Articles

Electrochemical Study of Nickel(II) Complexes with Diaza-Macrocyclic Ligands in Acetonitrile

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The electrochemical behavior and the complex formation between Ni^{2+} and 1,7-diaza-15-crown-5 and 1,10-diaza-18-crown-6 in acetonitrile solution have been studied by DC polarography, differential pulse polarography and cyclic voltammetry. Nickel(II) complexes gave a single well-defined wave. The formation constants of their complexes were $10^{4.89}$ and $10^{3.86}$, respectively. Nickel(II) ion was found to form complexes of 1-to-1 composition with 1,7-diaza-15-crown-5 and 1,10-diaza-18-crown-6. In addition, reduction steps were irreversible and the reduction current were diffusion controlled. The electrochemical reduction mechanism of Ni(II)-macrocyclic diaza-crown complexes in acetonitrile solution is estimated.

Introduction

The alkaline and alkaline earth metal ion selectivity of polyether macrocyclic ligands have been well investigated[1-3]. Along a given series of ligands, maximum stability is usually observed when optimum macrocyclic ring (or cavity) size is reached for a particular metal ion.

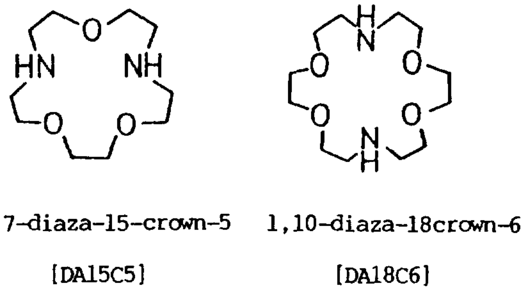
In contrast, such discrimination on the size of macrocyclic ring containing transition metal ions has been much less documented[4-7]. A major difficulty with these systems when the macrocyclic ligand contains an N-donor set is that traditional methods of determining stability constants (such as potentiometric titration) are not satisfactory with such complexes because thermodynamic equilibrium is often extremely slow to be established[7-9].

Nevertheless, studies involving potentiometric determination of stability constants for nickel complexes of a number of mixed donor macrocyclic ligands have been carried out. Also, the electrochemical behavior or complexes with a number of macrocyclic ligands have been extensively studied in the aqueous solution[10-12]. But relatively few studies on the electrochemical behavior have been reported in the nonaqueous solution.

Hence, this study is to investigate the complex formation and electrochemical behavior of nickel complexes of 1,7-diaza-15-crown-5 and 1,10-diaza-18-crown-6 as shown Figure 1 in acetonitrile solution by DC polarography, differential pulse polarography and cyclic voltammetry.

Experimental

Reagent. 1,7-Diaza-15-crown-5[DA15C5] and 1,10-diaza-18-crown-6[DA18C6] was obtained from Aldrich Co. and was used without further purification. Also, nickel nitrate used as a nickel ion source was obtained from Junsei Chemical Co. Acetonitrile (AN) used as solvent was purified by Coetzee method[13] and tetraethylammonium perchlorate (TEAP) used as supporting electrolyte was synthesized and purified by Kolthoff method[14].



1,7-diaza-15-crown-5 1,10-diaza-18crown-6

[DA15C5] [DA18C6]

Figure 1. Structual formulas of macrocyclic ligands.

Polarographic and Cyclic Voltammetric Measurement. Polarographic and cyclic voltammetric measurements of complex are made with a EG & G PAR (Princeton Applied Reserch) Model 264A Polarographic Analyzer/Sripping Voltammeter using 1.0×10^{-1} M TEAP as supporting electrolyte. The voltammograms were recorded with X-Y recorder (Houston Series X-Y recorder).

