A Conductance Study of Macrocyclic Schiff Base Metal(II) Complexes in Methanol

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(Received February 10, 1990)

The first ionic association constants between five macrocyclic Schiff base metal(II) complexes (cation and perchlorate or thiocyanate anion) were determined by conductometric measurements in methanol at 25 °C by using a modified Onsager limiting equation, according to Fuoss and Edelson method. The limiting equivalent conductivities of the chelate cations of these complexes were calculated. These results were used to evaluate the performance of coated-wire perchlorate ion-selective electrodes (PCWE) based on these complexes.

Increasing interest has recently developed to obtain information concerning the selectivity and ion exchange of some macrocyclic Schiff base metal complexes. Part of this interest is due to studies concerning the role and application of these complexes to an ion-selective electrode (ISE).[1] The ionic transport behavior contained in a polymeric membrane of ISE was found to be largely dependent on the nature of both the selectivity and stability of these metal complexes on the metal or counter anion. The selectivity of these macrocyclic complexes is strongly affected by the solvent media, the stability of complexes and their interactions with a cation or counter anion.[2] The ionic selectivity and performance of the electrode increases with the degree of stability of these complexes, namely what relationship it has between the performance of the electrode and the stability of these complexes. There is much interest to investigate ion selective electrodes.

In previous papers[3] we reported characterizations of perchlorate ion-selective coated-wire electrodes (PCWE) based on metal(II) complexes of macrocyclic Schiff bases (Fig. 1) as a new ion exchanger meterial derived from the condensation of 1, 3-diamino-2-propanol and 2,6-diacetylpyridine involving each metal(II) salt. In these complexes, the stable chelate cation formed by the divalent metal ion (Ba^{2+}, Pb^{2+}, and Cu^{2+}) and the nitrogen and oxygen atoms of the macrocyclic ligand (Fig. 1) is again associated with two anions, ClO_4^- or SCN^-. Continuing our work, the ionic association constants of these complexes were studied by conductometry. A review concerning electrolytic conductance and parameters derived from conductance measurements has been reported by Miyoshi.[4,5] Jenkins, and Monk[6] suggested that a conductance measurement of mixtures is a useful method for determining the formation constants. Katayama and Tamamushi[7,8] studied the ion-paired formation constants of tris(ethylenediamine)cobalt(III) complexes with maleate and fumarate based on a continuous variation method for a conductometric determination. A conductometric study of the ionic association constants of cobalt(II), nickel(II), copper(II), and zinc(II) perchlorates in methanol-ethylene glycol mixtures has been made by Doe and Kitagawa.[9] Koryta and Dvorak[10] have introduced a method for the conductometric determination of dissociation constants. A conductometric study concerning ion association in aqueous solutions has been reported by Katayama.[11] In present study, conductometric measurements in methanol were made and conductometric data were treated by using a modified Onsager limiting equation according to the Fuoss and Edelson method.[12] The thermodynamic ionic association constants of the macrocyclic Schiff base metal(II) complexes have been determined. The free energies of the first association reaction on these metal(II) complexes have also been calculated. The performance of PCWE could be evaluated using these results.

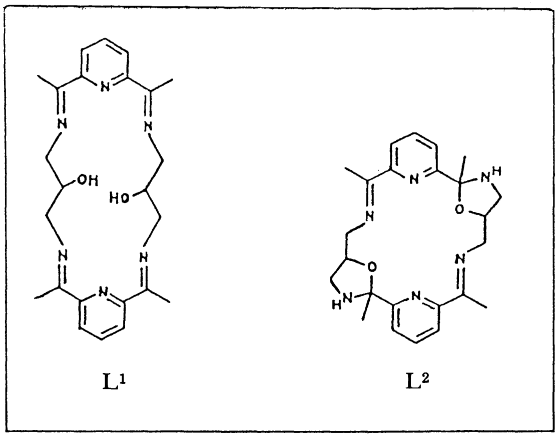

Fig. 1. Ligand constitution of macrocyclic Schiff bases metal(II) complexes derived from condensation of 1,3-diamino-2-propanol and 2,6-diacetylpyridine.

