Extraction Properties of *p*-Methyloxacalix[3]arene Methyl Ether for Alkali Metal Ions

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(Received March 7, 2014; Accepted May 9, 2014)

A neutral macrocyclic ligand, *p*-methyloxacalix[3]arene methyl ether (MOC3A-Me), was synthesized and its extraction properties for alkali metal picrates was investigated in a dichloromethane/water system at 25°C. The alkali metal ions were extracted by MOC3A-Me with a selectivity sequence $\text{Li}^+ < \text{Na}^+ < \text{K}^+ \leq \text{Rb}^+ \leq \text{Cs}^+$, whereas they were little extracted by the parent oxacalix[3]arene which contains free hydroxyl groups. From extraction equilibrium analysis, MOC3A-Me (L) was found to extract each alkali metal picrate (M^+A^-) by the reaction $\text{M}^+_{\text{w}} + \text{L}_{\text{o}} + \text{A}^-_{\text{w}} \rightleftharpoons \text{ML}^+\text{A}^-_{\text{o}}$, where subscripts 'o' and 'w' denote the organic and aqueous phases, respectively. The logarithmic values of the extraction equilibrium constants were determined to be 1.73, 2.12, 2.89, 3.01, and 3.07 for Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ , respectively. The structures and thermodynamic stabilities of the ML^+ complexes in the gas phase were evaluated by DFT calculations to discuss factors determining the cation selectivity of MOC3A-Me.

1. Introduction

Crown ethers and calixarenes are widely studied as synthetic ionophores. In contrast, hexahomotrioxacalixarenes, commonly called oxacalix[3]arene, have not yet been studied well but are attracting increasing interest [1]. The solvent extraction properties of *p*-*tert*-butoxycalix[3]arene derivatives for various metal ions were investigated qualitatively based on the percent extraction for given conditions [2–8]. For example, methyl and ethyl ethers of *p*-*tert*-butoxycalix[3]arene are known to show K^+ selectivity in the extraction of alkali metal picrates in a dichloromethane/water system [3,5]. To obtain more insight into the cation selectivity of oxacalix[3]arenes, quantitative data based on the equilibrium constants are necessary. In this study, we synthesized *p*-methyloxacalix[3]arene methyl ether (MOC3A-Me, Figure 1) and its extraction properties for alkali metal picrates were investigated in the dichloromethane/water system at 298 K (25°C). The extraction equilibrium constants were determined from analysis of the equilibria. To enable discussion of the factors determining the cation selectivity of MOC3A-Me, the structures and thermodynamic stabilities of MOC3A-Me – alkali

Figure 1. Structural formula of MOC3A-Me.

metal ion complexes in the gas phase were evaluated by DFT calculations.

2. Experimental

2.1 Reagents and instruments

Water was deionized and further purified through a Milli-Q Labo system (Millipore). Dichloromethane of guaranteed-reagent grade was distilled before use. Acetone of guaranteed-reagent grade was dried over molecular sieves 4A and distilled just before use. Potassium carbonate of guaranteed reagent grade was dried over phosphorus pentoxide under vacuum for one day. Aqueous solutions of alkali metal picrates were prepared as described previously [9]. Hydrochloric acid of super special grade (Kanto Chemical Co.) was used as received. All other reagents were obtained from commercial sources as guaranteed or extra-pure grade and used without further purification.

Characterization of MOC3A-Me was carried out using a JEOL JNM-ECS400 FT-NMR spectrometer, a Thermo Fisher Exactive mass spectrometer, and a Perkin-Elmer PE2400II elemental analyzer at the Center for Analytical Instrumentation, Chiba University. UV-Vis absorption spectra were recorded on a Beckman DU-640 spectrophotometer. Determination of alkali metals was performed with a Hitachi Z-5000 polarized Zeeman atomic absorption spectrophotometer in flame atomic absorption mode (K and Rb) or emission mode (Li, Na, and Cs).

