Ion-Pair Formation of 3*m*-Crown-*m* Ether ($m = 5, 6$) and Its Monobenzo Derivative Complex Ions with Several Pairing Anions in Water

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Ion-pair formation constants (K_{MLX} in $mol^{-1}\cdot dm^3$) for $M(B18C6)^+$, $M(15C5)^+$, or $M(B15C5)^+$ with pairing anions (X^-) in water were determined by potentiometry with ion-selective electrodes at 25 °C over wide ranges of the ionic strength (I). The symbols B18C6, 15C5, and B15C5 denote benzo-18-crown-6 ether, 15-crown-5 ether, and benzo-15C5, respectively; metal salts, MX, used are sodium picrate (NaPic), KPic, $NaBPh_4$, $NaMnO_4$, and $KMnO_4$. The K_{MLX} values at $I = 0$ mol dm^{-3} ($K_{MLX}°$) were evaluated from analyzing the I dependence of the log K_{MLX} values determined. Then, effects of shapes of X^-, the benzo group of the ethers, their ring sizes, and the shielding of the metal ions, M^+, by the ethers on these $K_{MLX}°$ values were discussed in comparison with the values previously reported on M(18C6)X, M(15C5)Pic, and M(B15C5)Pic. Also, center-to-center distances in the M(18C6 derivatives)$^+$-X^- or M(15C5 ones)$^+$-X^- pairs were estimated from Bjerrum's equation.

Introduction

Ion-pair formation of crown ether-complex ions (ML^{z+} with a charge magnitude of z) with pairing anions (X^-) in water is required to elucidate extraction-ability and -selectivity of crown ethers, L, against the metal ions, M^{z+}, in solvent extraction. This is based on the fact that its overall extraction equilibrium is expressed as combination of this ion-pair formation with other component equilibria,[1] such as the complex formation of M^{z+} with L in water and the distribution of L. Since a pioneering work[1] in which one of the authors used solvent extraction to determine an ion-pair formation constant (K_{MLX} in $mol^{-1}\cdot dm^3$) for K(benzo-18-crown-6 ether)$^+$ {$K(B18C6)^+$} with picrate ion (Pic^-) in water, several studies have been developed by other methods, such as capillary zone electrophoresis (CZE)[2,3] and potentiometry[4−8] with ion-selective electrodes (ISEs). Then, many constants have been determined so far by potentiometry for Pic^- (at M = Na, K, Ag),[4−7] nitrated phenolates (Na),[8] tetraphenylborate (Na),[6] and permanganate ions (Na, K)[4] with M(18-crown-6 ether)$^+$ {$M(18C6)^+$} and by CZE for Pic^-,[2,3] nitrated benzoates, nitrated benzenesulfonates, nitrated phenolates, perchlorate, and thiocyanate ions[3] (at M = Na, K) with $M(18C6)^+$, $M(B18C6)^+$, or M(dibenzo-18C6)$^+$ {$M(DB18C6)^+$}. Whereas, from the extraction experiments, the K_{MLX} have been reported anew on the ion-pair formation of Pic^- or perchlorate ion with $M(18C6)^+$ of M = Li−Cs,[9] $M(B18C6)^+$ of Na, K (reevaluated), and Rb,[10,11] $M(DB18C6)^+$ of Na−Cs,[11,12] and on that of Pic^- with ML^+ containing L of smaller sizes.[13,14] Nevertheless, discussion about influences of X^- or L on the magnitude of K_{MLX} seems to be insufficient.

In the present paper, we determined potentiometrically the K_{MLX} values for some alkali metal salts (MX = $NaMnO_4$, $KMnO_4$, NaPic, KPic, $NaBPh_4$) with B18C6, 15-crown-5 ether (15C5), and benzo-15C5 (B15C5) in water at 25 °C over wide ranges of the ionic strength (I). Also, the K_{MLX} values at $I = 0$ $mol\cdot dm^{-3}$ ($K_{MLX}°$) were evaluated from a nonlinear regression analysis[6] of I dependence of the determined log K_{MLX} values. Using these values and those reported before on M(18C6)X, M(15C5)Pic, and M(B15C5)Pic, changes of an interaction of ML^+ with X^- caused by changing kinds of X^- and L were discussed. Besides, center-to-center distances in the ML^+-X^- pairs were estimated from Bjerrum's equation.

