 ppm and one singlet at about 3.5 ppm.

The incremental additions of diamagnetic ions, K^+ and Ag^+ to the solutions of crown were found to lead to down field shift in respective resonances. The observed resonance lines are the population averaged signal indicating a fast exchange of ion between free and complexed ligand. The stoichiometry of complex formation could be obtained by plotting the shift of ligand proton resonance positions as function of ion/crown mole ratio.²⁶ According to Figure 5 and 6 cation induced diamagnetic shift varies linearly with the mole ratio until the ratio of 1:1 reached. It could be deduced that these ions form the 1:1 complex with crown. Therefore, the ob-

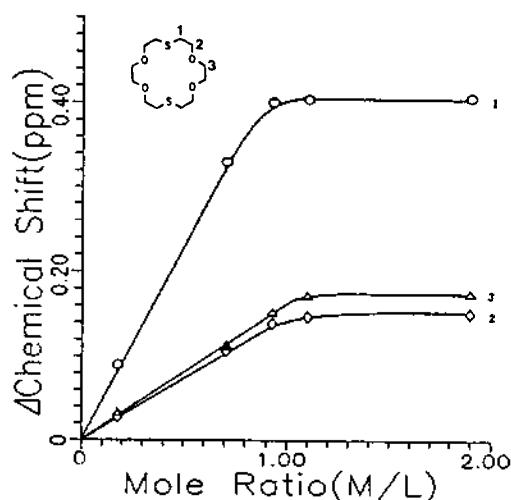


Figure 6. The plots of cation induced shifts of proton signals of DT18C6 by incremental addition of silver perchlorate.

served chemical shifts of a ligand proton is the weight average of proton in free and complexed ligands as in eq. (7).²⁶

$$\delta_{\text{obsd}} = \frac{[L]_0 - [ML^+]}{[L]_0} \delta_{\text{free}} + \frac{[ML^+]}{[L]_0} \delta_{\text{complex}} \quad (7)$$

In Figure 6, among the ether ring protons of DT18C6 larger $\Delta\delta$ values were observed for proton adjacent to sulfur donor atom. Since the chemical shifts of methylene protons of ether ring depend mainly on the strength of the interactions between nearest neighboring donor atoms and ionic species, this observation means that for the $\text{Ag}^+ - \text{DT18C6}$ complex, silver ion does not equally interact with the donor atoms, but preferentially does with the sulfur donor atoms. Thus, these results are consistent with Parker's^{11,23} thermodynamic data for the specific solvation of sulfur containing solvents with silver ion by soft-soft interaction.²⁵

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Kinetic Investigation on the Reaction between Cu(II) and Excess D-penicillamine in Aqueous Media

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The kinetics and mechanism of reduction of Cu(II) with an excess D-penicillamine have been examined at pH = 6.2 and 0.60M in ionic strength. The reaction at the initial stage is biphasic with a rapid complexation process to give "red" transient complex of [Cu(II)(pen)₂]²⁻ that is partially reduced to another transient "brown" intermediate. The "brown" intermediate is finally reduced to diamagnetic "yellow" complex, [Cu(I)(Hpen)]_n. The final reduction process is pseudo-first order in ["brown" transient] disappearance with $k = \{k_{3a} + k_{3b}[\text{pen}]^{2-}\}$, where $k_{3a} = (5.0 \pm 0.8) \times 10^{-3} \text{sec}^{-1}$ and $k = (0.14 \pm 0.02) \text{M}^{-1} \text{sec}^{-1}$ at 25°C. The activation parameters for the [H₂pen]-independent and [H₂pen]-dependent paths are $\Delta H^\ddagger = (52 \pm 5) \text{kJmol}^{-1}$, and $\Delta S^\ddagger = (-27 \pm 3) \text{Jk}^{-1} \text{mol}^{-1}$, and $\Delta H^\ddagger = (56 \pm 2) \text{kJmol}^{-1}$ and $\Delta S^\ddagger = (-18 \pm 0.7) \text{Jk}^{-1} \text{mol}^{-1}$ respectively. The nature of "brown" intermediate is not clearly identified, but this intermediate seems to be in the mixed-valence state, judging from the kinetic and spectroscopic informations.

Introduction

D-penicillamine, HS(CH₂)₂CH(NH₂)COOH (H₂pen) has been used as a medicinal chelating agent¹ and the oral administration of D-penicillamine to patients with Wilson's disease promotes the urinary excretion of excess copper^{2,3}, but the reaction between copper(II) and D-penicillamine has not been well characterized.

Unusual complications have been observed by previous workers^{2,4-6} as D-penicillamine reacts with copper(II) to cause partial or complete reduction to produce paramagnetic "purple" complex anion, [Cu(II)₆Cu(I)₆(pen)₁₂Cl]⁵⁻ or diamagnetic "yellow" complex, [Cu(I)(Hpen)]_n, depending on concentration ratio of Cu(II) to D-penicillamine⁴. Moreover, the presence of halide ions (Cl⁻ or Br⁻) is reported to be essential for the formation of "purple" complex ion in the mixed valence state⁴.

The reduction of copper(II) with an excess thiol such as D-penicillamine is known to produce the appropriate disulfide⁷ and it has been suggested on the basis of an investiga-

tion employing polarography and electronic absorption spectroscopy that the stoichiometry is as in the following reaction⁸.



Although the stoichiometry of this type of reaction is relatively well established, there are controversies about the nature of transient intermediates produced in the initial stage of the reaction and the reaction mechanism for the formation of Cu(I) complexes which has not been identified with certainty.

In this study, we reexamined the reduction of Cu(II) with an excess D-penicillamine in the acetate buffer (pH = 6.2) to elucidate the reaction mechanism for the formation of "yellow" complex.

Experimental Section

Materials. Doubly distilled water was further purified by a passage through anion and cation resins (Dowex-1-hy-