2.2 Preparation of MOC3A-Me

The synthetic work was conducted under a nitrogen atmosphere and the solvents used were degassed by ultrasound just before use. *p*-Methyloxacalix[3]arene was synthesized according to the literature [4]. A mixture of *p*-methyloxacalix[3]arene (0.188 g, 4.17×10^{-4} mol dm⁻³), potassium carbonate (1.15 g, 8.32×10^{-3} mol dm⁻³) and iodomethane (4.56 g, 3.21×10^{-2} mol dm⁻³) was stirred under reflux in acetone (20 cm³) for 24 h. The reaction mixture was poured into dilute hydrochloric acid (0.12 mol dm⁻³, 10 cm³) and the product was extracted with dichloromethane (20 cm³). The dichloromethane solution was washed three times with water, and then evaporated and dried under vacuum, leaving MOC3A-Me as a white powder (0.158 g, yield 74 %). ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.27 (s, 9H, CH₃), 3.18 (s, 9H, OCH₃), 4.45 (s, 12H, CH₂), 7.07 (s, 6H, CH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 20.76, 62.11, 66.47, 155.86, 131.17, 131.48, 132.71. HR MS (ESI) found: *m/z* 515.2396. Calc. for C₃₀H₃₆O₆Na [M+Na]⁺: *m/z* 515.240960 (the sodium detected in the ESI-MS spectrum came from the instrument system). Anal. found: C, 72.47; H, 7.33%. Calc. for C₃₀H₃₆O₆: C, 73.17; H, 7.32%. UV: λ_{max} (CH₂Cl₂) 281 nm ($\epsilon = 3.9 \times 10^3$ dm³ mol⁻¹ cm⁻¹).

2.3 Extraction of alkali metal picrates with MOC3A-Me

Equal volumes of a dichloromethane solution of MOC3A-Me ($6 \times 10^{-4} - 1 \times 10^{-2}$ mol dm⁻³) and an aqueous solution of an alkali metal picrate ($2 \times 10^{-3} - 7 \times 10^{-3}$ mol dm⁻³, pH 7.0 – 7.4) were placed in a Teflon FEP centrifuge tube. The two-phase mixture was equilibrated by shaking the tube mechanically for 1 h at 250 strokes per min at 298.2 ± 0.2 K. After the organic and aqueous phases were separated by centrifugation at 3000 rpm, the concentration of the alkali metal in the organic phase was determined as follows. An aliquot of the organic phase was transferred to another centrifuge tube in which water of the same volume as the organic phase was placed, and the tube was shaken for 30 min; by this operation, the alkali metal in the organic phase was completely back extracted into the water. The alkali metal

concentration was determined with an atomic absorption spectrophotometer after addition of hydrochloric acid (final concentration of HCl, 0.06 mol dm⁻³). The concentration of the alkali metal in the aqueous phase was calculated based on the mass balance, and the distribution ratio (*D*) of the alkali metal was determined as the ratio of the molar concentration in the organic phase to that in the aqueous phase. Blank extraction with pure dichloromethane was negligibly small.

2.4 DFT calculations

DFT (B3LYP [10,11]) calculations for MOC3A-Me and its complexes with alkali metal ions (Na⁺, K⁺, Rb⁺, and Cs⁺) in the gas phase were performed with the Gaussian 03 program package [12]. The equilibrium geometries and electronic energies were calculated with a 6-31G(d) standard basis set for C, H, O, and Na atoms and a LANL2DZ effective core potential basis set [13] for K, Rb, and Cs atoms. The thermal corrections to Gibbs free energies at 298 K and 1 atm were obtained from frequency calculations using a scaling factor of 0.9804 [14]. Equilibrium geometry in dichloromethane was also calculated using the Onsager model [15,16] for MOC3A-Me and its Na⁺ complex; the geometries in dichloromethane were confirmed to be almost the same as those in the gas phase.

3. Results and Discussion

Initially, the distribution of MOC3A-Me was evaluated in the dichloromethane/water system. When the dichloromethane solution of MOC3A-Me (9×10^{-3} mol dm⁻³) was equilibrated with an equal volume of water at 298 K (shaking time, 1 h), the UV-Vis absorption spectrum of MOC3A-Me in the organic phase practically did not change and no light absorption of MOC3A-Me was observed in the aqueous phase. This result shows that MOC3A-Me is stable in this system and so hydrophobic that the distribution from the dichloromethane phase to the aqueous phase is negligible.

