

Extraction-ability and -selectivity of tetra-aza-crown ethers for transition metal cations

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Abstract

In order to investigate the relative effects of the differences between the structures and lipophilicities of 1, 10-dioxa-4, 7, 13, 16-tetra-azacyclo-octadecane (TA-18-crown-6) and the tetrabenzyl derivative of 1,10-dioxa-4, 7, 13, 16-tetra-azacyclo-octadecane (TBTA-18-crown-6) on their extraction-abilities and -selectivities for transition metal cations, constants of the overall extraction ($\log K_{\text{ex}}$) of 1:1 (M:L) complexes, the distribution (K_{D}) for two diluents (CH_2Cl_2 and CHCl_3) with different dielectric constants have been determined at 25 ± 0.1 °C. The magnitude of $\log K_{\text{ex}}$ is largely determined by that of K_{D} . The equilibrium constants of TA-18-crown-6 have been compared with those of TBTA-18-crown-6. It is found that: (i) $\log K_{\text{ex}}$ sequences of TA-18-crown-6 and TBTA-18-crown-6 for transition metals in CH_2Cl_2 lie in order: $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$ and $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ respectively; (ii) the stability sequences of two types of tetra-aza-crown ethers with the transition metal cations in CHCl_3 are the same as follows: $\text{Fe}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}$, and (iii) unusual selectivities are observed for transition metal-tetra-aza-crowns, e.g. the high $\text{Fe}^{3+}/\text{M}^{n+}$ selectivity factors (S_{f}) of TA-18-crown-6, except for the competitive-extractions for the special case in CHCl_3 of TBTA-18-crown-6, it was found that the $\text{Mn}^{2+}/\text{M}^{n+}$ values were relatively higher according to the other transition metal cations. A systematic sequence in these two types of solvents is not found for a given transition metal cation in terms of the variation of selectivity with the tetra-aza-crown ethers. The results provide alternatives for the rational design of other specific ligands on the transition metal cations.

Introduction

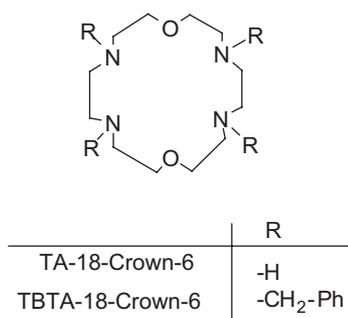
Investigation of metal complexes containing macrocyclic ligands has been an area of active research for many years [1], and a variety of macrocyclic and macropolycyclic compounds have been examined in the search for synthetic host molecules. Crown ethers and analogues thereof [2], based upon 1,2-disubstituted ethane units, have proved to be suitable hosts for a range of cationic species and a few neutral molecules [3], and the rigid, predictably structured, spherands [4] have been used, more recently, as hosts for cations. Most of the applications of the synthetic macrocyclic ligands are based on their ability to form stable complexes with metal ions and their selectivity toward metal cations. Of the several tetradentate macrocyclic ligands known, by far the largest number contain 14 members and perturbations on the simplest, 1, 4, 8, 11-tetra-azacyclo-tetradecane, commonly known as cyclam [5]. Tetra-aza-crown ethers are versatile complexing agents because their properties (e.g. affinity for cations, hydrophobicity, etc.) can be optimized by introducing suitable substituents on the nitrogen atoms. To date only a few derivated tetra-aza-analogues of crown ethers and their

metal complexes have been prepared and characterized [6–14]. These ligands have also been applied as solvent extractants [15], selective reagents for the colorimetric determination of transition metals [16], and chelate adsorbents [17]. The saturated macrocycles have produced much interesting information on the stabilities and structures of metal complexes [18–20].

