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A Novel Extractant Based on *D*-Glucosamine for the Extraction of Molybdenum and Tungsten

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A novel *D*-glucosamine based extractant, 2-deoxy-2-aminio-1,3,4,6-tetra-O-decanoyl-*D*-glucopyranose, has been synthesized and employed for the extraction of Mo(VI) and W(VI) in chloride, nitrate, and sulphate media using a mixture of toluene and 1-octanol as the diluent. At low pH, W(VI) is selectively extracted, while Mo(VI) is poorly extracted with this extractant. Little extraction of both metals takes place at high pH. The extraction is affected by the coexisting inorganic anions, Cl^-, NO_3^-, and SO_4^{2-}. The selectivity for W(VI) against Mo(VI) is the result of steric hindrance caused by the bulky alkyl chain covered the amine ligand site, compared with commercial amine type extractants, TOA and Primene JM-T.

1. Introduction

A large number of extractants have been developed from the viewpoint of separation of metal values and/or removal of toxic metals from waste water. Extractants based on biomolecules, such as chitosan and chitin have become quite attractive in recent years, and the extractants have been demonstrated to have unique behaviors in metal extraction [1], though there are few reports of biomolecule-based extractants for metals extraction. One of the biomolecules, having the potential as the framework for an extractant, is *D*-glucosamine which is shown in Fig. 1. *D*-Glucosamine is a type of amino sugar, and is widely used in health foods while the monomer unit of chitosan has an anion-exchangeable primary amino group. In addition, *D*-glucosamine can be easily lipophilized by introducing long-chain alkyl groups to its hydroxyl groups and a *D*-Glucosamine-based extractant consisting of carbon, hydrogen, oxygen, and nitrogen atoms would be completely combustible.

Anion exchange extractants have generally high extractability for anionic metal complexes, such as molybdenum, tungsten, and vanadium. Many studies of the anion exchange extraction of these metals have been conducted with Primene JM-T (primary amine) [2], diisododecylamine (DIDA, secondary amine) [3], Alamine336 (tertiary amine) [4], and TOMAC (quaternary ammonium salt) [5].

In the present work, a novel extractant, 2-deoxy-2-aminio-1, 3,4,6-tetra-O-decanoy-*D*-glucopyranose (C9GLN), has been synthesized from *D*-glucosamine as the extractant for the anionic forms of Mo(VI) and W(VI). The extraction behavior of these metals was investigated in conventional batch extraction tests. The effect of the aqueous media on the extraction behavior of Mo(VI) and W(VI) was also investigated. The extraction and separation ability of the extractant is compared with commercial amine type extractant, and the potential of the new extractant is discussed.

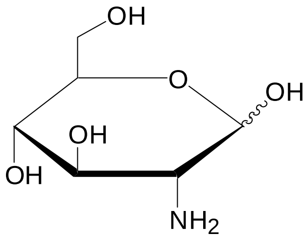


Fig.1 Chemical structure of *D*-glucosamine.

2. Experimental

2.1 Materials

D-Glucosamine hydrochloride, *n*-decanoic anhydride, and 4-dimethylaminopyridine were supplied by Tokyo Chemical Industry Co., Ltd. Pyridine, *p*-anisaldehyde, all inorganic reagents, and organic solvents were supplied by Wako Pure Chemical Industries. Commercial extractants, tri-*n*-octylamine (TOA) and Primene JM-T (mixture of highly branched C_{16} to C_{22} tertiary alkyl primary amine isomers) were supplied by Wako Pure Chemical Industries and Rohm and Hass Company, respectively. These extractants were used without further purification.

2.2 Synthesis of the extractant

The extractant was synthesized according to the procedures reported by Silva *et al.*, as shown in Scheme 1 [6].