Experimental Section

Chemicals. Procedures for preparing the MX salts employed and purifying B18C6, 15C5, and B15C5 were the same as those[5,6] described before. All aqueous solutions were prepared by using water that passed through a Milli-Q Labo ultrapure water system (Millipore).[7]

Measurements of emf. Cells used for emf measurements at 25 ± 0.3 °C were as follows: Ag|AgCl|0.1 $mol\cdot dm^{-3}$ $(C_2H_5)_4NCl$ or 0.05 $mol\cdot dm^{-3}$ $MgCl_2$|test solution|ISE.[4,6] In every measurements, the emf reading after 1 min from immersing ISE in the test solution was recorded for the $NaBPh_4$-15C5 system, while those were recorded after 5 min for the other systems: in the former system, a gradual decrease in the emf was observed over 5 min. The ratios, $[L]_t/[MX]_t$, of total concentrations of L = B18C6, 15C5, or B15C5 to those of MX in the test solutions were fixed at unity. The K_{MLX} values were obtained in I ranges of (1.1 to 6.8) × 10^{-3} $mol\cdot dm^{-3}$ for MLX = Na(B18C6)Pic, (0.1 to 2.2) × 10^{-3} $mol\cdot dm^{-3}$ for K(B18C6)Pic, (0.9 to 4.3) × 10^{-4} $mol\cdot dm^{-3}$ for $Na(B18C6)BPh_4$, (0.5 to 2.5) × 10^{-3} $mol\cdot dm^{-3}$ for $Na(B18C6)MnO_4$, (0.6 to 6.0) × 10^{-3} $mol\cdot dm^{-3}$ for $K(B18C6)MnO_4$, (0.2 to 2.2) × 10^{-3} $mol\cdot dm^{-3}$ for $Na(15C5)BPh_4$, (0.1 to 1.3) × 10^{-3} $mol\cdot dm^{-3}$ for $Na(B15C5)BPh_4$, (0.4 to 8.3) × 10^{-3} $mol\cdot dm^{-3}$ for $Na(15C5)MnO_4$, (0.4 to 10) × 10^{-3} $mol\cdot dm^{-3}$ for $Na(B15C5)MnO_4$, (0.2 to 4.1) × 10^{-3} $mol\cdot dm^{-3}$ for $K(15C5)MnO_4$, and (0.2 to 4.4) × 10^{-3} $mol\cdot dm^{-3}$ for $K(B15C5)MnO_4$. Fine precipitates were found in the emf measurements of M(B18C6)Pic (M = Na, K), $NaLBPh_4$ (L = B18C6, 15C5, B15C5), and $K(B15C5)MnO_4$, when the I values were beyond the upper limits described. Measurement method, a pH/ion meter, the ISEs for Na^+ and K^+, and the reference electrodes employed were the same as those reported before.[6]

Calculation. Data sets of the concentration ion-pair formation constant, K_{MLX}, and I have been obtained as a result of a

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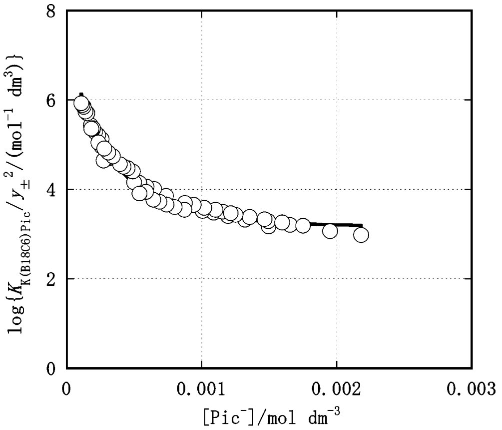

Figure 1. Plot of log($K_{K(B18C6)Pic}$/$y_{\pm}^2$) vs [Pic$^-$]. Solid line shows the curve fitted to eq 1 by the nonlinear regression using $K_{KPic}° = 5.8$ [6] and $K_{KB18C6} = 10^{1.664}$ mol^{-1}·dm^3.[15]

successive approximation with an estimate of the liquid junction potential between the test solution and the aqueous one of $(C_2H_5)_4NCl$ or $MgCl_2$.[6] Calculations of $K_{MLX}°$ from these data sets were performed by using the procedure[6] described previously.