The cation complexing ability of tetra-aza-crown ethers can be modified by the substituents attached to the nitrogen atoms, and the interactions between a transition metal ion and tetra-aza-crown ethers can be increased by substituting nitrogen atoms for some of the donor oxygen atoms in the ligand. The extraction-ability and -selectivity and the change in those with the diluent of a tetra-aza crown ether for metal salts can be quantitatively and comparatively elucidated by using the fundamental equilibrium constants. In a previous study [21], constants for the overall extraction, distribution, aqueous ion-pair formation of 18-crown-6, dibenzo-18-crown-6, 15-crown-5 and 12-crown-4 – sodium dyes (1:1:1 complexes) were determined; partition constants of these crown ethers were also measured. In the present work, a study of the two different solvents dependence of the complexation equilibria and the metal selectivity of synthesized tetra-azacrowns with transition metal ions has been made. The complexing abilities of

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TA-18-crown-6 with some transition metal ions (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) have been investigated, earlier by the potentiometric method in the literature [22], but there is no complete information on the comparative stability constants and selectivities of their complexations, and investigations have been carried out in different solvents. TA-18-crown-6 and TBTA-18-crown-6 compounds have been synthesized as earlier described in the literature [23, 24].



Experimental

Reagents

TA-18-crown-6 and TBTA-18-crown-6 were prepared according to published procedures [23, 24]. CHCl_3 , CH_2Cl_2 , $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were analytical-grade reagents from Merck. The purity of all the metal nitrates was determined by EDTA titration. Chloroform and dichloromethane were used without further purification.

Extraction procedure and determination of extraction constants

For K_{ext} determination, the extraction measurements were done in a 100 cm³ glass thermostated cell com-

partment with a mechanical stirrer in which a 25 cm³ solution of any aqueous metal salt (4×10^{-5} M) and tetra-aza-crown ether in organic solvents (same concentration) were placed and stirred for 30 min at 25 ± 0.1 °C, and subsequently allowed to stand for 30 min to complete the phase separation. The extractions were performed at the natural pH's of the aqueous metal solution which were *ca.* 6.5–7.8. For selective extraction, observing S_f values of the transition metal cations by the tetra-aza-crown ethers, a changed extraction technique was derived. An aqueous solution of the transition metal mixtures at a certain concentration (4×10^{-5} M) and a separate organic solution of the each tetra-aza-crown ether in the same concentration (4×10^{-5} M) were used. Competitive transition metal salt extractions were conducted with 5.00 cm³ of an aqueous solution containing Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} nitrates, and 5.00 cm³ of an organic solution of the tetra-aza-crown ether.

After extraction, the transition metal salt concentration in the aqueous phase was determined using a Perkin-Elmer 3100 model ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectrometer) and FIAS 90 autosampler. Each value was the average of three subsequent measurements. The complexation and distribution constants, and the S_f values of the tetra-aza-crown ethers are summarized in Tables 1 and 2. The distribution coefficients ($K_{D,L}$) of the tetra-aza-crown ethers in the solvents used in the study were determined according to the method given by Takeda and Kato [25].

Theory, results and discussion

In this work we have studied the common formalism of Equations (1–24) [25]. The equilibrium processes taking place during the extraction between an aqueous solution containing the transition metal cation, $M_{(w)}^{m+}$, and organic anion, $A_{(w)}^-$, and an organic solution containing crown ethers $L_{(\text{org})}$, can be written:

Table 1. Equilibrium constants for extractions of transition metal cations with tetra-aza-crown ethers in CH_2Cl_2 and CHCl_3 at 25 °C^a