2-*p*-Methoxybenzylideneamino-*D*-glucosamine (1)

D-Glucosamine hydrochloride (20.0 g, 92.8 mmol) was dissolved in 100 mL of 1 mol/L sodium hydroxide solution, and *p*-methoxybenzaldehyde (13.1 g, 95.9 mmol, 1.0 eq.) was slowly added to the solution in an ice bath under a nitrogen atmosphere. The mixture was stirred vigorously for 12 h. The resulting white solid was collected by filtration, and then was washed with deionized water and mixture of methanol and diethyl ether. The white solid was dried *in vacuo* overnight (19.5 g, 70.5 % yield). The product was identified by ^{1}H-NMR spectrometry (JEOL, JMM-ECP500). ^{1}H-NMR (500 MHz, DMSO-d6) δ 8.11 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.52 (d, J = 6.9 Hz, 1H), 4.92 (d, J = 5.0 Hz, 1H), 4.81 (d, J = 6.0 Hz, 1H), 4.69 (t, J = 7.1 Hz, 1H), 4.54 (t, J = 6.0 Hz, 1H), 3.80 (s, 3H), 3.72 (m, 1H), 3.44 (m, 1H), 3.24–3.14 (m, 2H), 2.79 ppm (t, J = 8.5 Hz, 1H). An elemental analysis (YANACO, MT-6 Corder) was carried out as: found C, 56.33, H, 6.36, N, 4.51 %, calculated for $C_{14}H_{19}NO_6$: C, 56.56, H, 6.44, N, 4.71 %.

2-Deoxy-2-*p*-methoxybenzylimideneaminio-1,3,4,6-tetra-O-decanoyl-*D*-glucopyranose (2)

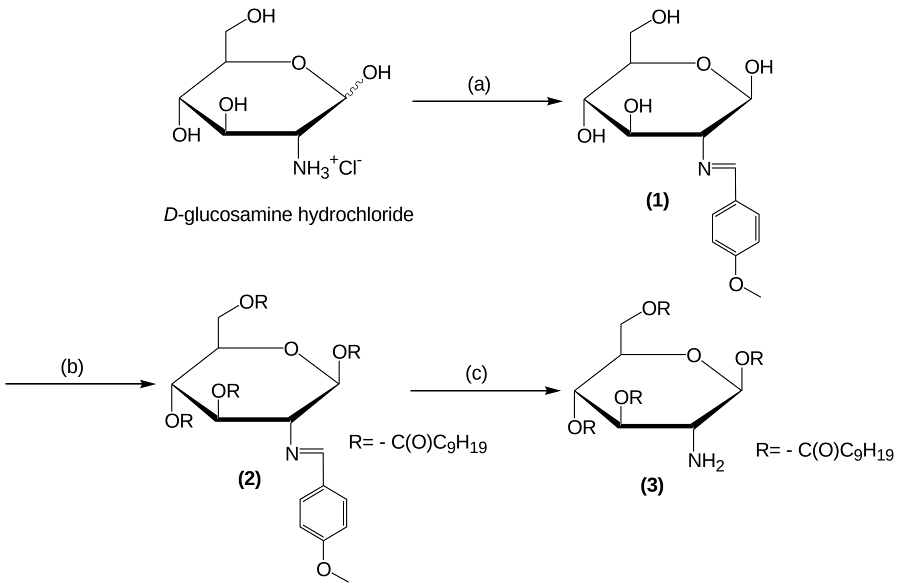
The product **1** (1.0 g, 3.36 mmol) was suspended in pyridine (10.5 g, 133 mmol, 39.5 eq.), and *n*-decanoic anhydride (5.49 g, 16.8 mmol, 5.0 eq.) and 4-dimethylaminopyridine (0.05 g, catalyst quantity) were slowly added to the suspension in an ice bath under a nitrogen atmosphere. The mixture was stirred at room temperature, followed by the dissolution of the suspension, for more than 12 h, and then the solution was poured into deionized water. Ethyl acetate was added to the resulting solution to extract the organic product. The organic solution was washed with saturated sodium chloride solution and deionized water, and then was dried with anhydrous magnesium sulfate. After filtration, the solvent was evaporated and the resulting solid dried *in vacuo*. This product was used in the final step without purification.