Results and Discussion

Determination of $K_{MLX}°$ for ML$^+$ with X$^-$ in Water. Figure 1 shows a plot of log($K_{K(B18C6)Pic}$/$y_{\pm}^2$) vs [Pic$^-$]. Here, [Pic$^-$] denotes an equilibrium concentration of Pic$^-$ in the test solution and is equivalent to the I value of the test solution in practice: namely, $I = (1/2)\{[K^+] + [K(B18C6)^+] + [Pic^-]\} = [Pic^-]$ with a charge balance equation of $[K^+] + [K(B18C6)^+] = [Pic^-]$.[6] Since this [Pic$^-$] value is expressed as the function of [K$^+$] (see eq 3), it was immediately calculated from the experimental [K$^+$] value by the successive approximation with the estimate of the liquid junction potential.[6] Also, $y_{\pm}$ refers to a mean ionic activity coefficient for the electrolyte ML$^+$X$^-$ or M$^+$X$^-$ and was estimated by using either the Debye−Hückel limiting law (DHL)[16] or the Davies equation.[17] A hyperbola-like tendency was observed in this plot, as shown in that of the KPic-18C6 system.[6] Namely, the log($K_{K(B18C6)Pic}$/$y_{\pm}^2$) values, obtained from eq 2 (see below) and DHL, seem to approach an asymptotic limit of about three with an increase in [Pic$^-$].

For the $K_{MLX}°$ determination, the plot has been analyzed using the following equation:[6]

$$\log\frac{K_{MLX}}{y_{\pm}^{2}} = \log\left(K^{\circ}_{MLX} + \frac{b_m}{y_{\pm}^{2}[ML^+][X^-]}\right) \qquad (1)$$

with

$$K_{MLX} \equiv \frac{[MLX]}{[ML^+][X^-]} = \frac{[MX]_t - [X^-](1 + K_{MX}[M^+])}{([X^-] - [M^+])[X^-]} \qquad (2)$$

and

$$[X^-] = \frac{[M^+](1 + K_{ML}[M^+])}{1 - K_{ML}K_{MX}[M^+]^2} \qquad (3)$$

at the conditions of $1 + K_{ML}[M^+] \gg K_{ML}(b_m - b')$ and $[MX]_t = [L]_t$.[6,7] Here, K_{ML} and b_m (or b') are referred to a complex formation constant (mol^{-1}·dm^3) of ML$^+$ in water and a curve-fitting parameter reflecting a mean amount (mol·dm^{-3}) of some species with MX (or L) lost from the bulk of the test solution,[6] respectively. A derivation of eq 1 is grounded on mass balances with b_m (and b') and the following three equilibria:[6] $M^+ + X^- \rightleftharpoons MX$, $M^+ + L \rightleftharpoons ML^+$, and $ML^+ + X^- \rightleftharpoons MLX$. Also, the K_{MX} value in eqs 2 and 3 is defined as $[MX]/[M^+][X^-]$ and expressed as the usual function[5,6] of I, $K_{MX} = y_{\pm}^2 K_{MX}°$, from the extended Debye−Hückel law.[16] In many cases, this function has been employed for calculation of the K_{MLX} value,[6] because the K_{MX} values experimentally obtained in the range of a lower I have a positive deviation from values proper. Determining [M$^+$] potentiometrically and utilizing literature values of $K_{MX}°$ (or K_{MX}) and K_{ML}, then we could easily calculate [X$^-$] from eq 3 and obtain the experimental K_{MLX} values from eq 2. Moreover, the $K_{MLX}°$ value was determined by the nonlinear regression fitting of eq 1 to the plot together with the parameter b_m.[4−6] In a previous study,[18] it was differentially demonstrated that the $K_{MLX}°$ value, obtained from such an analysis of the plot, is not influenced by the magnitude of b_m. Namely, the $K_{MLX}/y_{\pm}^2$ value, which is equivalent to the $K_{MLX}°$ one, at $[X^-] \rightarrow +\infty$ in eq 1 is equal to that at $b_m \rightarrow 0$.