| Cation | Solvent | TA-18-crown-6 | | | TBTA-18-crown 6 | | | |
|------------------|--------------------------|-----------------|-------|-----------------------|------------------|-------|-----------------------|------------------|
| | | $K_{D,L}$ | K_D | $\log K_{\text{ext}}$ | $K_{D,L}$ | K_D | $\log K_{\text{ext}}$ | |
| Mn^{2+} | CH_2Cl_2 | 1.00 | 0.21 | 11.39 ± 0.06 | 5.74 | 0.21 | 12.24 ± 0.55 | |
| Fe^{3+} | | | 12.33 | 19.65 ± 1.65 | | 19.00 | 22.71 ± 1.65 | |
| Co^{2+} | | | 0.33 | 11.37 ± 0.31 | | 0.33 | 12.56 ± 0.55 | |
| Ni^{2+} | | | 0.14 | 11.17 ± 0.83 | | 0.18 | 12.22 ± 0.49 | |
| Cu^{2+} | | | 0.43 | 11.85 ± 0.63 | | 1.35 | 12.56 ± 0.77 | |
| Zn^{2+} | | | 0.29 | 11.05 ± 1.26 | | 0.48 | 11.62 ± 0.20 | |
| Cd^{2+} | | | | 0.03 | 11.33 ± 0.06 | | 0.18 | 12.12 ± 0.74 |
| Mn^{2+} | | CHCl_3 | 0.55 | 0.03 | 10.48 ± 0.26 | 3.79 | 0.03 | 10.13 ± 0.33 |
| Fe^{3+} | | | | 4.71 | 19.96 ± 0.98 | | 1.50 | 18.38 ± 1.35 |
| Co^{2+} | | | | 0.91 | 12.58 ± 1.17 | | 1.11 | 13.71 ± 1.10 |
| Ni^{2+} | | | 0.34 | 13.59 ± 1.70 | | 2.64 | 14.80 ± 1.05 | |
| Cu^{2+} | | | 2.33 | 13.17 ± 0.62 | | 1.22 | 13.82 ± 0.37 | |
| Zn^{2+} | | | | 0.11 | 11.88 ± 0.04 | | 0.21 | 12.62 ± 0.31 |
| Cd^{2+} | | | | 0.08 | 11.02 ± 0.35 | | 0.22 | 11.19 ± 0.16 |

^a Corr. coefficient: 0.999.

Table 2. Selectivity factor values, S_F , determined for pairs of transition metal cations in the competitive extraction of transition metal nitrates from aqueous solution into CH_2Cl_2 and CHCl_3 with TA-18-crown-6 and TBTA-18-crown-6

| Tetra-aza-crown ether | Solvent | $\text{M}^{\text{m}+}$ | $\text{Mn}^{2+}/\text{M}^{\text{m}+}$ | $\text{Fe}^{3+}/\text{M}^{\text{m}+}$ | $\text{Co}^{2+}/\text{M}^{\text{m}+}$ | $\text{Ni}^{2+}/\text{M}^{\text{m}+}$ | $\text{Cu}^{2+}/\text{M}^{\text{m}+}$ | $\text{Zn}^{2+}/\text{M}^{\text{m}+}$ | $\text{Cd}^{2+}/\text{M}^{\text{m}+}$ |
|-----------------------|--------------------------|------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| TA-18-crown-6 | CH_2Cl_2 | Mn^{2+} | 1.00 | 58.71 | 1.57 | 0.67 | 2.05 | 1.38 | 0.14 |
| | | Fe^{3+} | 0.02 | 1.00 | 0.03 | 0.01 | 0.03 | 0.02 | 0.00 |
| | | Co^{2+} | 0.64 | 37.36 | 1.00 | 0.42 | 1.30 | 0.88 | 0.09 |
| | | Ni^{2+} | 1.50 | 88.07 | 2.36 | 1.00 | 3.07 | 2.07 | 0.21 |
| | | Cu^{2+} | 0.49 | 28.67 | 0.77 | 0.33 | 1.00 | 0.67 | 0.07 |
| | | Zn^{2+} | 0.72 | 42.51 | 1.14 | 0.48 | 1.48 | 1.00 | 0.10 |
| | | Cd^{2+} | 7.00 | 411.00 | 11.00 | 4.67 | 14.33 | 9.67 | 1.00 |
| | CHCl_3 | Mn^{2+} | 1.00 | 157.00 | 30.33 | 11.33 | 77.67 | 3.67 | 2.67 |
| | | Fe^{3+} | 0.01 | 1.00 | 0.19 | 0.07 | 0.49 | 0.02 | 0.02 |
| | | Co^{2+} | 0.03 | 5.18 | 1.00 | 0.37 | 2.56 | 0.12 | 0.09 |
| | | Ni^{2+} | 0.09 | 13.80 | 2.68 | 1.00 | 6.85 | 0.32 | 0.24 |
| | | Cu^{2+} | 0.01 | 2.02 | 0.39 | 0.15 | 1.00 | 0.05 | 0.03 |
| | | Zn^{2+} | 0.27 | 42.82 | 8.27 | 3.09 | 21.18 | 1.00 | 0.73 |
| | | Cd^{2+} | 0.36 | 58.87 | 11.38 | 4.25 | 29.13 | 1.38 | 1.00 |
| TBTA-18-crown-6 | CH_2Cl_2 | Mn^{2+} | 1.00 | 90.48 | 1.57 | 1.33 | 6.43 | 2.29 | 0.86 |
| | | Fe^{3+} | 0.01 | 1.00 | 0.02 | 0.01 | 0.07 | 0.03 | 0.01 |
| | | Co^{2+} | 0.64 | 57.56 | 1.00 | 0.85 | 4.09 | 1.45 | 0.55 |
| | | Ni^{2+} | 1.17 | 68.72 | 1.18 | 1.00 | 4.82 | 1.71 | 0.64 |
| | | Cu^{2+} | 0.16 | 14.07 | 0.24 | 0.21 | 1.00 | 0.36 | 0.13 |
| | | Zn^{2+} | 0.44 | 39.58 | 0.69 | 0.58 | 2.81 | 1.00 | 0.38 |
| | | Cd^{2+} | 1.17 | 105.56 | 1.83 | 1.56 | 7.50 | 2.67 | 1.00 |
| | CHCl_3 | Mn^{2+} | 1.00 | 50.00 | 37.00 | 88.00 | 40.67 | 7.00 | 7.00 |
| | | Fe^{3+} | 0.02 | 1.00 | 0.74 | 1.76 | 0.81 | 0.14 | 0.14 |
| | | Co^{2+} | 0.03 | 1.35 | 1.00 | 2.37 | 1.10 | 0.19 | 0.19 |
| | | Ni^{2+} | 0.01 | 0.57 | 0.42 | 1.00 | 0.46 | 0.08 | 0.08 |
| | | Cu^{2+} | 0.02 | 1.23 | 0.91 | 2.16 | 1.00 | 0.17 | 0.17 |
| | | Zn^{2+} | 0.14 | 7.14 | 5.29 | 12.57 | 5.81 | 1.00 | 1.00 |
| | | Cd^{2+} | 0.14 | 7.14 | 5.29 | 12.57 | 5.81 | 1.00 | 1.00 |