2-Deoxy-2-aminio-1,3,4,6-tetra-O-decanoyl-*D*-glucopyranose (3), C9GLN

The crude product **2** was dissolved in 80 mL of acetone, and the solution was slowly added to 0.6 mL of 6 mol/L hydrochloric acid solution in an ice bath. The mixture was stirred for more than 12 h at room temperature. The resulting white gel was filtered and washed with acetone. The crude product was dried *in vacuo* overnight. The white solid was dissolved in toluene, and then was contacted with a 28 % ammonia solution to liberate the amino group. The mixture was stirred for more than 3 h. The organic layer was collected and washed with deionized water. The organic solution was dried with anhydrous magnesium sulfate. After filtration, the solvent was evaporated and the resulting solid dried *in vacuo* to obtain a white powder (1.86 g, 69.4 % yield). The product was identified by ^{1}H-NMR spectrometry and FT-IR spectrometry (SHIMADZU, FTIR-8400S). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.46 (d, J = 8.7 Hz, 1H), 5.04 (m, 2H), 4.25 (dd, J = 4.58 Hz, 1H), 4.09 (dd, J = 1.8 Hz, 1H), 3.82 (m, 1H), 3.00 (t, J = 9.4 Hz, 1H), 2.42-2.19 (m, 8H), 1.68-1.53 (m, 8H), 1.26 (br, 48H), 1.14 (s, 2H), 0.88 ppm (t, J = 6.8 Hz, 12H); FT-IR (KBr) 3387, 3317, 2960, 2926, 2860, 1738, 1607, 1292, 1178 cm^{-1}. The elemental analysis was as follows: found: C, 69.04, H, 10.69, N, 1.98 %, calculated for $C_{46}H_{85}NO_9$: C, 69.39, H, 10.76, N, 1.76 %.

2.3 Extraction procedure

Organic solutions were prepared by dissolving the extractant in a mixture of 95 wt% of toluene and 5 wt% of 1-octanol. 1-Octanol was added as a modifier in order to improve the solubility of the extractant in toluene as well as to prevent third-phase formation during extraction. Aqueous feed solutions of Mo(VI) and W(VI) were prepared by dissolving $Na_2MoO_4 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$ in deionized water, respectivery. The aqueous media (Cl^-, NO_3^-, and SO_4^{2-}) and anion concentration were controlled by adding appropriate amounts of NaCl, $NaNO_3$, and Na_2SO_4, respectively. The pH was adjusted by adding the appropriate amount of inorganic acids (HCl, HNO_3, and H_2SO_4) or sodium hydroxide solution to the aqueous solution. Feed solutions of the cationic metals (Ni^{2+}, Co^{2+} and Cu^{2+}) were also prepared for investigating the selectivity of the extractant. In this case metal, chlorides, nitrates, and sulfates were dissolved in deionized water, and the concentration of anions (Cl^-, NO_3^-, and SO_4^{2-}) and the pH values were adjusted in the same manner as for Mo(VI) and W(VI). Equal volumes of the aqueous and organic solutions were shaken vigorously at 298 K for more than 12 h to attain equilibrium. After phase separation, the equilibrium pH value was measured using a pH meter (HORIBA, F-23). The concentration of metal ions and anions were analyzed by means of an inductively coupled plasma atomic emission spectrometer (ICP-AES; SHIMADZU, ICPS-7000) and an ion chromatography (Metrohm, Compact IC 761 type), respectively. The concentrations in organic solutions were calculated from the material valance.



Scheme 1 Synthetic route for the present extractant; (a) *p*-methoxybenzaldehyde, 1 mol/L NaOH, (b) *n*-decanoic anhydride, 4-dimethylaminopyridine, pyridine, (c) (i) 6 mol/L HCl, acetone, (ii) 28 % NH_3, toluene (two steps).

3. Results and Discussion

3.1 Extraction equilibria of molybdenum and tungsten in single systems

Figure 2 shows the effect of equilibrium pH values on the percentage extraction of Mo(VI) and W(VI) in chloride, nitrate, and sulfate media with C9GLN. W(VI) is effectively extracted at low pH, while Mo(VI) is only poorly extracted. At pH >6, both metals are hardly extracted at all. Figure 3 shows the dissociation behavior of *D*-glucosamine [7]. If the pK_a value of the amino group is assumed not to be affected by the introduction of decanoyl groups into the hydroxyl groups, the extractant forms the ammonium salt of inorganic anions ($R\text{-}NH_3^+A^-$ for chloride and nitrate media or $(R\text{-}NH_3^+)_2SO_4^{2-}$ for sulphate medium, R is glucosamine matrix) at low pH. The extraction behavior is therefore concluded to be affected by the species of the extractant.