The working electrode used for voltammetry was EG & G PARC Model 303A SMDE (static mercury drop electrode) system. The auxilary electrode was platinium wire. The reference electrode with glass frit tip was Ag/Ag^+ [0.1 M $AgNO_3$ in AN] electrode. Then nonaqueous internal filling solution was 0.1 M $AgNO_3$ AN solution obtaining from EG & G PAR Co. All test solution were throughly degassed with nitrogen gas saturated wih acetonitrile and a continuous stream of nitrogen gas was passed over the solution while measurement were being taken.

Results and Discussion

Polarographic and Voltammetric Behavior of Nickel Complexes. The Figure 2 shows typical DC polarograms and differential pulse polarograms of nickel(II) ion

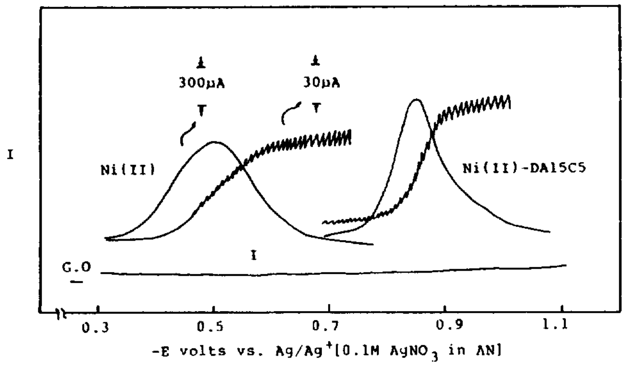


Figure 2. DC and differential pulse polarograms of 1.0×10^{-3} M Nickel(II) and Nickel(II) complex with DA15C5 in 1.0×10^{-1} M TEAP-AN solution at 25℃. Curve (I) is DC polarographic residual current.

Table 1. Differential Pulse Polarographic Potentials (E_p) and Peak Currents (i_p) of 1.0×10^{-3} M Nickel(II) and Nickel(II) Complexes in 1.0×10^{-1} M TEAP-AN Solution at 25℃

Compounds	E_p (volts *vs* Ag/Ag$^+$ [0.1 M $AgNO_3$ in AN])	i_p (mA)
Ni(II)	−0.50	0.68
Ni(II)-DA15C5	−0.85	0.93
Ni(II)-DA18C6	−0.77	0.90

and its complex with DA15C5 in a AN solution containing 1.0×10^{-1} M tetraethyl-ammonuim perchlorate (TEAP). Nickel(II) ion and nickel(II) complex exhibited one well-defined wave.

The differential pulse polarographic peak potentials (E_p) and peak currents (i_p) of each compound are given in Table 1. The peak currents for each complex is linearly varied at the concentraction range of 2.5×10^{-4} M-1.0×10^{-3} M.

Also, the typical cyclic voltammograms of two each complexes in acetonitrile solution at HMDE are shown in Figure 3. The cyclic voltammetric data at different scan rate (v) for each complex are given in Table 2. The plot of peak current (i_p) verses the square root of scan rate ($v^{1/2}$) is linear for each complex. These results indicate that the waves are diffusion controlled.

For an irreversible system, peak potential (E_p) is shifted to a negative direction according to increase in scan rate (for a reduction process). Thus the plot of peak potential (E_p) versus log (v) is linear. We can obtain the transfer coefficients (α) from slope of plots. The transfer coefficients (α) determined from a slopes of these plots are given in Table 3[15]. In general, deviation of transfer coefficient (α) from unity is indicative of reversibility. Thus, the result of Table 3 indicate that each reduction step is irreversible.

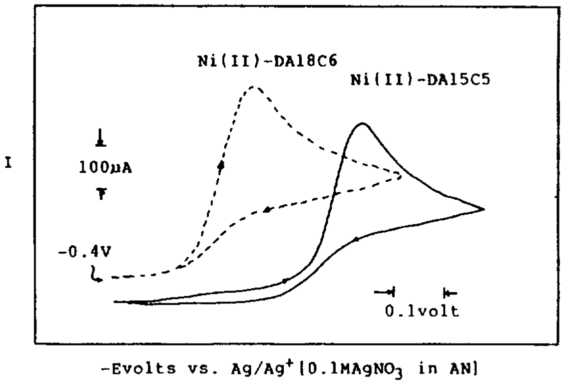


Figure 3. Cyclic voltammograms of 1.0×10^{-3} M Nickel(II) complexes in 1.0×10^{-1} M TEAP-AN solution on HMDE at 25℃, scan rate 200 mV/sec.