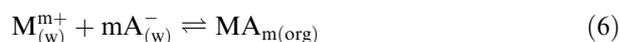
$$K_{\text{ext,w}} = [\text{MLA}_{\text{m}(\text{org})}] / [\text{M}^{\text{m}+}]_{\text{w}} [\text{A}^-]_{\text{w}}^{\text{m}} [\text{L}]_{\text{w}} \quad (2)$$

and

$$K_{\text{D}} = [\text{MLA}_{\text{m}(\text{org})}] / [\text{M}^{\text{m}+}]_{\text{w}} \quad (3)$$



$$K_{\text{D,L}} = [\text{L}]_{\text{org}} / [\text{L}]_{\text{w}} \quad (5)$$



$$K_{\text{MA}} = [\text{MA}_{\text{m}(\text{org})}] / [\text{M}^{\text{m}+}]_{\text{w}} [\text{A}^-]_{\text{w}}^{\text{m}} \quad (7)$$

and

$$K'_{\text{D}} = [\text{MA}_{\text{m}(\text{org})}] / [\text{M}^{\text{m}+}]_{\text{w}} \quad (8)$$



$$K_{\text{HA}} = [\text{HA}]_{\text{org}} / [\text{H}^+]_{\text{w}} [\text{A}^-]_{\text{w}} \quad (10)$$

for the extraction process of an acid, HA, with the metal salt in the above, $[\text{M}^{\text{m}+}]_{\text{w}}$, $[\text{A}^-]_{\text{w}}$ and $[\text{ML}_n\text{A}]_{\text{org}}$ denote the concentrations of uncomplexed cation and anion in

the aqueous phase and the complex ion-pair extracted in the organic phase, respectively. Mass balances for these processes are expressed as