Mo(VI) mainly exists as MoO_4^{2-} in alkaline aqueous solution, and forms several oxoanion species even at pH values < 6, e.g., $HMoO_4^-$, H_2MoO_4, $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, and MoO_2^{2+} [8]. Alternatively, W(VI) is mainly present as WO_4^{2-} in alkaline aqueous solution, and also forms several oxoanion species in weakly acidic aqueous solution, e.g., HWO_4^-, H_2WO_4, $W_6O_{21}^{6-}$, $HW_6O_{21}^{5-}$, and

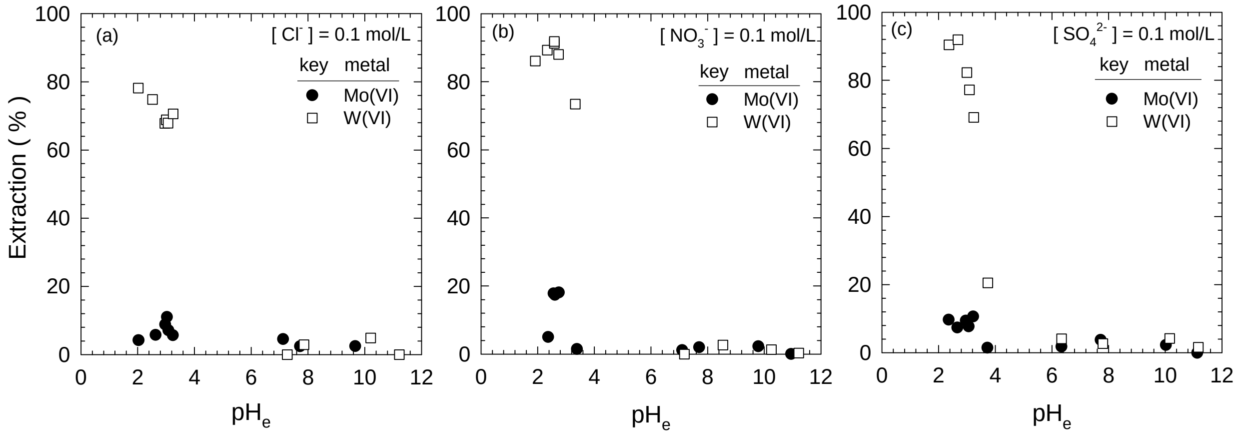


Fig. 2 The effect of equilibrium pH on the percentage extraction of Mo(VI) and W(VI) in (a) chloride, (b) nitrate, and (c) sulfate media; [M] = 1.0×10^{-4} mol/L, $\overline{[\text{extractant}]}$ = 1.0×10^{-2} mol/L.

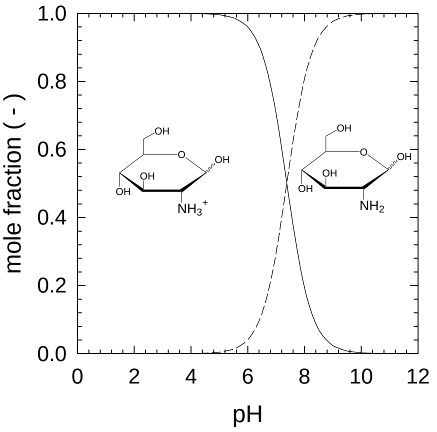


Fig. 3 Distribution diagram for species of *D*-glucosamine as a function of pH (pK_a = 7.38).

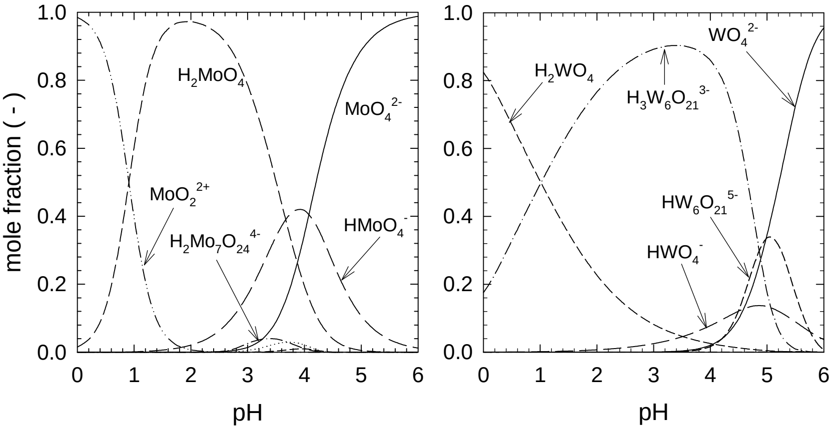


Fig. 4 The mole variation of Mo(VI) and W(VI) species in aqueous solution, [M] = 1.0×10^{-4} mol/L.