A curve calculated by the nonlinear regression with eq 1[4−6] is shown with a solid line in Figure 1. It has correlation coefficient (R) of 0.993 at $n = 56$ (n = the data number of K_{MLX}) and yields the parameters: $K_{K(B18C6)Pic}° = (1.37 \pm 0.12) \times 10^3$ mol^{-1}·dm^3 and $b_m = (7.4 \pm 0.3) \times 10^{-5}$ mol·dm^{-3}. Thus, eq 1 reproduces well the tendency that the plot approaches constant value in the range of the higher [Pic$^-$].[4−6] Similar results were also obtained in the other MX-L systems. Table 1 summarizes the $K_{MLX}°$ values together with those reported before on M(18C6)X,[4−6] M(15C5)Pic, and M(B15C5)Pic.[5,18] These $K_{MLX}°$ values, except for the $K_{K(15C5)Pic}°$ and $K_{K(B15C5)Pic}°$ ones, were much larger than the $K_{MX}°$ ones[4−6] reported on the corresponding MX salts in water. This fact indicates that the hydrated ion, Na$^+$ or K$^+$, dehydrates in complex formation with B18C6, 15C5, and B15C5, as described often for various L.[19]

The other data (b_m, R, and n) obtained from the regression analysis were as follows: $b_m = (1.8 \pm 0.08) \times 10^{-4}$ mol·dm^{-3} and $R = 0.990$ for the curve of the $NaMnO_4$-B18C6 system ($n = 30$); $(1.0 \pm 0.07) \times 10^{-4}$ mol·dm^{-3} and 0.953 for that of $KMnO_4$-B18C6 ($n = 84$); $(3.4 \pm 0.2) \times 10^{-4}$ mol·dm^{-3} and 0.946 for that of NaPic-B18C6 ($n = 65$); $(2.2 \pm 0.2) \times 10^{-4}$ mol·dm^{-3} and 0.970 for that of $NaBPh_4$-B18C6 ($n = 31$); $(1.3 \pm 0.1) \times 10^{-4}$ mol·dm^{-3} and 0.975 for that of $NaMnO_4$-15C5 ($n = 52$); $(1.8 \pm 0.2) \times 10^{-4}$ mol·dm^{-3} and 0.972 for that of

Table 1. Ion-Pair Formation Constants $K_{MLX}°$ of ML$^+$ with X$^-$ in Water at T = 298 K

	$K_{MLX}°$ [a]/(mol^{-1}·dm^3)		$K_{MLX}°$ [a]/(mol^{-1}·dm^3)	
MX	L = 18C6	B18C6	L = 15C5	B15C5
$NaMnO_4$	231[b]	$(1.63 \pm 0.41) \times 10^3$	38 ± 21	354 ± 75
$KMnO_4$	93[b]	72 ± 12	239 ± 80	137 ± 110
NaPic	62[c]	642 ± 96	34[e]	517[e]
AgPic	191[d]	157[d]	556[d]	1.6×10^3 [d]
KPic	738[c]	$(1.37 \pm 0.12) \times 10^3$	6.0[e]	12[e]
$NaBPh_4$	2.9×10^5 [c]	$(1.24 \pm 1.02) \times 10^5$	$(7.36 \pm 1.51) \times 10^3$	$(9.07 \pm 6.30) \times 10^3$

[a] Values at $I = 0$ mol·dm^{-3}. [b] Ref 4. [c] Ref 6. [d] Ref 5. [e] Ref 18.

Table 2. Center-to-Center Distances a of ML^+ with Pic^- Estimated at $T = 298$ K from the $K_{MLX}°$ and $K_{MLX}{}^{a,b}$ Values by Bjerrum's Equation

		a/Å $\{K_{MLX}/(mol^{-1}·dm^3)\}$		
MX	L	solvent = H_2O	$CH_2Cl_2{}^c$	DCE^d
NaPic	18C6	0.6	6.0 $\{1.1 \times 10^4\}^{b,f}$	4.9 $\{10^{4.07}\}^{b,e}$
	B18C6	0.4	$-^g$	4.5 $\{10^{4.38}\}^{b,e}$
	DB18C6	$-^h$	4.4 $\{1.11 \times 10^5\}^{b,i}$	4.0 $\{10^{4.70}\}^{b,j}$
KPic	18C6	0.4	4.6, 5.7^i $\{7.44 \times 10^4\}^{a,i}$	5.0, 4.9 $\{9.68 \times 10^3\}^{a,k}$, $\{10^{4.06}\}^{b,e}$
	B18C6	0.4	$-^g$	4.4 $\{10^{4.46}\}^{b,e}$
	DB18C6	$-^h$	3.8, 4.3^i $\{5.06 \times 10^5\}^{a,i}$	4.1 $\{10^{4.58}\}^{b,j}$