Experimental

Preparation of the Macrocyclic Schiff Base Barium(II), Copper(II), and Lead(II) Complexes. 2,6-Diacetylpyridine and 1, 3-diamino-2-propanol were supplied by the Nakarai Chemical Co., Ltd. The complexes were prepared by using

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the following general method:[13] 2,6-Diacetylpyridine (0.01 mol) and the each metal salt, [$Ba(ClO_4)_2$, $Ba(NCS)_2$, $Pb(ClO_4)_2$, or $Pb(NCS)_2$] (0.005 mol), were dissolved in refluxing dry methanol (150 cm^3). To this was added a solution of 1,3-diamino-2-propanol (0.01 mol) dissolved in methanol(50 cm^3) dropwise over 15 min. The resulting solution or suspension was then refluxed further for 3 h. Macrocyclic complexes were deposited upon cooling and collected by filtration. Further, batches of each complex were obtained by evaporation of the filtrate under reduced pressure. Recrystalizations of these complexes were carried out with methanol three times. The samples were then dried in vacuo over silica gel; the elemental analysis and yields for several preparations are as follows:

$BaL^1(ClO_4)_2$: Colorless crystals (Found: C, 35.54; H, 4.48; N, 10.52%. Calcd for $C_{24}H_{34}BaCl_2N_6O_{12}$: C, 35.7; H, 4.3; N, 10.4 %). Yields for several preparations 60—65%.

$BaL^1(NCS)_2$: White powder (Found: C, 43.24; H, 4.65; N, 15.60%. Calcd for $C_{26}H_{34}BaN_8O_4S_2$: C, 43.1; H, 4.7; N, 15.5%). Yield for several preparations 40%.

$PbL^2(ClO_4)_2$: Colourless crystals (Found: C. 33. 65; H. 3.71; N, 9.76%. Calcd for $C_{24}H_{32}Cl_2N_6O_{11}Pb$: C, 33.6; H, 3.8; N, 9.8%). Yields for several preparations 72%.

$PbL^2(NCS)_2$: Light yellow crystals (Found: C, 41.60; H, 4.67; N, 13.9%. Calcd for $C_{27}H_{34}N_8O_3PbS_2$: C, 41.1; H, 4.3; N, 14.2%). Yield 78%.

$CuL^1(ClO_4)_2$: Blue crystals (Found: C, 40.04; H, 4.62; N, 11.51%. Calcd for $C_{24}H_{34}CuCl_2N_6O_{12}$: C, 39.33; H, 4.68; N, 11.47%). Yields for several preparations 38%.

The $\mathbf{L}^1$ or $\mathbf{L}^2$ among the molecular formulas of these complexes indicate the ligand on the left or right of Fig. 1, respectively.

Conductivity Measurements. Conductivity measurements were carried out at a frequency of 1 K Hz, by a 4291A LCR meter (Yokogawa-Hewlett Packard Co., Ltd) and a Yanagimoto cell in a complex solution using distilled methanol as a solvent. The cell content was thermostated at 25±0.5 °C, and the conductivity measuring cell constant was determined by using 0.01 and 0.1 mol dm^{-3} of potassium chloride as standard solutions in 0.427. The concentration range of the complexes studied was in general from 10^{-3} to 10^{-5} mol dm^{-3}. These solutions were prepared in an air-conditioned room at about 25 °C.

Results and Discussion

Conductometric data were treated according to the modified Onsager limiting equation, which for very low concentrations[14] is

$$\Lambda = \Lambda^0 - S \cdot C_0^{1/2}. \tag{1}$$

Here, Λ is the equivalent conductance at each apropriate concentration; C_0, and Λ^0 are the limiting equivalent conductances, respectively. For a 2-1 electrolyte, the Onsager slope is as follows:[12]

$$S = \alpha\Lambda^0 + \beta, \tag{2}$$

where

$$\alpha = 6.86 \times 10^6(\varepsilon T)^{-2/3}q(1 + q^{1/2})^{-1},$$

$$\beta = 151.6\eta^{-1}(\varepsilon T)^{-1/2},$$

$$q = 2/3(1 + \lambda_{0-}/\Lambda^0).$$

Here, ε is the dielectric constant of the solvent, η is the viscosity of the solvent, and T is the test temperature. A plot of Λ versus $C_0^{1/2}$ yields a straight line with an intercept of Λ^0 on the Λ-axis. The Onsager slope, S is obtained by Λ^0. It is considered that the consecutive association equilibria of the prepared complexes are according to