Although the alkali metal picrates were more or less extracted by MOC3A-Me as described below, they were little extracted by the parent oxacalix[3]arene which contains free hydroxyl groups (*p*-methyloxacalix[3]arene). This result is the same as that reported for *p*-*tert*-butyloxacalix[3]arene [4]. It appears that the strong intramolecular hydrogen bonds between the hydroxyl groups make the oxygen atoms unable to bind to the alkali metal ions.

The extraction of an alkali metal ion (M⁺) with MOC3A-Me as a ligand (L) and picrate as a counter ion (A⁻) can be expressed as

$$K_{ex} = [ML^+A^-]_o / ([M^+]_w [L]_o [A^-]_w) \quad (2)$$

where ML⁺A⁻ represents the ion pair of the ML⁺ complex with A⁻; the subscripts 'o' and 'w' refer to the organic and aqueous phases, respectively; *K_{ex}* is the extraction equilibrium constant. When the distribution ratio, *D*, of the alkali metal is approximately equal to [ML⁺A⁻]_o / [M⁺]_w, the following equation is derived from Eq. (2):

$$D / [A^-]_w = K_{ex} [L]_o \quad (3)$$

The $[L]_o$ and $[A^-]$ values can be calculated from the following equations:

$$[L]_o = [L]_t - [ML^+A^-]_o \quad (4)$$

$$[A^-]_w = [A]_t - [ML^+A^-]_o \quad (5)$$

where the subscript 't' denotes the total concentration. The $\log (D/[A^-]_w)$ vs. $\log [L]_o$ plots are shown in Figure 2. Each plot gives a straight line of slope 1 as expected from Eq. (3), proving that the extracted species are of the form ML^+A^- . The $\log K_{ex}$ values were determined and are given in Table 1.

Figure 2. Plots of $\log (D/[A^-]_w)$ vs. $\log [L]_o$ for the extraction of alkali metal picrates with MOC3A-Me in dichloromethane.

Table 1. Equilibrium constants and standard Gibbs free energy changes in the extraction system for alkali metal picrates (M^+A^-) with MOC3A-Me (L) in dichloromethane (o) at 298 K.

M^+	$\log K_{ex}$	ΔG_{ex}° (kJ/mol)	$\Delta G_{tr,M+A}^\circ$ ^a (kJ/mol)	$\Delta G_{MLA,o}^\circ$ ^b (kJ/mol)
Li ⁺	1.73 ± 0.02	-9.88	—	—
Na ⁺	2.12 ± 0.06	-12.1	61.8	-73.9
K ⁺	2.89 ± 0.03	-16.5	36.0	-52.5
Rb ⁺	3.01 ± 0.02	-17.2	27.6	-44.8
Cs ⁺	3.07 ± 0.04	-17.5	25.7	-43.2

^a Standard Gibbs free energy change for the reaction $M^+_w + A^-_w \rightarrow M^+_o + A^-_o$; Ref. 18.

^b Standard Gibbs free energy change for the reaction $M^+_o + L_o + A^-_o \rightarrow ML^+A^-_o$.

The selectivity of MOC3A-Me for the alkali metal ions is as follows: $\text{Li}^+ < \text{Na}^+ < \text{K}^+ \leq \text{Rb}^+ \leq \text{Cs}^+$. This selectivity is different from that of the methyl and ethyl ethers of *p-tert*-butyloxacalix[3]arene [3,5], the reason for which is not clear at this stage. The selectivity shown by MOC3A-Me is quite similar to that for dibenzo-24-crown-8, although the former is inferior to the latter in extraction power; the $\log K_{\text{ex}}$ values for the extraction of alkali metal picrates with dibenzo-24-crown-8 in dichloromethane are 3.56 (Na^+), 4.341 (K^+), 4.41 (Rb^+), and 4.69 (Cs^+) at 298 K [17].

