Effects of Water Molecules on Metal Complexes of Hydroxyoxime and Carboxylic Acid Extractants

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Water molecules around the cobalt(II) (Co) and manganese(II) (Mn) complexes of the hydroxyoxime extractant, LIX63 and/or of the carboxylic acid extractant, Versatic acid 10 (VA10), in cyclohexane solvent were investigated using molecular dynamics calculations with simulated annealing. For the complexes of VA10, water molecules were coordinated to the metal ions, and VA10 molecules were found around the complexes. For the complexes of LIX63, a few water molecules were located at ~ 0.4 nm from the metal ions, in addition to the LIX63 molecules were also coordinated to the metal ions. Our trajectory analysis indicates that the water molecules at ~ 0.4 nm are hydrogen-bonded to LIX63 or other water molecules, suggesting that the hydrogen bonding contributes to the stabilization of the metal complex.

1. Introduction

In solvent extraction processes for separation and purification of critical metal ions in aqueous solution, it has been reported that water molecules play an important role in the stabilization of the metal complexes formed in the organic solvent. The stability of the metal-extractant complex in the organic solvent is theoretically known to be related to the extraction efficiency, and the stabilization mechanism has been researched experimentally and theoretically. Consequently, it is useful to specify the position of one water molecule around the metal ion in order to understand the extraction mechanism at an atomic level.

Although synergistic extraction using the multiple extractants has been researched and the mechanisms have been elucidated in some cases [1-5], several aspects remain undefined at an atomic level. It has been reported experimentally that the efficiency curve, representing the pH-dependence, of the extraction of cobalt(II) by the hydroxyoxime extractant, LIX63 used in combination with the carboxylic acid extractant, Versatic acid 10 (VA10), is shifted by two pH units compared to LIX63 alone [6], called synergistic effect. However, the 3-dimensional structure of the metal complexes formed by these extractants is unclear.

In this paper, the distribution of molecules/ions around the cobalt(II) (Co) or manganese(II) (Mn) ions was investigated by using molecular dynamics (MD) calculations with simulated annealing (SA). All

Figure 1. Structures of LIX63 and VA10.
calculations were carried out in cyclohexane (CHX) as diluent. LIX63 and VA10 (Figure 1) were selected as the hydroxyoxime and carboxylic acid extractants, as experimental data for these were available [6]. We performed the calculations with six systems (Co-LIX63, Mn-LIX63, Co-VA10, Mn-VA10, Co-(LIX63+VA10) and Mn-(LIX63+VA10)). In addition to the extractants, all systems contained ten water molecules to examine their distribution around the metal ion. The SA trajectories were analyzed and revealed that water molecules not coordinated to the metal ions contribute to the stability of the metal complexes.

2. Methods

MD simulations were performed with the GROMACS software package [7,8] using the general AMBER Force Field [9] (for CHX, LIX63 and VA10), TIP3P water model [10] (for H2O) and parameters developed by Li and Merz [11, 12] (for Co2+, Mn2+ and Cl−) and by Sagnella and Voth [13] (for H3O+). The atomic charges of CHX, LIX63 and VA10 were calculated using the AM1-BCC method [14,15]. The initial model systems were constructed by using one Co2+ or Mn2+ ion and 10 water molecules with 10 LIX63 and/or 10 VA10 molecules. These systems were embedded in rectangular boxes solvated with 508 CHX molecules in a periodic boundary condition, and H3O+ and Cl− were added to neutralize the system. The box sizes were set to be 4.6 nm x 4.6 nm x 4.6 nm.

To avoid the coordination of Cl− to the metal ions in the Co- and Mn-VA10 systems, the distances between metal ions and Cl− were restrained. Our pre-calculations with the Co- and Mn-VA10 systems containing free Cl−, which were 500-ns MD calculations and SA calculations, showed that free Cl−’s were coordinated to the metal ions immediately and not exchanged with other molecules. The structures of the metal complexes were very similar with that in aqueous solution including no extractant. Thus, to focus on the effect of water molecules on the complexes, we used the distance restraints. For applying the restraints, the restraint potential form $V(r)$ is

\[
V(r) = \begin{cases} 
\frac{1}{2}k(r - r_0)^2 & \text{for } r < r_0 \\
0 & \text{for } r \geq r_0 
\end{cases}
\]

where $r$ is the distance between the metal ion and the chloride ion, $r_0$ is set to be 1.5 nm, and $k$ is the force constant, 500 kJ/mol/nm².