[a] K_{MLX} values estimated from conductance data. [b] K_{MLX} values estimated from extraction data. [c] Saturated with water. [d] 1,2-Dichloroethane saturated with water. [e] Ref 22. [f] Ref 26. [g] Not estimated, since K_{MLX} is not available. [h] Not estimated, since K_{MLX} could not be determined potentiometrically from less solubility of DB18C6 to water. [i] Ref 24. [j] Ref 23. [k] Ref 25.

$NaMnO_4$-B15C5 ($n = 42$); $(4.5 \pm 0.4) \times 10^{-5}$ mol·dm^{-3} and 0.992 for that of $KMnO_4$-15C5 ($n = 29$); $(6.4 \pm 0.5) \times 10^{-5}$ mol·dm^{-3} and 0.989 for that of $KMnO_4$-B15C5 ($n = 44$); $(5.8 \pm 0.7) \times 10^{-5}$ mol·dm^{-3} and 0.960 for that of $NaBPh_4$-15C5 ($n = 37$); and $(8.1 \pm 0.7) \times 10^{-5}$ mol·dm^{-3} and 0.975 for that of $NaBPh_4$-B15C5 ($n = 35$). A further treatment of b_m will be omitted because its physical meaning is not clear yet, as described previously.[6]

Center-to-Center Distances of ML^+ with X^- in Water. Based on Bjerrum's model,[20,21] we tried estimating the center-to-center distances in the ML^+-X^- pairs from the $K_{MLX}°$ values in Table 1. According to this model, an ion-pair formation constant (K_B in mol^{-1}·dm^3) at 25 °C has been expressed as

$$K_B = \frac{1.332 \times 10^6}{D^3} Q(b) \qquad (4)$$

with

$$Q(b) = \int_2^b \frac{\exp(x)}{x^4} dx$$

and

$$b = \frac{560.5}{aD}$$

where D and a denote a dielectric constant of a solvent and the center-to-center distance (Å unit) of the ions in contact, respectively. In calculation, we assumed $K_B = K_{MLX}°$ and $D =$ the dielectric constant of the pure solvent and then estimated the b value from calculating numerically the $Q(b)$ value by Simpson's rule with $(b - 2)/N = 0.2$ ($N = 1, 2, 3, ...$).

Table 2 summarizes the a values calculated from the $K_{MLX}°$ values for M(18C6 derivatives)Pic (M = Na, K) together with those from the K_{MLX} values of other solvent systems reported by conductometric or solvent extraction experiments.[22-26] Their uncertainties were presumed to be about ± 0.1 Å from calculation errors of $Q(b)$. The a values estimated for water-saturated CH_2Cl_2 and 1,2-dichloroethane (DCE) systems appear reasonable. Also, although exceptions are present, the K_{MLX} values for the DCE system seem to decrease with an increase in the ionic radii, evaluated by Shannon,[27] of central M^+: NaLPic > KLPic > RbLPic > CsLPic for L = DB18C6,[23] KLPic > NaLPic > CsLPic > RbLPic for B18C6,[26] LiLPic > RbLPic > CsLPic > NaLPic ≥ KLPic for 18C6,[26] or $NaLPicCl_2$ > $KLPicCl_2$ > $CsLPicCl_2$ for 18C6, where the symbol $PicCl_2{}^-$ denotes dichloropicrate ion.[24] These results indicate that the major interaction between ML^+ and X^- is Coulombic in the DCE system.