$$[\text{L}_0] = [\text{L}]_{\text{w}} + [\text{MLA}_{\text{m}(\text{org})}] + [\text{L}]_{\text{org}} \quad (11)$$

$$[\text{M}_0^{\text{m}+}] = [\text{M}^{\text{m}+}]_{\text{w}} + [\text{MLA}_{\text{m}(\text{org})}] + [\text{MA}_{\text{m}(\text{org})}] \quad (12)$$

and

$$[\text{A}_0^-] = \text{m}[\text{M}_0^{\text{m}+}] = \text{m}[\text{MLA}_{\text{m}(\text{org})}] + \text{m}[\text{MA}_{\text{m}(\text{org})}] + [\text{HA}]_{\text{org}} + [\text{A}^-]_{\text{w}} \quad (13)$$

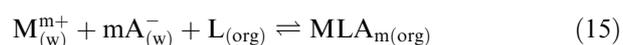
where the subscript (0) designates the initial concentrations.

$$[\text{MLA}_{\text{m}(\text{org})}] \gg [\text{MA}_{\text{m}(\text{org})}] + [\text{HA}]_{\text{org}}$$

then,

$$[\text{A}^-]_{\text{w}} \cong [\text{A}_0^-] - \text{m}[\text{MLA}_{\text{m}(\text{org})}] \quad (14)$$

Therefore, for the overall extraction process, the following equation can be written by adding Equation (1) to the reverse of Equation (4),



$$K_{\text{ext.org}} = [\text{MLA}_m]_{\text{org}} / [\text{M}^{m+}]_{\text{w}} [\text{A}^-]_{\text{w}}^m [\text{L}]_{\text{org}} \quad (16)$$

and

$$[\text{MLA}_m]_{\text{org}} + [\text{M}^{m+}]_{\text{w}} \gg [\text{MA}_m]_{\text{org}}$$

Equations (12) and (14) can be modified, respectively:

$$[\text{MLA}_m]_{\text{org}} = [\text{M}_0^{m+}] - [\text{M}^{m+}]_{\text{w}} \quad (17)$$

$$[\text{A}^-]_{\text{w}} \cong [\text{A}_0^-] - m([\text{M}_0^{m+}] - [\text{M}^{m+}]_{\text{w}}) \quad (18)$$

and hence,

$$[\text{A}^-]_{\text{w}} \cong m[\text{M}^{m+}]_{\text{w}} \quad (19)$$

and, in this case, the equilibrium constant of the extraction process can be written in a modified form:

$$K_{\text{ext.org}} = [\text{MLA}_m]_{\text{org}} / m^m [\text{M}^{m+}]_{\text{w}}^{(m+1)} [\text{L}]_{\text{org}} \quad (20)$$

The following equations can be derived by adding Equations (11) to (5),

$$[\text{L}]_{\text{org}} = K_{\text{D,L}}([\text{L}_0] - [\text{MLA}_m]_{\text{org}}) / (1 + K_{\text{D,L}}) \quad (21)$$

hence Equation (11) can be written in a modified form:

$$K_{\text{ext.org}} = (1 + K_{\text{D,L}})[\text{MLA}_m]_{\text{org}} / K_{\text{D,L}} m^m [\text{M}^{m+}]_{\text{w}}^{(m+1)} ([\text{L}_0] - [\text{MLA}_m]_{\text{org}}) \quad (22)$$

Therefore, the relationship between K_{ext} and K_{D} from the Equations (1), and (21) can be written as

$$K_{\text{ext.org}} = K_{\text{D}} / m^m [\text{M}^{m+}]_{\text{w}}^m [\text{L}]_{\text{org}} \quad (23)$$

From selective extractions performed for two different transition metal cations under identical conditions (*i.e.*, the same ligand and anion and the same concentrations of the ligand and metal salt), the selectivity factor, S_{f} , for $\text{M}_{(1)}^{m+}$ over $\text{M}_{(2)}^{m+}$ is determined as a ratio of $K_{\text{D}\{\text{M}_{(1)}^{m+}\}}$ and $K_{\text{D}\{\text{M}_{(2)}^{m+}\}}$, as described by equation [26]:

$$S_{\text{f}} = K_{\text{D}\{\text{M}_{(1)}^{m+}\}} / K_{\text{D}\{\text{M}_{(2)}^{m+}\}} \quad (24)$$