$$M^{2+} + X^- \rightleftharpoons MX^+ \ (K_1) \tag{3}$$

and

$$MX^+ + X^- \rightleftharpoons MX_2 \ (K_2), \tag{4}$$

where M indicates one of the metal(II) chelate cations, $(BaL^1)^{2+}$, $(PbL^2)^{2+}$, and $(CuL^1)^{2+}$, X^- indicates either ClO_4^- or SCN^-, respectively. The ionic consecutive association constants, K_1 and K_2 are defined by

$$K_1 = [MX^+]f_+/[M^{2+}][X^-]f_{2+}f_- \tag{5}$$

and

$$K_2 = [MX_2]f/[MX^+][X^-]f_+f_-, \tag{6}$$

where, f_{2+}, f_+, f, and f_- are the activity coefficients of M^{2+}, MX^+, MX_2, and X^-, respectively. It is generally thought that $K_1 \gg K_2$. The conductometric data were treated by the Fuoss and Edelson method.[12] This method works very well to determine the ionic association constants or the stability constants.[15—17] Using their method, only the ionic equlibrium of Eq. 3 was considered on the assumption that $K_1 \gg K_2$. They derived the following equation based on the Onsager limiting law:

$$\Lambda F = \Lambda^0 - DK_1/\Lambda^0, \tag{7}$$

where

$$D = C_0 f_{2+}\Lambda F(\Lambda F - \Lambda^0/2)$$

and

$$F = [(1 - SC_0^{1/2})^{-1} + (\Lambda^0 - \lambda_{0-})/2\Lambda]/[1 + [\Lambda^0 - \lambda_{0-})/2\Lambda^0]$$

are defined. Here, F is a function which approximately corrects the conductance ratio, Λ/Λ^0, for the effect of interionic forces on the mobility, λ_{0-} is the limiting equivalent conductance of X^-, S is Onsager's slope, and C_0 is the molar concentration of X^-. The ion activity coefficient of M^{2+}, f_{2+} was estimated by the Debye–Hückel equation:

$$-\log f_{2+} = 1.82 \times 10^6(\varepsilon T)^{-3/2}z_i^2 I^{1/2},$$

where I is the ionic strength (I=1.5 C_0). The values of λ_{0-} are 70.9 S cm^2 mol^{-1} for ClO_4^- and 61.0 S cm^2 mol^{-1} for SCN^- in methanol at 25.0 °C respectively. For calculations in methanol systems, a dielectric constant of ε=32.66 and a viscosity of η=0.005445 P[18] (1 P=10^{-1} Pa s) were used, respectively.

The experimental data of the equivalent conductances for each complexes in methanol are summarized in Table 1. The equivalent conductance, Λ, were calculated using 1000 $\kappa/2C_0$. Figure 2 shows a plot of Λ vs. $C_0^{1/2}$ according to Eq. 1 for $BaL^1(ClO_4)_2$ methanol solution. The limiting equivalent conductance, Λ^0, value was obtained from extrapolating the plot of Λ vs. $C_0^{1/2}$; the Onsager theoretical slope for each complex solution could be calculated acorrding to Eq. 2 by using the Λ^0 value (for example, 120.9 S cm^2 mol^{-1} for $1/2BaL^1(ClO_4)_2$). Figure 2 also gave an Onsager theoretical curve for $BaL^1(ClO_4)_2$. Table 2 shows several parameters: the specific conductivity (κ), the equivalent conductance (Λ), the activity coefficients (f_{2+}) and D for $BaL^1(ClO_4)_2$ in methanol at 25 °C. If the plots of ΛF vs. D, are further written according to Eq. 7, the K_1 value can be obtained from the slope (K_1/Λ^0) of the plot. Figure 3 shows a plot of ΛF vs. D for $BaL^1(ClO_4)_2$ and $BaL^1(SCN)_2$. Their K_1 was calculated as 1874 dm^3 mol^{-1} and 2684 dm^3 mol^{-1}, respectively. In addition, several results concerning the conductivity of all complexes are summarized in Table 3.