Initial structures for the SA calculations were prepared as follows; after minimization, gradual heating to 300 K in 500 ps and equilibration at 300 K for 10 ns were carried out. The pressure of the systems was maintained at 1 bar by Parrinello-Rahman approach [16,17] and the temperature was controlled by the velocity-rescaling thermostat [18]. The final structures in the simulations were used for the next SA calculations.

The structure sampling was carried out with 8 cycles of the SA calculations. Each cycle consisted of five steps; (i) equilibration at 300 K for 250 ps, (ii) heating from 300 to 800 K for 500 ps, (iii) equilibration at 800 K for 500 ps, (iv) cooling from 800 to 300 K for 500 ps and (v) equilibration at 300 K for 250 ps. We analyzed the SA trajectories in step (i) and (v) during the last 5 cycles. The volume of the systems was fixed, and the temperature was controlled by the velocity-rescaling thermostat [18].

In all MD simulations, the particle-mesh Ewald algorithm [19] was used for long-range electrostatic interactions.
interactions, and other short-ranged nonbonding interactions were calculated using a cut-off of 1.2 nm. A time step was set to be 1.0 fs and conformations were saved every 1 ps.

3. Results and Discussion

The structures of the Co or Mn complexes containing LIX63 and/or VA10 were estimated using the SA trajectories during last 5 cycles (see above). During the SA calculations, the molecules coordinated to the metal ions were exchanged frequently according to the system temperature. Because these observed structures might be in metastable states, not stable states, we performed six 500-ns MD calculations starting from the configurations chosen from each SA trajectory. These MD results showed that the structures of the metal complexes did not changed and were in stable states. Consequently, the snapshots of the SA trajectories were analyzed to compare the structures of the metal complexes.

3.1 Complexes coordinated with LIX63

Our analysis of the SA trajectories shows that there are several coordination structures of the Co-LIX63 complexes. The appearance frequency of the Co-LIX63 complexes is classified in Table 1 according to the number of coordinated molecules and the coordination number. The coordination number is defined as the number of the atoms in the sphere of 0.30 nm radius centered on the metal ion, and the appearance frequency, $f_{ij}$, was calculated from:

$$f_{ij} = \frac{n_{ij}}{N_{\text{total}}}$$

where $n_{ij}$ is the number of the MD snapshots with the number of the coordinated molecules $i$ and the coordination number $j$, and $N_{\text{total}}$ is the total number of the snapshots. The 3-dimensional descriptions of the structure of the Co-LIX63 complexes are listed in Table 1. Despite water molecules being present in the system, the Co-LIX63 complex with the highest appearance frequency, that is, the most stable complex, contained only LIX63 molecules.

| System | Number of coordinated molecules a) | Coordination number | Appearance frequency | Geometry b) |
|--------|-----------------------------------|--------------------|----------------------|-------------|
| Co-LIX63 | 3 (3,0) | 5 | 0.60 | square pyramidal |
| | 3 (2,1) | 5 | 0.20 | square pyramidal |
| | 4 (2,2) | 5 | 0.10 | square pyramidal |
| | 4 (3,1) | 6 | 0.10 | octahedral |
| Mn-LIX63 | 4 (3,1) | 6 | 0.30 | octahedral |
| | 5 (4,1) | 6 | 0.20 | octahedral |
| | 5 (3,2) | 6 | 0.20 | octahedral |
| | 5 (2,3) | 6 | 0.20 | octahedral |
| | 5 (1,4) | 6 | 0.10 | octahedral |

a) $(m,n)$ represents the numbers of LIX63 and water molecules, respectively.

b) The square pyramidal geometry is distorted.
To define the 3-dimensional structures of the metal complexes, the angular distribution of ligands was calculated. Values are presented in Figure 2. Figure 2 (d) shows that the 6-coordinated structures of the Co complexes containing 3 LIX63 and 1 H2O molecules are pseudo-octahedral. When the coordinated H2O

Figure 2. Angular distribution of ligands in the complexes containing LIX63: (a) Co complex with 3 LIX63 and 0 H2O, (b) Co complex with 2 LIX63 and 1 H2O, (c) Co complex with 2 LIX63 and 2 H2O, (d) Co complex with 3 LIX63 and 1 H2O, (e) Mn complex with 3 LIX63 and 1 H2O, (f) Mn complex with 4 LIX63 and 1 H2O, (g) Mn complex with 3 LIX63 and 2 H2O, (h) Mn complex with 2 LIX63 and 3 H2O and (i) Mn complex with 1 LIX63 and 4 H2O.