The standard Gibbs free energy change of the extraction reaction $\text{M}^+_{\text{w}} + \text{L}_{\text{o}} + \text{A}^-_{\text{w}} \rightarrow \text{ML}^+\text{A}^-_{\text{o}}$ can be calculated by $\Delta G^\circ_{\text{ex}} = -2.303RT \log K_{\text{ex}}$. The values at 298 K are shown in Table 1. The $\Delta G^\circ_{\text{ex}}$ value can be considered as the sum of the standard Gibbs free energy change for the transfer of dissociated M^+ and A^- from the aqueous phase to the organic phase ($\Delta G^\circ_{\text{tr,M+A}}$) and that of the formation of the ML^+A^- complex from M^+ , L, and A^- in the organic phase ($\Delta G^\circ_{\text{MLA,o}}$). The values of $\Delta G^\circ_{\text{tr,M+A}}$ [18] and $\Delta G^\circ_{\text{MLA,o}}$ ($= \Delta G^\circ_{\text{ex}} - \Delta G^\circ_{\text{tr,M+A}}$) are also listed in Table 1. It should be noted that the contributions from the dehydration of M^+ and A^- are not included in the $\Delta G^\circ_{\text{MLA,o}}$ values but in the $\Delta G^\circ_{\text{tr,M+A}}$ values, because the cited values of $\Delta G^\circ_{\text{tr,M+A}}$ correspond to the transfer of M^+ and A^- from water to dry dichloromethane in which the ions are not hydrated [18]. The sequence in $\Delta G^\circ_{\text{tr,M+A}}$, $\text{Na}^+ \gg \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, indicates that the larger alkali metal ions are more extractable owing to the lower hydration in the aqueous phase. On the other hand, the $\Delta G^\circ_{\text{MLA,o}}$ values vary in the reverse sequence, $\text{Na}^+ \ll \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, indicating that the ternary complex ML^+A^- of the smaller alkali metal ions is more stable in the organic phase. The sequence in $\Delta G^\circ_{\text{ex}}$, $\text{Na}^+ > \text{K}^+ \geq \text{Rb}^+ \geq \text{Cs}^+$, is consistent with that in $\Delta G^\circ_{\text{tr,M+A}}$. This is because the difference in the $\Delta G^\circ_{\text{MLA,o}}$ values between two alkali metal ions is smaller than the corresponding difference in $\Delta G^\circ_{\text{tr,M+A}}$. Namely, the extraction selectivity of MOC3A-Me for the alkali metal ions is governed by the extractability of the metal ions themselves.

The $\Delta G^\circ_{\text{MLA,o}}$ values are, further, the sum of the standard Gibbs free energy change of complexation between M^+ and L in the organic phase and that of association of ML^+ and A^- in the organic phase. Here we discuss the ability of MOC3A-Me to complex with alkali metal ions in the gas phase with the aid of DFT calculations. It is known that tri-*O*-alkylated oxacalix[3]arenes have two typical conformations, *cone* and *partial-cone*, as illustrated in Figure 3. By analogy from the results for *p-tert*-butyloxacalix[3]arene alkyl ethers [3], a rapid conversion between the conformations should occur in the case of MOC3A-Me. The standard Gibbs free energies at 298 K of these conformations were calculated by DFT. The results showed

Figure 3. Typical conformations of MOC3A-Me.

Table 2. Thermodynamic values calculated from DFT calculations to evaluate the standard Gibbs free energy change ($\Delta G_{\text{ML}^+, \text{gas}}^\circ$) of the reaction $\text{M}^+ + \text{L} \rightarrow \text{ML}^+$ in the gas phase at 298 K.

	Electronic energy (a.u.) ^a	Thermal correction to Gibbs free energy ^b (a.u.) ^a	G_{298}° ^c (a.u.) ^a	$\Delta G_{\text{ML}^+, \text{gas}}^\circ$ ^d (kJ/mol)
$\text{M}^+ =$				
Na ⁺	−162.08123	−0.01415	−162.09538	—
K ⁺	−27.97063	−0.01488	−27.98550	
Rb ⁺	−23.70578	−0.01596	−23.72174	
Cs ⁺	−19.73152	−0.01659	−19.74811	
L^e	−1615.61202	0.52718	−1615.61202	—
$\text{ML}^+ =$				
NaL ⁺	−1778.37117	0.53119	−1777.83998	−348
KL ⁺	−1644.17952	0.52739	−1643.65213	−143
RbL ⁺	−1521.50318	0.52735	−1639.37213	−101
CsL ⁺	−1517.51485	0.52629	−1635.38459	−64.2

^a 1 a.u. (hartree) = 2625.5 kJ/mol

^b Multiplied with a scaling factor of 0.9804.

^c Standard Gibbs free energy at 298 K; $G_{298}^\circ = (\text{electronic energy}) + (\text{thermal correction})$.