On the other hand, the limiting equivalent ionic conductivity of perchlorate (ClO_4^-) and thiocyanate

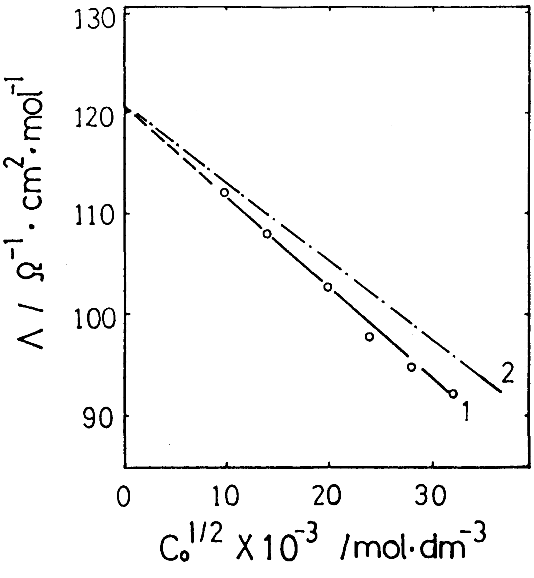

Fig. 2. Ploting of Λ versus $C_0^{1/2}$ for $BaL^1(ClO_4)_2$ solution using methanol as solvent at 25 °C.

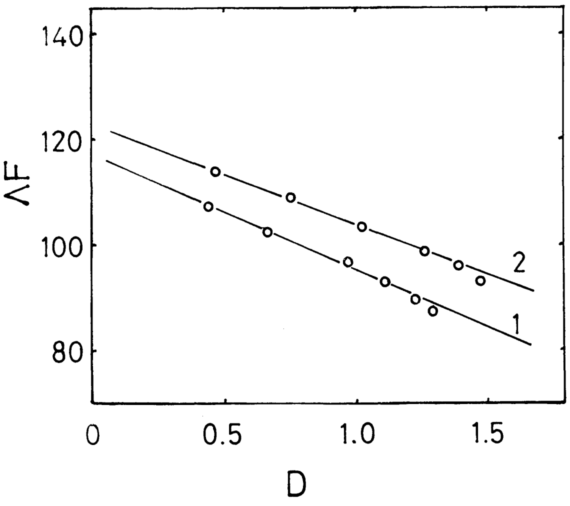

Fig. 3. The plots of ΛF vs. D for 1: $BaL^1(ClO_4)_2$ and 2: $BaL^1(SCN)_2$ in methanol as solvent at 25 °C.

Table 1. Equivalent Conductance (Λ) of Different Concentrations of Metal Complexes in Methanol (25 °C)

Concn.	Λ/S cm^2 mol^{-1}				
mol dm^{-3}	$BaL^1(ClO_4)_2$	$BaL^1(SCN)_2$	$PbL^2(ClO_4)_2$	$PbL^2(SCN)_2$	$CuL^1(ClO_4)_2$
1.0X10^{-4}	112.9	105.1	106.1	103.7	106.7
2.0X10^{-4}	108.2	101.2	101.3	99.4	102.1
4.0X10^{-4}	102.8	96.1	96.5	90.6	89.7
6.0X10^{-4}	97.9	91.9	92.1	86.2	88.1
8.0X10^{-4}	95.0	88.9	86.6	84.1	82.4
1.0X10^{-3}	92.4	86.1	85.4	81.1	80.4

Table 2. Several Parameter about $BaL^1(ClO_4)_2$ in Methanol at 25 °C

Concn.	κX10^4	Λ	f_{2+}	D
mol dm^{-3}	S cm^{-1}	S cm^2 mol^{-1}		
1.0X10^{-4}	0.2258	112.9	0.7978	0.474
2.0X10^{-4}	0.4326	108.2	0.7266	0.749
4.0X10^{-4}	0.8227	102.8	0.6365	1.110
6.0X10^{-4}	1.1748	97.9	0.5750	1.260
8.0X10^{-4}	1.5202	95.0	0.5278	1.385
1.0X10^{-3}	1.8481	92.4	0.4900	1.477