To define the 3-dimensional structures of the metal complexes, the angular distribution of ligands was calculated. Values are presented in Figure 2. Figure 2 (d) shows that the 6-coordinated structures of the Co complexes containing 3 LIX63 and 1 H2O molecules are pseudo-octahedral. When the coordinated H2O
molecule is removed, the Co complexes become the 5-coordinate. The angular distribution of ligands of these structures is drawn in Figure 2 (a). The peak at 180° is broad and shifted, and the peak at 90° is broad. This suggests that these structures have distorted 5-coordinate geometries. The space where one H2O molecule was coordinated is occupied with the hydrocarbon groups of LIX63 ligand. Visual inspection of some of these 5-coordinated structures of the Co complexes suggests that they are distorted square pyramidal or approximately trigonal bipyramidal. On the other hand, the 5-coordinated structures in Figure 2 (b) and (c) have more nearly regular square pyramidal. The distortion of the 5-coordinated structures is mainly caused by the steric hindrance of the LIX63 hydrocarbon groups, but also might be a consequence of the inadequacy of the force field parameters used in the calculations.

In case of the 5-coordinated structures of the Co complexes, a few H2O molecules are found near the complexes of a few H2O ligands, though there are no H2O molecules near the complexes of no H2O ligands. The contribution of these H2O molecules around Co2+ to the stabilization of the Co complexes will be discussed later.

The structures of the Mn-LIX63 complexes are different from those of their Co analogues. Table 1 and Figure 2 (e-i) show that all of the Mn-LIX63 complexes are 6-coordinated and pseudo-octahedral. All contained the coordinated water molecule(s). This suggests that water molecules are important in contributing to their stabilization.

To examine the role of the water molecules, we compared results with those from our previous study where MD simulations with no water molecules were performed [20]. This comparison shows that the appearance frequency of 6-coordinated structures of the Mn complexes is increased by the presence of water molecules, indicating that the interaction of water molecules with Mn2+ and LIX63 enhances stability. However, though the frequency of the 5-coordinated structures in the Co systems with H2O is found to be greater, the most prevalent Co complex was one of no H2O ligands (see also Table 1). This suggests that the water molecules not coordinated to metal ions can also contribute to the stabilization of the complexes. In order to examine how H2O/H3O+ molecules not coordinated to the metal ion contribute to the stabilization of the metal complexes, we calculated the various radial distribution functions \( g(r) \) with \( r \) being the distance from the metal ion (Figure 3) and defined the positions of the molecules which were not coordinated to the metal ions.

From Figure 3 (a) and (b), the first peaks of \( g(r) \) indicate that the LIX63 and H2O were coordinated to Co2+ at \( r \sim 0.19 \) nm. It should be noted that there were one or two molecules of LIX63 and H2O/H3O+ at \( r \sim 0.4 \) nm, depicted by the second peak of \( g(r) \). The second peak at \( r \sim 0.4 \) nm in Figure 3 (a) represents one O atom of LIX63 of which another O atom was directly coordinated to Co2+ because the steric hindrance by the hydrocarbon chains of LIX63 ligands prevent other LIX63 molecules from being in this region. The second peaks at \( r \sim 0.4 \) and 0.5 nm in Figure 3 (b) show that H2O/H3O+ were hydrogen-bonded to H2O/H3O+ and LIX63, respectively (see also Figure 4). The second peaks in Figure 3 (b) are caused by the 5- and 6-coordinated structures of the Co-LIX63 complexes with the low appearance. Hydrogen bonding might contribute to the stabilization of the Co-LIX63 complexes, and this is similar to the second solvation shell in the bulk liquid.
Figure 3 (a) and (b) also show that LIX63 and H$_2$O/H$_3$O$^+$ molecules/ions were located less frequently in the ranges $r$ ~ 0.5 to 1.2 nm. This indicates that the Co-LIX63 complexes are surrounded by CHX molecules and the stability of the complex is enhanced by hydrophobic interactions with CHX molecules and the hydrocarbon groups of coordinated LIX63 molecules, leading the exclusion of H$_2$O/H$_3$O$^+$.