The complexation of transition cations Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} have been examined with the tetra-aza-crown ethers and extracting solvents. The stability constants of various metal complexes of these ligands are listed in Table 1, as the interactions of these ligands with the transition metal ions in two different solvent media. The macrocyclic ligands, TA-18-crown-6 and TBTA-18-crown-6, form with the transition metal cations (1:1)-complexes of unexpected high stability even in an extraction study [27]. Assuming that formation of 1:1 complexes of the transition metal cations have been extracted at the natural pH of the

aqueous metal salt solutions (*ca.* 6.5–7.8). In this paper, the extractability of the transition metal cations from aqueous solutions into solutions of TA-18-crown-6 in two different organic solvents was investigated. The $\log K_{\text{ext}}$ values of TA-18-crown-6 and TBTA-18-crown-6 for the transition metal cations in dichloromethane have decreased in the order: $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$ and $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ respectively (Table 1), and the $\log K_{\text{ext}}$ sequence of TA-18-crown-6 in chloroform has been found: $\text{Fe}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mn}^{2+}$, which is completely consistent with that of TBTA-18-crown-6 (Table 1). Thus, extraction-selectivity tendencies of TA-18-crown-6 and TBTA-18-crown-6 for the transition metal cations are found to be identical in chloroform.

The difference in $\log K_{\text{ext}}$ values of TA-18-crown-6 between neighbouring transition metal ions in the Periodic Table is close to TBTA-18-crown-6. In addition, the $\log K_{\text{ext}}$ values of TBTA-18-crown-6-transition metal complexes in these two types of solvent are relatively larger than the $\log K_{\text{ext}}$ values of TA-18-crown-6-transition metal complexes. These tetra-aza-crown ether transition metal complexes are less stable in dichloromethane than in chloroform, except in cases of Mn^{2+} and Cd^{2+} complexes. TBTA-18-crown-6, bearing benzyl side-groups on the four nitrogen atoms, was relatively able to form more stable complexes with all of the transition metals, and the extractability of this ligand for the same metal ion was much higher than that of TA-18-crown-6. The $K_{\text{D,L}}$ value of TA-18-crown-6 for the same metal ion is found to be much smaller than that of TBTA-18-crown-6, resulting in the much lower extractability of TA-18-crown-6 compared with TBTA-18-crown-6. This indicated that the lower lipophilicity of TA-18-crown-6 has caused much less stable complexation for the transition metal ions compared to TBTA-18-crown-6 in these types of extracting solvents. It is found that the values of stability constants were nearly in the same range for most transition metal cations except for the Fe^{3+} cation, but that the stability in dichloromethane was generally lower than in chloroform, except for the Mn^{2+} and Cd^{2+} cations.

Fe^{3+} is found to be the best extracted metal cation for these two types of organic solvents and tetra-aza-crown ethers. This is followed by the Cu^{2+} and Ni^{2+} for the both tetra-aza-crown ethers in dichloromethane and chloroform, respectively.

In order to probe the potential differences in selectivities for competitive solvent extraction of transition metal cations by tetra-aza-crown ethers, we have carried out solvent extractions on seven transition metal nitrates [manganese(II) nitrate, iron(III) nitrate, cobalt(II) nitrate, nickel(II) nitrate, copper(II) nitrate, zinc(II) nitrate and cadmium(II) nitrate] present in aqueous solution individually and as an equimolar mixture, into these two types of organic solvents (dichloromethane and chloroform) with TA-18-crown-6 and TBTA-18-

crown-6. Values of the selectivity factors, S_f , calculated for pairs of transition metal cations as $K_{D(M1^{m+})}/K_{D(M2^{m+})}$ in dichloromethane and chloroform are presented in Table 2 for the tetra-aza-crown ether and its benzyl substituted derivative, respectively. The data contained in these tables unequivocally demonstrate that the selectivities determined from the competitive extraction experiments were generally different although the same cavity size and the number of oxygens and nitrogens in the macrocyclic ring for both of the tetra-aza-crowns examined.