The estimated a values of the ML^+-Pic^- pairs in water were much smaller than those[22-26] in both CH_2Cl_2 and DCE saturated with water (Table 2). These facts suggest that, in addition to the Coulombic interaction, there are interactions such as hydrophobic or ion-dipole one, coming from specificity of water structure, for the ML^+-Pic^- pairs in water. Similar values were obtained for the AgLPic systems (a/Å = 0.5 for both the L), $NaLMnO_4$ (0.5 for L = 18C6 and 0.4 for B18C6), $KLMnO_4$ (0.5), and $NaLBPh_4$ (0.3). The NaL^+-$BPh_4{}^-$ pairs have the smallest a values of all the L employed. This fact is in agreement with the speculation that the hydrophobic interactions are present between these component ions or around the pairs. Values from a/Å = 0.4 to 0.9 were obtained for the M(15C5)X and M(B15C5)X systems.

Effect of an Addition of a Benzo Group on $K_{MLX}°$. From Table 1, the ratios of $K_{M(B18C6)X}°/K_{M(18C6)X}°$ were calculated to be 7.1 for MLX = $NaLMnO_4$, 0.77 (or its inverse = 1.3) for $KLMnO_4$, 10 for NaLPic, 0.82 (or 1.2) for AgLPic, 1.9 for KLPic, and 0.43 (or 2.3) for $NaLBPh_4$. This order was $NaLBPh_4$ < $KLMnO_4$ < AgLPic (<1) < KLPic < $NaLMnO_4$ < NaLPic. Taking account of simply these L sizes and the major interaction of the ML^+-X^- pairs and assuming that the size is a dominant factor determining the $K_{MLX}°$ value, we have the relation, $K_{M(B18C6)X}° < K_{M(18C6)X}°$, namely, $K_{M(B18C6)X}°/K_{M(18C6)X}° < 1$. The ratios were close to unity in medial cases, such as $KLMnO_4$, KLPic, and AgLPic. This fact means that the interaction of AgL^+ or KL^+ with X^- does not largely change in the addition of a benzo group to 18C6 and also that a steric hindrance of the benzo groups on $K(B18C6)^+$ and $Ag(B18C6)^+$ against Pic^- or $MnO_4{}^-$ does not drastically decrease the K_{MLX} values. Hence, there must be similarity in conformation around M^+ between $K(18C6)^+$ and $K(B18C6)^+$ or $Ag(18C6)^+$ and $Ag(B18C6)^+$. Moreover, this suggests a close resemblance in structure between $K(B18C6)^+$ and $Ag(B18C6)^+$ in water. The higher cases can indicate that 18C6 shields more effectively the electric charge of Na^+ trapped in its cavity than B18C6 does, resulting comparatively a decrease in the $K_{Na(18C6)X}°$ values ($X^- = MnO_4{}^-$ and Pic^-). Only the $NaBPh_4$-L systems suggest the steric hindrance of the benzo group in $Na(B18C6)^+$ against $BPh_4{}^-$.

The same ratios, $K_{M(B15C5)X}°/K_{M(15C5)X}°$, for the ion-pair complexes of MX with the 15C5 derivatives were calculated: 9.4 for MLX = $NaLMnO_4$, 0.62 (or its inverse = 1.6) for $KLMnO_4$, 15 for NaLPic, 2.0 for KLPic, 2.8 for AgLPic, and 0.94 (or 1.1) for $NaLBPh_4$ (Table 1). This order was $KLMnO_4$ < $NaLBPh_4$ (≤1) < KLPic < AgLPic < $NaLMnO_4$ < NaLPic.

From the fact that the lower cases from $KLMnO_4$ to KLPic are close to unity, it is clear that the benzo group attached to 15C5 does not change the interaction between KL^+ and X^- (= MnO_4^- and Pic^-) or NaL^+ and BPh_4^- in the pairs. On the other hand, the higher cases suggest that the shielding against Na^+ trapped in 15C5 is higher than in B15C5.

Effect of X^- on K_{MLX}°. To compare strength of the interaction of X^- with a fixed NaL^+, we calculated the ratio of $K_{\mathrm{NaLX}}^\circ/K_{\mathrm{NaLPic}}^\circ$ based on the NaPic-L systems. The ratios were in the order $X^- = Pic^-$ ($K_{\mathrm{NaLX}}^\circ/K_{\mathrm{NaLPic}}^\circ = 1.0$) < MnO_4^- (3.7) < BPh_4^- (4.7×10^3) for $Na(18C6)^+$ and Pic^- (1.0) ≤ MnO_4^- (1.1) < BPh_4^- (2.6×10^2) for $Na(15C5)^+$ (Table 1). The same order was also observed for $Na(B18C6)^+$ and the free Na^+,[6] though the magnitude of each ratio decreased; while the order of MnO_4^- (0.68) < Pic^- (1.0) < BPh_4^- (18) was for $Na(B15C5)^+$. From these orders, we can see immediately that, among X^- employed, the tetrahedral and bulky BPh_4^- most strongly interacts with the NaL^+.