^d $\Delta G_{\text{ML}^+, \text{gas}}^\circ = G_{298}^\circ(\text{ML}^+) - \{G_{298}^\circ(\text{M}^+) + G_{298}^\circ(\text{L})\}$

^e L = MOC3A-Me in the *partial-cone* conformation.

that the free MOC3A-Me molecule in the gas phase is 22.5 kJ mol^{−1} more stable in the *partial-cone* conformation than in the *cone* conformation; this finding agrees with the experimental results reported for *p*-*tert*-butyloxacalix[3]arene propyl ether [3]. It was also found that MOC3A-Me in the *partial-cone* conformation forms much more stable complexes with all the alkali metal ions than that in the *cone* conformation. Therefore, the dominant conformation of MOC3A-Me in both the free and complex forms is *partial-cone*. The standard Gibbs free energy change for the reaction $\text{M}^+ + \text{L} (\text{partial-cone}) \rightarrow \text{ML}^+ (\text{partial-cone})$ in the gas phase at 298 K ($\Delta G_{\text{ML}^+, \text{gas}}^\circ$) was calculated from the standard Gibbs free energies of M^+ , L, and ML^+ . The thermodynamic values obtained are given in Table 2. The $\Delta G_{\text{ML}^+, \text{gas}}^\circ$ value becomes more negative for the smaller alkali metal ions, which is explained in terms of the electrostatic interaction between the alkali metal ion and the ligand oxygen atoms. Such a variation of $\Delta G_{\text{ML}^+, \text{gas}}^\circ$ is consistent with that of $\Delta G_{\text{MLA}, 0}^\circ$ in dichloromethane (Table 1), suggesting that the $\Delta G_{\text{MLA}, 0}^\circ$ value is governed by the intrinsic stability of ML^+ .

The equilibrium geometries of free MOC3A-Me and its complexes with Na⁺ and Cs⁺ are shown in Figure 4, where the ligand is in the *partial-cone* conformation. It is seen from the geometries that the ligand changes its conformation flexibly to effectively bind to the alkali metal ions of different sizes, where the number of the ligand oxygen atoms surrounding an alkali metal atom is always five. The standard Gibbs free energy at 298 K of the ligand having the conformation identical to that in the complex was calculated; the Gibbs free energy was found to vary with the complexing metal ion in the sequence, Na⁺ (−1615.59808

Figure 4. Equilibrium geometries of L, NaL^+ , and CsL^+ in the gas phase determined by DFT calculations (L = MOC3A-Me).

Upper drawing: ball and stick models

Lower drawing : space filling models

a.u.) $> \text{K}^+$ (-1615.60101 a.u.) $\approx \text{Rb}^+$ (-1615.60031 a.u.) $> \text{Cs}^+$ (-1615.60291 a.u.). This shows that the steric strain of the ligand arising from complexation is greater when the alkali metal ion is smaller. Such a steric strain should reduce the difference in the $\Delta G_{\text{ML}^+, \text{gas}}^\circ$ values between the alkali metal ions.

4. Conclusion

p-Methyloxacalix[3]arene methyl ether exhibits an extraction selectivity for the larger alkali metal ion such as Cs^+ . The selectivity is governed by the extractability of the alkali metal ions themselves. The ligand has a flexible structure and changes its conformation to complex effectively with the alkali metal ions of different sizes. The ligand interacts more strongly with the smaller alkali metal ions having a higher charge density, but the ligand conformational strain upon complexation is also larger for the smaller alkali metal ions. Consequently, the complexation of the ligand with the alkali metal ions makes only a minor contribution to the extraction selectivity, although it should be effective in enhancing the extractability of the alkali metal ions. A similar explanation may hold true for the extraction selectivity of dibenzo-24-crown-8 [17]. On the other hand, we have recently reported a more highly Cs^+ -selective ionophore, the 1,1,1-tris[(salicylideneamino)methyl]ethane – aluminium(III) complex, which has a rigid cavity suited for accommodating Cs^+ [9]. It appears certain that the rigidity of the ligand structure is an important factor for enhancing the selectivity.

Acknowledgement

This research was partially supported by research grants from the Futaba Electronic Memorial Foundation and AGSST of Chiba University.

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