Table 2. Cyclic Voltammetric Data of 1.0×10^{-3} M Nikel(II) Complexs in 1.0×10^{-1} M TEAP-AN Solution at 25℃ and HMDE

Scan rates (mV/sec)	Ni(II)-DA15C5		Ni(II)-DA18C6	
	$-E_p$ (mV)	i_p (μA)	$-E_p$ (mV)	i_p (μA)
100	852	382	750	345
200	872	554	780	460
500	917	863	835	715
1,000	942	1,171	900	964

Table 3. Transfer Coefficients (α) of Nickel(II) Complexs at 25℃ and HMDE

Compounds	Transfer coefficients (α)
Ni(II)-DA15C5	0.16
Ni(II)-DA18C6	0.10

Polarographic Determination of Stability Constants. The mole ratio of complex between Ni^{2+} and DA15C5 and DA18C6 are 1-to-1 in acetonitrile solution[18]. In the polarographic study the significant quantity for the stability of the complex is the half-wave potential difference of the complex and the free metal ion. The half-wave potentials of the polarographic wave of the complex are shifted to more negative potentials when the concentration of the ligand in solution is increased[16]. Particularly, in view of the irreversible process for the reduction step, the stability constant. K_{ML} can be obtained from following equation[17].

$$\Delta E_{1/2} = -RT/(n_a\alpha F)\ln(1+K_{ML}[L])$$

The values of logarithm of stability constant, log K_{ML} are 4.89 for DA15C5 and 3.86 for DA18C6 in 0.1 M tetraethylammonium perchlorate-acetonitrile solution, respectively. In acetonitrile solution nickel complexes of DA15C5 and DA18C6 have considerably higher stability than in protic solvent[18,19]. This result is termed effect due to solvation[20]. Thus, ligands exist as a protonated form in protonic solvent. Also, comparing to stability of Ni(II)-DA15C5 complex is higher than those of Ni(II)-DA18C6 complex. This result can be evaluted from the relationship between ring of ligand and radius of metal ion[21].

Change of Reduction Peak Potential of Complex by Adding Acid. To gain insight into the reduction mechanism of each complex, the change of reduction peak potential of complex by adding acid was examined. The change of reduction peak potential of differential pulse polarogram

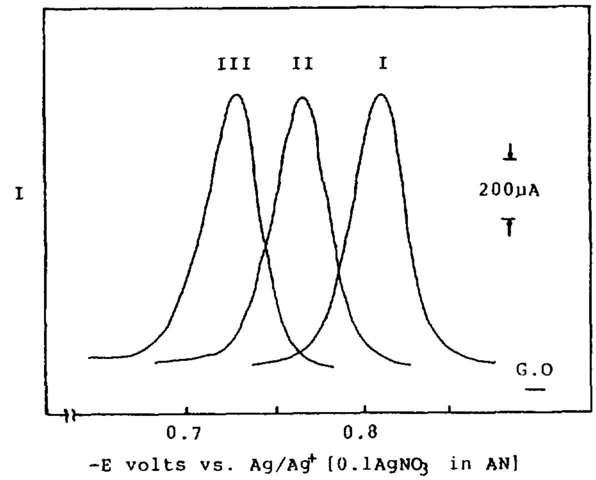
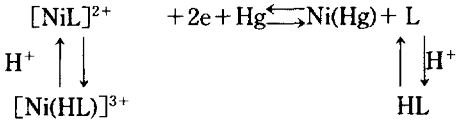