(SCN^-) is used at 70.9 and 61.0 S cm^2 mol^{-1},[19] respectively. Therefore, the limiting equivalent ionic conductance (λ_{0+}) of the cation($1/2M^{2+}$) of the macrocyclic metal complex can be calculated according to the Kohlrausch law:[20]

$$\Lambda^0 = \lambda_{0+} + \lambda_{0-}. \qquad (8)$$

All of these results concerning the limiting equivalent ionic conductivities of $1/2M^{2+}$ in methanol are also given in Table 3. It has been found that a slight difference exists between both of the limiting equivalent ionic condutivities of $1/2(BaL^1)^{2+}$ or $1/2(PbL^2)^{2+}$ or $1/2(CuL^1)^{2+}$, respectively, corresponding to the existing ClO_4^- and SCN^-. This might be the reason why the construction of these complexes and the interactions of their cations, M^{2+}, is affected by these two anions. Further, the free-energy changes due to first ionic association reactions were also calculated, according to

$$\Delta G = -RT \ln K_1. \qquad (9)$$

Table 4 shows the calculated results for five complexes in methanol. No conductivity data concerning the cations of macrocyclic Schiff base metal(II) complexes have been obtained so far. The ionic association constants obtained from this conductivity data can be used to evaluate the performance of coated-wire perchlorate ion-selective electrodes (PCWE) based on these macrocyclic Schiff base metal(II) complexes. The mobility of ions between the membrane of ISE and the solution is concerned. As described in a recent paper,[3] the PCWE based on $BaL^1(ClO_4)_2$ and DBP has better response characteristics than electrodes based on other complexes. The ionic association constants are compared with the potential response performance of PCWE based on five complexes as ion-exchanger materials in Table 5. All of the ionic association constants of these prepared complexes were large, and in order $BaL^1(ClO_4)_2 < PbL^2(ClO_4)_2 < CuL^1(ClO_4)_2$ and $BaL^1(ClO_4)_2 < BaL^1(SCN)_2$. The performance, for example, the response slope or the Nernstian responding range shown in Table 5, gave the order $Bal^1(ClO_4)_2 > PbL^2(ClO_4)_2 > CuL^1(ClO_4)_2$ for these complexes containing the ClO_4^- anion; $BaL^1(SCN)_2 > PbL^2(SCN)_2$ for those containing the SCN^- anion. Of course, the complexes containing ClO_4^- used as ion-exchanger materials were better for perchlorate selective electrode than that containing SCN^-. We considered that a complex of large solubility makes a better ion-exchanger material of ISE when the ionic association constant or stability constant of the complex is sufficiently large. The size and symmetry of the space construction of a macrocyclic Schiff base metal complex and its distribution in a membrane may affect the ion exchange and selectivity of the electrode.

Table 4. Free Energy of First Ionic Association Reactions of Five Complexes in Methanol

Complex	ΔG / kJ mol^{-1}
$BaL^1(ClO_4)_2$	−8.11
$PbL^2(ClO_4)_2$	−8.66
$CuL^1(ClO_4)_2$	−9.56
$BaL^1(SCN)_2$	−8.40
$PbL^2(SCN)_2$	−8.85

Table 3. Limiting Equivalent Conductivities (Λ^0) and Ionic Association Constants (K_1) of the Five Metal Complexes (25 °C)

Complex	Λ^0 / S cm^2 mol^{-1}	K_1 / dm^3 mol^{-1}	λ_{0-}/Anion / S cm^2 mol^{-1}	$\lambda_{0+}/1/2M^{2+}$ / S cm^2 mol^{-1}
$BaL^1(ClO_4)_2$	120.9	1874	70.9	50.0
$BaL^1(SCN)_2$	112.5	2684	61.0	51.5
$PbL^2(ClO_4)_2$	117.3	3122	70.9	46.4
$PbL^2(SCN)_2$	108.5	3715	61.0	47.5
$CuL^1(ClO_4)_2$	115.8	7216	70.9	44.9

Table 5. Potential Response Properties of the PCWEs Based on Five Complexes as Ion Exchanger Materials in $NaClO_4$ Aqueous Solution (pH=7.0)

Complex		Electrode properties[3]	
Component	$\log K_1$ dm^3 mol^{-1}	Slope / mV/pClO_4^-	Nernstian responding range / mol dm^{-3}
$BaL^1(ClO_4)_2$	3.27	58	1.0×10^{-1}—4.0×10^{-6}
$PbL^2(ClO_4)_2$	3.49	52	1.0×10^{-1}—2.5×10^{-5}
$CuL^1(ClO_4)_2$	3.86	49	1.0×10^{-1}—1.0×10^{-5}
$BaL^1(SCN)_2$	3.43	40	1.0×10^{-1}—2.0×10^{-5}
$PbL^2(SCN)_2$	3.57	25	1.0×10^{-1}—1.0×10^{-4}

This work was presented in part at the 40th ISE Meeting, Kyoto, Japan, September 1989.

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