Figure 3 (d-f) shows values of $g(r)$ between the Mn$^{2+}$ and the O atoms of LIX63 and H$_2$O/H$_3$O$^+$ or C atoms of CHX. The first peaks of $g(r)$ in Figure 3 (a) and (d) indicate LIX63 molecules coordinated to Co$^{2+}$ at $r$ ~ 0.19 and Mn$^{2+}$ at $r$ ~ 0.20 nm, respectively. This difference corresponds to the difference of the ion radii. Figure 3 (d) and (e) give the numbers of the LIX63 and H$_2$O/H$_3$O$^+$ molecules in the range $r$ ~ 0.4 to 0.8 nm from the Mn$^{2+}$ ions. These molecules form the hydrogen bonds in a similar manner to those in the Co complex as shown in Figure 4, suggesting that these interactions help to compensate for the weaker coordination of LIX63 to the Mn$^{2+}$ ion.

Figure 3 (c) and (f) show that the positions of the first peak or shoulder of $g(r)$ are 0.55 and 1.07 nm in the Co-LIX63 and Mn-LIX63 systems, respectively. This clear difference in the positions indicates that
the CHX-excluded volume, that is, the effective size of the metal complex depends on the metal ion. We define the effective radius of the metal complex ($r_{\text{eff}}$, see below) as the position of the first peak or the shoulder of $g(r)$ with CHX.

### 3.2 Complexes coordinated with VA10

The appearance frequency distributions of the Co- and Mn-VA10 complexes are listed in Table 2. All these complexes have 6-coordinated pseudo-octahedral structures. In these systems, H$_2$O molecules are mainly coordinated to the metal ions and the number of coordinated VA10 molecules is 2 or less.

| System   | Number of coordinated molecules a) | Coordination number | Appearance frequency | Geometry   |
|----------|-----------------------------------|---------------------|----------------------|------------|
| Co-VA10  | 6 (0,6)                            | 6                   | 0.50                 | octahedral |
|          | 6 (1,5)                            | 6                   | 0.30                 | octahedral |
|          | 6 (2,4)                            | 6                   | 0.20                 | octahedral |
| Mn-VA10  | 6 (0,6)                            | 6                   | 0.60                 | octahedral |
|          | 6 (1,5)                            | 6                   | 0.30                 | octahedral |
|          | 6 (2,4)                            | 6                   | 0.10                 | octahedral |

a) $(m,n)$ represents the numbers of VA10 and H$_2$O molecules, respectively.

It should be noted that the coordination of H$_2$O depends on extractant molecules. More H$_2$O molecules are coordinated to the metal ions in the VA10 system, than in system with just LIX63. Because the metal complex of H$_2$O ligands in organic solvent is unstable, we investigated the surroundings of the metal complex.

Figure 5 depicts the radial distribution function, $g(r)$. It is found that 6 water molecules are coordinated to Co$^{2+}$ or Mn$^{2+}$ at $r \sim 0.2$ nm (see also Figure 6). The values of the mean coordination numbers, $N(r)$, of O atoms of VA10 and H$_2$O are higher in the range $r \sim 0.4$ to 1.0 nm. Approximately 7 VA10 molecules are found when $r < 1.0$ nm. This indicates that the metal ions are surrounded with VA10
molecules outside $r \sim 0.4$ nm (Figure 6) and this surrounding may stabilize the metal complexes. The difference of the stabilization mechanism seems to be one of the reasons for the dependence of the extract efficiency and the time for extraction on the species of extractants and metal ions.

The effective radius of the metal complex, $r_{\text{eff}}$, was estimated from the $g(r)$ values in Figure 5(c) and (f). The values of $r_{\text{eff}}$ in the Co-VA10 and Mn-VA10 system are 0.71 nm and 0.57 nm, respectively. It should be noted that, in the VA10-only system, $r_{\text{eff}}$ for Mn$^{2+}$ is shorter than for Co$^{2+}$, but in the LIX63-only system, $r_{\text{eff}}$ for Co$^{2+}$ is shorter than for Mn$^{2+}$. This relationship is consistent with the efficiency tendency reported by experiments [6].

Figure 5. Radial distribution function, $g(r)$, plots between: (a) Co$^{2+}$ and O atoms in VA10, (b) Co$^{2+}$ and O atoms in H$_2$O, (c) Co$^{2+}$ and C atoms in CHX, (d) Mn$^{2+}$ and O atoms in VA10, (e) Mn$^{2+}$ and O atoms in H$_2$O, and (f) Mn$^{2+}$ and C atoms in CHX. Solid and dashed lines represent $g(r)$ and the mean coordination number, $N(r)$, respectively.
3.3 Complexes coordinated with LIX63 and VA10

The appearance frequencies of the Co-(LIX63+VA10) complex are listed in Table 3. LIX63 molecules were mainly coordinated to Co\(^{2+}\). It is noteworthy that all of the complexes contain no VA10 molecules coordinated to Co\(^{2+}\). This suggests that VA10’s role is in controlling the environment around the Co complexes (see below).