Similarly, the ratios of $K_{\mathrm{KLX}}^\circ/K_{\mathrm{KLPic}}^\circ$ were estimated: a relation in the magnitude for $K(18C6)^+$ was $X^- = MnO_4^-$ (0.13) < Pic^- (1.0) (Table 1). A similar result was obtained for the ratio, $K_{\mathrm{K(B18C6)X}}^\circ/K_{\mathrm{K(B18C6)Pic}}^\circ$. The reverse, $Pic^- < MnO_4^-$, is true of the relation for $K(15C5)^+$, $K(B15C5)^+$, and the free K^+.[6] These facts show that the planar Pic^- is easy to bind $K(18C6)^+$ and $K(B18C6)^+$.

Effects of the Ring Size of L and a Shielding of the Charge of M^+ on K_{MLX}°. We calculated from Table 1 $K_{\mathrm{M(18C6)X}}^\circ/K_{\mathrm{M(15C5)X}}^\circ$ and $K_{\mathrm{M(B18C6)X}}^\circ/K_{\mathrm{M(B15C5)X}}^\circ$ ratios as follows: $K_{\mathrm{M(18C6)X}}^\circ/K_{\mathrm{M(15C5)X}}^\circ = 6.1$ for MLX = $NaLMnO_4$, 0.39 (or its inverse = 2.6) for $KLMnO_4$, 1.8 for NaLPic, 0.34 for AgLPic, 1.2×10^2 (or 0.008) for KLPic, and 39 for $NaLBPh_4$; $K_{\mathrm{M(B18C6)X}}^\circ/K_{\mathrm{M(B15C5)X}}^\circ = 4.6$, 0.53 (or 1.9), 1.2, 0.098, 1.1×10^2 (or 0.009), and 14 in the same order of MLX. These ratios were in the orders of $X^- = (1 <) Pic^- < MnO_4^- < BPh_4^-$ for NaLX and $MnO_4^- (<1) \ll Pic^-$ for KLX. Taking account of the ring sizes of L and the major interaction as described above, we obtain the following relation: $K_{\mathrm{M(18C6)X}}^\circ < K_{\mathrm{M(15C5)X}}^\circ$ and $K_{\mathrm{M(B18C6)X}}^\circ < K_{\mathrm{M(B15C5)X}}^\circ$. This shows the ratio < 1, when the ring size is a dominant factor determining the K_{MLX}° value. The systems satisfying this requirement are of $KLMnO_4$ and AgLPic. To us, the other systems suggest another factor: the larger the shielding effect of the charge of the M^+ trapped in L is, the smaller the K_{MLX}° value becomes. Such an effect can act in the case that the size of M^+ fits well the cavity of L: for example, Na^+ and K^+ fit into 15C5 and 18C6, respectively. By a relation between these two factors, therefore, a magnitude of K_{MLX}° should be determined.

The above results indicate that the shielding effect of M^+ is rather dominant than the effect of the ring size, except for the AgLPic system. The order of the NaLX system means that the effect of 15C5 shielding Na^+ from $X^- = Pic^-$, MnO_4^-, and BPh_4^- is apparently superior to that of 18C6. In addition to the size effect described above, the ratio of the $KLMnO_4$ system can be explained also in terms of the effect that 18C6 shields K^+ from MnO_4^-; its effect is superior to 15C5 one. On the other hand, the fact of $K_{\mathrm{K(18C6)Pic}}^\circ/K_{\mathrm{K(15C5)Pic}}^\circ \gg 1$ suggests any specific affinity between $K(18C6)^+$ and Pic^- over the shielding effect on $K(18C6)^+$. Similar discussions should hold essentially for the ion-pair complexes with the benzo derivatives.

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