$H_3W_6O_{21}^{3-}$ [8]. Figure 4 shows the speciation of Mo(VI) and W(VI) in aqueous solution. The distribution diagrams of Mo(VI) and W(VI) were calculated from stability constants [8]. Comparing the extraction behavior and the species fractions of the metals in aqueous solution, the predominant extracted species for Mo(VI) and W(VI) are suggested as $HMoO_4^-$ and $H_3W_6O_{21}^{3-}$, respectively. The lower extraction extent of Mo(VI) is due to the coexistence of cationic and neutral species. A mutual separation between Mo(VI) and W(VI) with C9GLN is therefore expected to be achieved in acidic aqueous solution.

Figures 5 and 6 show the effects of the concentrations of coexistent inorganic anions, Cl^-, NO_3^-, and SO_4^{2-}, on the percentage extraction of Mo(VI) and W(VI) with C9GLN, respectively. The extraction percentage of both metals was decreased with increasing concentration of the coexistent anions in the aqueous solution. This indicates that the anion exchange reactions between the counter anions of the ammonium salt and the oxoanions of Mo(VI) and W(VI) are suppressed by the excess amounts of inorganic anions in the aqueous solution. The order of extraction efficiency becomes less in the order of $SO_4^{2-} > NO_3^- > Cl^-$. Figure 7 shows the extraction isotherms for the inorganic acids, HCl, HNO_3 and H_2SO_4 with C9GLN. The extractability of the inorganic acids becomes greater in the order of HCl > HNO_3 > H_2SO_4, which agrees with the decreasing trend of extractability of the metals. This suggests that C9GLN initially reacts with the inorganic acid to form the ammonium salt, and then the oxoanions are extracted via competitive anion exchange with the counter anions. The proposed extraction equilibria of W(VI) from aqueous chloride, nitrate, and sulphate solution are therefore defined as follows.

$$n\overline{\mathrm{RNH_2}} + \mathrm{H}_n\mathrm{A} \leftrightarrow \overline{(\mathrm{RNH_3}^{+})_n\mathrm{A}^{n-}} \qquad (1)$$

$$\overline{(\mathrm{RNH_3}^{+})_n\mathrm{A}^{n-}} + n\mathrm{HMoO_4}^{-} \leftrightarrow \overline{(\mathrm{RNH_3}^{+})_n(\mathrm{HMoO_4}^{-})_n} + \mathrm{A}^{n-} \qquad (2)$$

$$3\,\overline{(\mathrm{RNH_3}^{+})_n\mathrm{A}^{n-}} + n\,\mathrm{H_3W_6O_{21}}^{3-} \leftrightarrow \overline{(\mathrm{RNH_3}^{+})_{3n}(\mathrm{H_3W_6O_{21}}^{3-})_n} + 3\mathrm{A}^{n-} \qquad (3)$$

where, RNH_2 and A^{n-} represents the extractant and the inorganic anions ($n = 1$ for Cl^-, NO_3^-, and $n = 2$ for SO_4^{2-}).