One of the most important findings was the increase in Fe^{3+} selectivity over the other transition metal cations for the two types of tetra-aza-crown ethers and the two solvent media. The highest selectivity factors of Fe^{3+} compared with other transition metal cations were achieved for the two extracting solvents. However, the two aza-crown ethers have been generally found to be much less selective for Fe^{3+} than for other transition metal cations in chloroform. For the Fe^{3+} cation, the S_f values, determined by competitive extraction, were approximately *ca.* 0.56–425 take times greater than those calculated from the results of selective extraction experiments of other transition metal cations. The selectivity factor sequence for the Fe^{3+}/M^{m+} ratio for TA-18-crown-6 and TBTA-18-crown-6 in dichloromethane have been found to lie in the order: $Fe^{3+}/Cd^{2+} > Fe^{3+}/Ni^{2+} > Fe^{3+}/Mn^{2+} > Fe^{3+}/Zn^{2+} > Fe^{3+}/Co^{2+} > Fe^{3+}/Cu^{2+}$ and $Fe^{3+}/Cd^{2+} > Fe^{3+}/Mn^{2+} > Fe^{3+}/Ni^{2+} > Fe^{3+}/Co^{2+} > Fe^{3+}/Zn^{2+} > Fe^{3+}/Cu^{2+}$, respectively (see Table 2). A similar tendency is observed for TA-18-crown-6 in chloroform, and the selectivity factor, S_f , sequence for Fe^{3+} decreases in order: $Fe^{3+}/Mn^{2+} > Fe^{3+}/Cd^{2+} > Fe^{3+}/Zn^{2+} > Fe^{3+}/Ni^{2+} > Fe^{3+}/Co^{2+} > Fe^{3+}/Cu^{2+}$. It is interesting to note that the selectivity order of the transition metal cations is quite different from the above sequences for TBTA-18-crown-6 in chloroform, and the most selective metal cation is the Ni^{2+} cation. The results of the selectivity sequence for TBTA-18-crown-6 in chloroform lie in the order: $Ni^{2+}/Mn^{2+} > Ni^{2+}/Zn^{2+}$, $Ni^{2+}/Cd^{2+} > Ni^{2+}/Co^{2+} > Ni^{2+}/Cu^{2+} > Ni^{2+}/Fe^{3+}$ (see Table 2). Furthermore, since the solvent effect is also studied in this paper, justification of the results should involve consideration of two different solvent properties and solvent–solute interactions. Two haloalkanes studied in this work have relatively low and different dielectric constants ($\epsilon^{20} CH_2Cl_2$: 9.080 and $\epsilon^{20} CHCl_3$: 4.806). Several correlations between the solvent properties and extraction efficiency were obtained in our previous work and by others [21, 28]. The selectivity factor, S_f , generally has decreased as the organic solvent is varied in the order: dichloromethane > chloroform. Excluding the cases of S_f parameters for Ni^{2+}/M^{m+} and Cd^{2+}/M^{m+} , for these types of the tetra-aza-crown ethers, the selectivity factor decrease as the diluent is varied in the same order as above. Although the effect of relative solvent polarity on the observed selectivity parameter of the transition metal cations was not

investigated systematically, preliminary results show that less polar solvent such as dichloromethane, give rise to enhanced selectivity ratios both for the seven transition metal cations and the tetra-aza-crown ethers (Table 2) [29–31].

In conclusion, the results concerning the study of the transition metal cations with these monocyclic tetra-aza-crown ethers are very important in two respects. First, in all cases of extraction studies, the Fe^{3+} cation has been found to be the best selective extracted for the extraction solvents and the given tetra-aza-crown ethers as shown in Tables 1 and 2. Second, this work has also shown that chloroform is a relatively better extracting solvent for single-species extraction of the transition metal cations by tetra-aza-crown ethers (Table 1). However, the best extractive solvent for the tetra-aza-crown ethers in competitive extractions is dichloromethane (Table 2).

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