Table 3. Properties of the Co- and Mn-(LIX63+VA10) complexes.

| System          | Number of coordinated molecules \((l,m,n)\) | Coordination number | Appearance frequency | Geometry b) |
|-----------------|---------------------------------------------|---------------------|----------------------|-------------|
| Co-(LIX63+VA10) | 5 (2,0,3)                                   | 6                   | 0.22                 | octahedral  |
|                 | 4 (2,0,2)                                   | 6                   | 0.22                 | octahedral  |
|                 | 4 (3,0,1)                                   | 6                   | 0.34                 | octahedral  |
|                 | 3 (2,0,1)                                   | 5                   | 0.22                 | square pyramidal |
| Mn-(LIX63+VA10) | 3 (3,0,1)                                   | 6                   | 0.89                 | octahedral  |
|                 | 3 (3,0,0)                                   | 6                   | 0.11                 | octahedral  |

a) \((l,m,n)\) represents the numbers of LIX63, VA10 and water molecules, respectively.
b) The square pyramidal geometry is distorted.

To examine the 3-dimensional structures of the Co-(LIX63+VA10) complexes, the angular distribution of the ligands was calculated. Figure 7 (a-c) indicates that the 6-coordinated structures are present in the stable complexes. However, Figure 7 (d) indicates that the 5-coordinated complexes can have square pyramidal geometries and the widths of the peaks at 90° and 180° suggests that these complexes are distorted.

The Mn-(LIX63+VA10) complexes have the two structures shown in Table 3. They are pseudo-octahedral (see also Figure 7 (e) and (f)) and contain 3 LIX63 molecules coordinated to Mn\(^{2+}\). In
comparison with the LIX63-only system, the appearance frequency of the complexes coordinated with H2O is decreased and LIX63 were mainly coordinated to Mn2+. This suggests that VA10 stabilizes the Mn complexes by excluding H2O around the metal ions.

In comparison with the LIX63-only system, the first peaks of \(g(r)\) with O atoms of LIX63 and H2O molecules are left-shifted, and their values are greater (see also Figure 3(a) and (d), and 8(a) and (e)). This indicates that the complexes with LIX63 and VA10 are more stable than ones with LIX63-only. Also, for the Co complexes, O atoms of not only H2O/H3O+ molecules, but also VA10 are found at \(r \sim 0.5\) nm. The VA10 molecules are hydrogen-bonded to the ligands which enhances the hydrophobic interactions with CHX solvent (see Figure 9). The hydrogen bonding and the hydrophobic interactions of VA10 in the systems with LIX63 and VA10 are likely to make the complexes more stable. Although it is difficult to estimate the hydrophobic interaction energy, the qualitative order: coordination energy > hydrogen bond energy > hydrophobic interaction energy usually applies and consequently, in these systems, hydrogen bonding is likely to enhance extraction efficiency more than the hydrophobic interaction.

Figure 7. Angular distributions of ligands in LIX63+VA10 complexes. (a) Co complexes with 2 LIX63, 0 VA10 and 3 H2O, (b) Co complexes with 2 LIX63, 0 VA10 and 2 H2O, (c) Co complexes with 3 LIX63, 0 VA10 and 1 H2O, (d) Co complexes with 2 LIX63, 0 VA10 and 1 H2O, (e) Mn complexes with 3 LIX63, 0 VA10 and 1 H2O, (f) Mn complexes with 3 LIX63, 0 VA10 and 0 H2O.
The synergistic effect is caused by excluding water molecules around the metal complex. The radial distribution functions in Figure 8 show that LIX63 molecules, not VA10 and H2O molecules, are mainly coordinated to Co2+ or Mn2+. In both Co and Mn systems, LIX63 molecules were mainly found in the range with \( r < 0.5 \) nm and \( r > 1.5 \) nm. However, the \( g(r) \)'s of VA10 and H2O/H3O+ in the Co-(LIX63+VA10) system are different from those in the Mn-(LIX63+VA10) system. Peaks at \( r \sim 0.4 \) nm are found in the Co-(LIX63+VA10) system (shown in Figure 8 (b) and (c)), but not in the Mn-(LIX63+VA10) system (shown in Figure 8 (f) and (g)). This difference shows that the hydrogen bonding might contribute to the