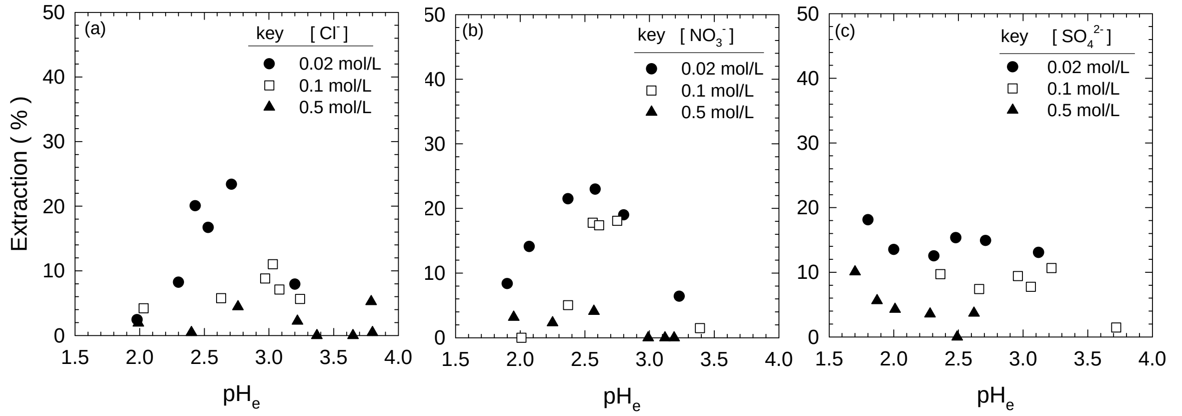


Fig. 5 The effect of concentration of coexisting inorganic anions on the percentage extraction of Mo(VI) in (a) chloride, (b) nitrate, and (c) sulphate media, $\overline{[\text{extractant}]} = 1.0\times10^{-2}$ mol/L.

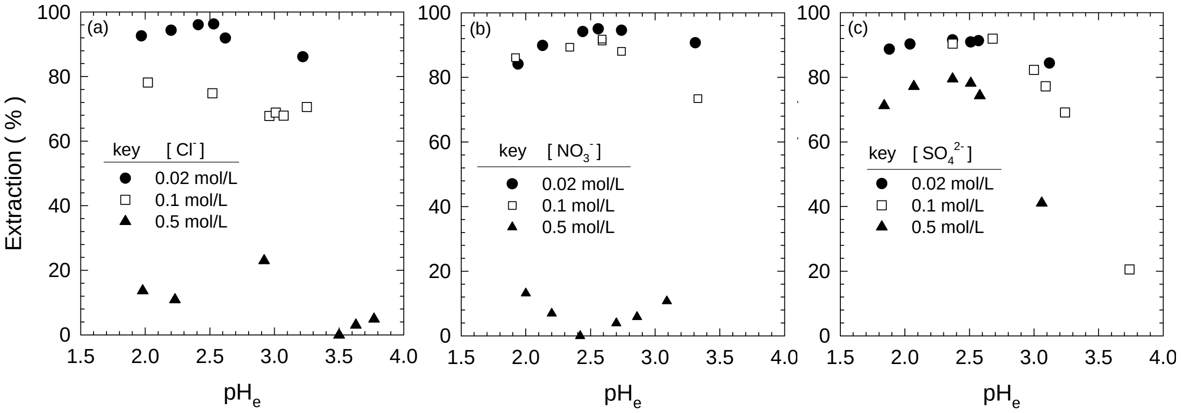


Fig. 6 The effect of concentration of coexisting inorganic anions on the percentage extraction of W(VI) in (a) chloride, (b) nitrate, and (c) sulphate media, $\overline{[\text{extractant}]} = 1.0\times10^{-2}$ mol/L.

Figure 8 shows the extraction behavior of cationic metals, Ni(II), Co(II) and Cu(II) with C9GLN in chloride, nitrate, and sulphate media, respectively. These cations were not extracted in any of the extraction systems, demonstrating that the present extractant has a high selectivity for oxoanions.

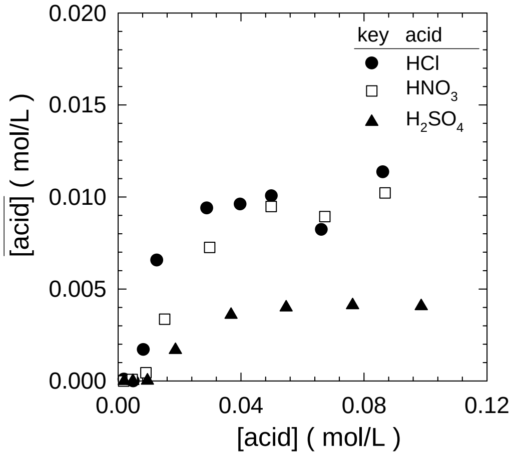


Fig. 7 The extraction isotherms of the inorganic acids, HCl, HNO_3, and H_2SO_4, with C9GLN, $\overline{[\text{extractant}]}$ = 1.0×10^{-2} mol/L.