Figure 4. The change of reduction peak potential of 1.0×10^{-3} M Ni(II)-DA15C5 complex in 1.0×10^{-1} M TEAP-AN solution by adding 1.0×10^{-5} M $HClO_4$ at 25℃. Amount of 1.0×10^{-5} M $HClO_4$ added; I=0.05, II=0.1, III=0.15 (m*l*) respectivery, Initial volume of AN solution; 5 m*l*.

of Ni(II)-DA15C5 complex by adding acid is showm in Figure 4. Then, 1.0×10^{-5} M $HClO_4$ aqeous solution was used as the adding acid. The peak potential of the differential pulse polarographic wave of the Ni(II)-DA15C5 complex is shifted to more positive potential when amounts adding acid in 5 m*l* AN Solution are increased. This result is due to the increase of of concentration of protonated ligand with the increase of amounts of adding acid. Thus, electrochemical reduction mechanism of Ni(II)-macrocyclic diaza-crown complexes in acetonitrile solution is estimated as follows[22].



$$\begin{array}{lcr} {[\mathrm{NiL}]^{2+}} & +2e+\mathrm{Hg} \rightleftarrows \mathrm{Ni(Hg)}+ & \mathrm{L} \\ \mathrm{H}^{+}\ \uparrow\downarrow & & \uparrow\downarrow\ \mathrm{H}^{+} \\ {[\mathrm{Ni(HL)}]^{3+}} & & \mathrm{HL} \end{array}$$

Conclusion

Based on the electrochemical experimental results for Ni (II)-macrocyclic diaza-crown complexes in acetonitrile solution, reduction steps are diffusion controlled and irreversible. Formation constants of complexes were $10^{4.89}$ and $10^{3.86}$, respectively. Nickel(II) ion was found to form complexes of 1-to-1 composition with DA15C5 and DA18C6.

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References

1. J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
2. R. M. Izatt *et al.*, *J. Am. Chem. Soc.*, **98**, 7620 (1976).
3. J. M. Lehn and J. P. Sauvace, *ibid.*, **97**, 6700 (1975).
4. D. H. Busch, *Acc. Chem. Res.*, **11**, 392 (1978).
5. T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, **97**, 7163 (1975).
6. M. Kodama and E. Kimura, *J. Chem. Soc. Dalton*, 1081 (1978).
7. A. Anichini, L. Fabbrizzi, P. Paolleti, and R. M. Clay, *ibid.*, 577 (1978).
8. F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, **13**, 2941 (1974).
9. I. Tabushi and M. Fujiyoshi, *Tetrahedron Lett.*, 2157 (1978).
10. A. Hofmanova, J. Koryta, M. Brezina, and M. L. Mittal, *Inorg. Chim. Acta*, **28**, 73 (1978).
11. M. Kodama and E. Kimura, *J. Chem. Soc. Dalton*, 1473 (1977).
12. D. P. Zollinger and M. Bos, *Anal. Chim. Acta*, **161**, 83 (1984).
13. J. F. Coetzee, *Anal. Chem.*, **34**, 1139 (1962).
14. I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1870 (1957).
15. A. J. Bard and L. R. Faulkner, "Electrochemical method, Fundamental and Application" pp. 222-224, John Wiley and Sons, New York, 1980.
16. *Idem.*, *ibid.*, pp. 163-164, John Wiley and Sons, New York, 1980.
17. K. Angelish, M. Brezina, and J. Koryta, *Electroanal. Chem. and Interf. Electrochem.*, **45**, 504 (1973).
18. E. Luboch, A. Cygan, and J. F. Biernat, *Inorg. Chim. Acta*, **68**, 201 (1983).
19. F. Arnaud-Neu, B. Spiess, and M. J. Schwing-weill, *J. Helv. Chim. Acta*, **60**, 2633 (1970).
20. *Idem.*, *J. Am. Chem. Soc.*, **104**, 5641 (1982).
21. M. Kodama and E. Kimura, *J. Chem. Soc. Dalton*, 2341 (1976).
22. *Idem.*, *ibid.*, 104 (1978).