Figure 8. Radial distribution function, \( g(r) \), plots between: (a) Co\(^{2+}\) and O atoms of LIX63, (b) Co\(^{2+}\) and O atoms of VA10, (c) Co\(^{2+}\) and O atoms of H\(_2\)O/H\(_3\)O\(^+\), (d) Co\(^{2+}\) and C atoms of CHX, (e) Mn\(^{2+}\) and O atoms of LIX63, (f) Mn\(^{2+}\) and O atoms of VA10, (g) Mn\(^{2+}\) and O atoms of H\(_2\)O/H\(_3\)O\(^+\), and (h) Mn\(^{2+}\) and C atoms of CHX. Solid and dashed lines represent \( g(r) \) and the mean coordination number, \( N(r) \), respectively.

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stabilization of the Co complex. However, H₂O/H₃O⁺ molecules cannot be found in the metal complex assembly between \( r \sim 0.8 \) and 1.5 nm, although VA10 molecules are found in this region. This indicates that H₂O/H₃O⁺ molecules were excluded by VA10. This exclusion might enhance the hydrophobic interactions between VA10 and LIX63 in the assembly, complementing the hydrogen bonding in the Co system. It seems that the combination of LIX63 and CHX does not exclude H₂O/H₃O⁺ molecules because additional LIX63 molecules are found in the range with \( r > 1.5 \) nm in the LIX63-only system. In spite of this difference in the mode of stabilization, the mixture of LIX63 and VA10 has a higher appearance frequency of the 6-coordinated complexes (see Table 3).

The structures of the Co- and Mn-(LIX63+VA10) complexes calculated in our SA simulations are not in agreement with the Ni complex formed by 5-hydroxy-4-octanone oxime (as an analogue of LIX63) and iso-propionic acid (as an analogue of VA10) [21]. This inconsistency might be due to the different length of hydrocarbon groups of these ligands. The smaller steric hindrance in the model complexes may cause the complexes to be stable. As mentioned above, the nature of the hydrocarbon groups and water molecules located at \( \sim 0.4 \) nm has an effect on the stabilization of the metal complex in the organic solvent. Our observation shows the importance of the water molecules located at \( \sim 0.4 \) nm.

The effective radius, \( r_{\text{eff}} \), of the Co and Mn complexes in the systems with LIX63 and VA10 are 0.53 nm and 0.55 nm, respectively. This difference is consistent with that of the efficiency for extraction of the two metal ions using either single or mixed extractants and indicates that \( r_{\text{eff}} \) values are useful in predicting relative extraction efficiencies and metal ion selectivities, i.e. screening combinations of potential extractants. In general, to do this, lots of knowledge about the chemistry of metal ions and the propeties of extractants is needed and the appropriate experimenal measurements sometime are time-consuming. On the other hand, selection using \( r_{\text{eff}} \) values could prove to be more efficient and effective.

In our simulations, only phenomena in the water-immiscible solvent have been considered. As solvent extraction involves two immiscible phases and it is also necessary to consider the effects of the interface between the phases. Such effects are being examined and will be reported elsewhere.
4. Conclusion

We have investigated the structures of Co(II) or Mn(II) complexes with LIX63 and/or VA10 extractants and the positions of uncoordinated water molecules using SA calculations. The Co and Mn complexes with LIX63 or VA10 contain a few water molecules located at ~0.4 nm from the metal ions. These water molecules are hydrogen-bonded to the LIX63/VA10 and water molecules coordinated to the metal ions. These hydrogen bonds might contribute to the stability of the complexes. In solvent extraction of Co and Mn using mixed LIX63 and VA10 extractants, the stabilization of the metal complexes is enhanced by the exclusion of the water molecules and the replacement of H₂O with VA10.

The effective radius, $r_{\text{eff}}$, calculated from the first peak or shoulder of $g(r)$ of C atoms of CHX correlates with experimentally observed extraction efficiency. The dependence of $r_{\text{eff}}$ on the nature of metal ions and the extractants shows that coordination energies and hydrophobic interactions play important roles in determining the extraction efficiency. Consequently, we could use $r_{\text{eff}}$ to predict relative extraction efficiencies and metal ion selectivities.

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