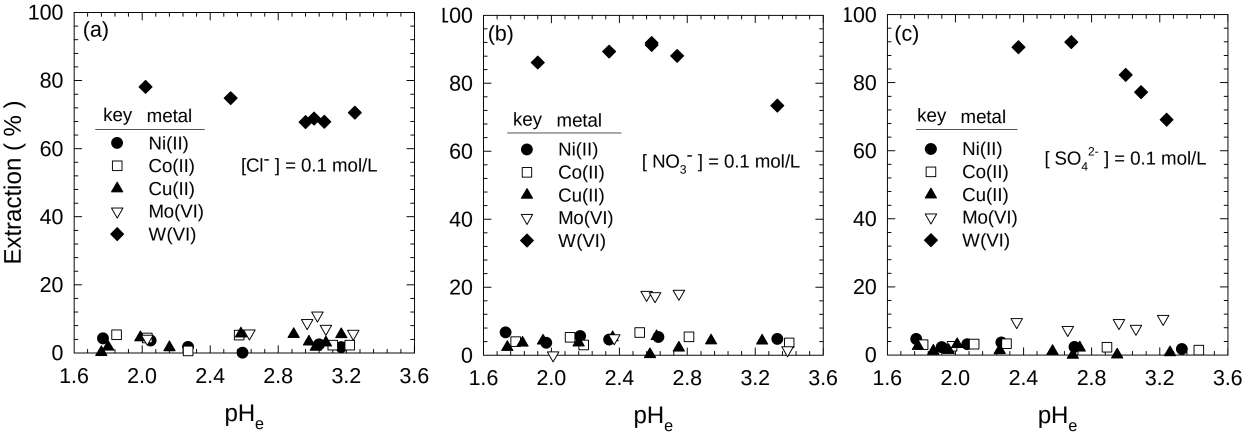


Fig. 8 The extraction behavior of cationic metals, Ni(II), Co(II), and Cu(II), with C9GLN in (a) chloride, (b) nitrate, and (c) sulphate media, $\overline{[\text{extractant}]}$ = 1.0×10^{-2} mol/L.

3.2 Stripping of molybdenum and tungsten

Table 1 lists the stripping yield of Mo(VI) and W(VI) with several reagents. Both metals were effectively stripped with sodium chloride solution, suggesting that the extracted anionic species were exchanged by an excess amount of chloride ion. The extracted W(VI) was also quantitatively stripped with sodium hydroxide solutions, because the ammonium salt in the organic phase was transformed to the free amine by the aqueous alkaline solution.

Table 1 Stripping tests for Mo(VI) and W(VI)

Stripping reagent	Concentration (mol/L)	Stripping (%)	
		Mo(VI)	W(VI)
water	-	30.4	31.8
H_2SO_4	0.5	13.8	3.66
H_2SO_4	1.0	10.9	4.56
NaCl	0.1	44.1	63.5
NaCl	0.5	82.9	78.6
NH_3	0.15	92.5	79.2
NH_3	0.3	69.0	80.5
NH_3	1.5	68.1	88.2
NaOH	0.1	56.0	94.6
NaOH	0.5	55.7	96.5
NaOH	1.0	54.4	98.7

3.3 Comparison of extraction performance with commercial extractants

Figure 9 shows the effect of pH on the percentage extraction of Mo(VI) and W(VI) in sulphate medium with C9GLN, Primene JM-T and TOA. Although the commercial extractants have higher extractability for both Mo(VI) and W(VI) than C9GLN, the separation ability for the metals with C9GLN is superior to the commercial extractants. The amino group in C9GLN is shielded by bulky alkyl side chains compared with the commercial extractants as shown in Fig. 10. Since the alkyl groups may interfere with the approach of large oxoanions to the amino group, C9GLN therefore possesses selective extractability for W(VI).

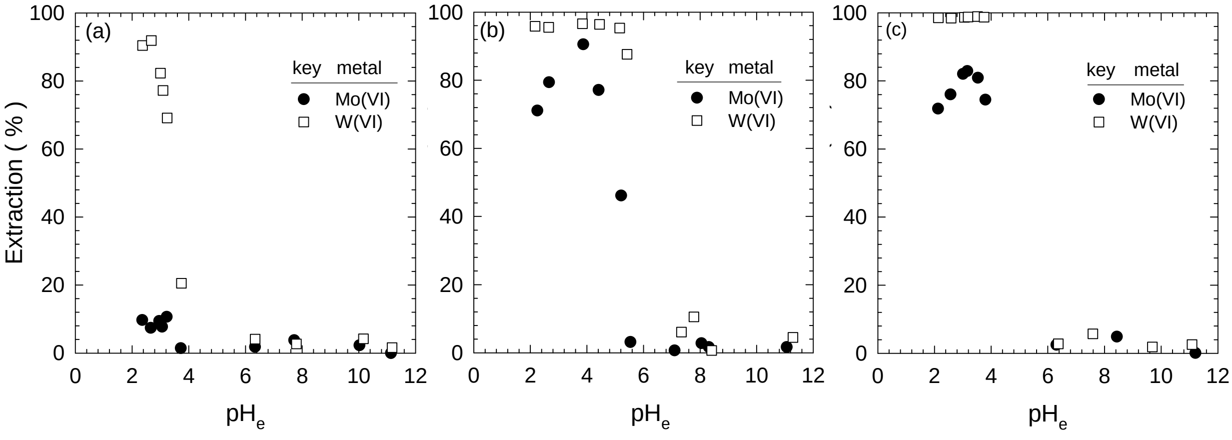


Fig. 9 The effect of pH on the percentage extraction of Mo(VI) and W(VI) in sulphate medium with (a) C9GLN, (b) Primene JM-T, and (c) TOA, $\overline{[\text{extractant}]}$ = 1.0×10^{-2} mol/L, $[SO_4^{2-}]$ = 0.1 mol/L.

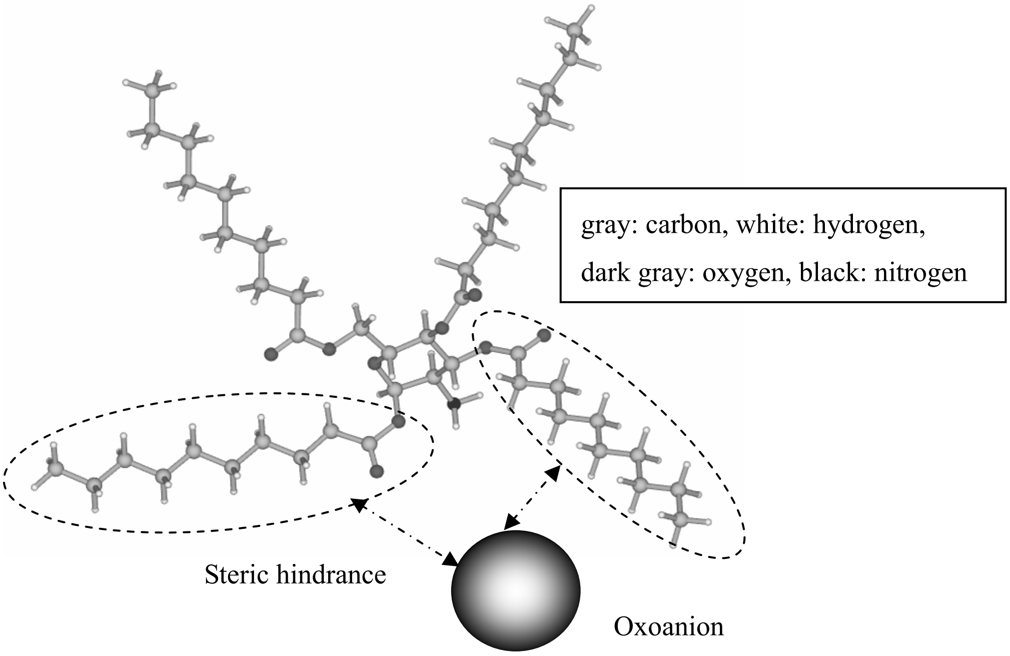


Fig. 10 The effect of steric hindrance in C9GLN on the anion exchange reaction.

4. Conclusion

The extraction behavior of Mo(VI) and W(VI) with 2-deoxy-2-aminio-1,3,4,6-tetra-O-decanoyl *D*-glucopyranose (C9GLN) has been investigated, with the following results. W(VI) is effectively extracted at low pH, while Mo(VI) is poorly extracted. At high pH values, the extraction of both metals is very few. The extraction of the metals is affected by coexisting inorganic anions, Cl^-, NO_3^-, and SO_4^{2-}, due to the competitive extraction between the inorganic anions and the anionic species of the metals. Since the separation ability for the metals shown by C9GLN is greater than those of the commercial extractants, C9GLN is thus concluded to have a good potential as an extractant for the separation of these anionic metal ions.

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