**Synergism of thiocyanate ions and microinterfacial surface as driving forces for heavy multi-metals extraction**

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Supporting Information

Abbreviation list:

W = water

W/Ac = water:acetone 1:1 (w:w)

BuOAc = Butyl Acetate

B30 0.3 mM = Brij 30 0.3mM aqueous solution

B30 1 mM = Brij 30 1 mM aqueous solution

mE = microemulsion

The cobalt nitrate hexahydrate dissolved in different solvents (S. 1a) is described as hexaaquacobalt(II) nitrate, [Co(H2O)6](NO3)2, as it consists of discrete [Co(H2O)6]2+ and [NO3]- ions. The cobalt ion has the oxidation state of +2, and it is a *d7* ion. From the high-spin (left) side of the *d7* Tanabe–Sugano (T-S) diagram, the ground state is 4T1g(4F), and the spin multiplicity is a quartet. The diagram shows that there are three quartet excited states: 4T2g, 4A2g, and 4T1g(4P). From the diagram one can predict that there are three spin-allowed transitions. However, the spectra of [Co(H2O)6]2+ does not show three distinct peaks that correspond to the three predicted excited states. Instead, the spectrum has a broad peak at around 510 nm. Based on the T-S diagram, the lowest energy transition is 4T1g to 4T2g, which is seen in the near IR and is not observed in the visible spectrum. The main peak corresponds to the energy transition 4T1g(4F) to 4T1g(4P) and the slightly higher energy transition (the shoulder) is predicted to be 4T1g(4F) to 4A2(4F). The small energy difference leads to the overlap of the two peaks, which explains the broad peak observed in the visible spectrum.

 The electronic spectra of cobalt thiocyanate complex (S. 1b) show that in a less polar solvent, the Co2+ ions occupy tetrahedral (*Td*) symmetry sites leading to the formation of [Co(SCN)4]2-. Tetrahedral Co2+ has the same energy level scheme as Cr3+ ion in octahedral symmetry. From T-S diagram, the ground state is a non-degenerated 4A2, and the spin multiplicity is a quartet. The visible ground-state absorption band centered at 623 nm is assigned to the spin- and electric-dipole-allowed 4A2 → 4T1(4P) transition, while the shoulder observed at 586 nm can be assigned to one of the doublet levels arising from the 2G free-ion level. The big difference between the very intense *d*-*d* bands in the blue *Td* complex [Co(SCN)4]2-, compared with the much weaker band in the pink octahedral complex [Co(H2O)6]2+ arises because the *Td* complex has no center of symetry, helping to overcome the g ↛ g Laporte selection rule.

S. 1. The electronic spectra of a) cobalt nitrate and b) cobalt thiocyanate complex in different media

The relatively complicated formula [Cr(H2O)6](NO3)3·3H2O typifies hydrated metal salt (S 2a). The chromium centers are bound to six water ligands and the remaining volume of the solid is occupied by three nitrate anions and three molecules of water of crystallization. The T-S diagram for octahedral *d3* shows that the ground state is 4A2g and the spin multiplicity is a quartet. From the diagram one can observe that there are three spin-allowed transitions. The two energy transitions observed in the visible domain of experimental spectra are 4A2g to 4T2g, which is assigned to the band at 576 nm and 4A2g to 4T1g(4F) at 410 nm. The third transition, 4A2g to 4T1g(4P), with high energy, should be located in the near-ultraviolet domain of the spectrum, but it is obscure by a very intense charge transfer band.

The electronic spectra of chromium thiocyanate complexes (S 2b) in different solvents show no changes in spectrum, maintaining an octahedral geometry; hence the same spin-allowed transitions are expected.

S. 2. The electronic spectra of a) chromium nitrate and b) chromium thiocyanate complex in different media

The aqueous solution of nickel nitrate hexahydrate usually refers to octahedral [Ni(H2O)6](NO3)2, wherein the nickel ion, with 2+ oxidation state and *d8* configuration is surrounded by six water molecules. The T-S diagram for octahedral *d8* shows that the ground state is 3A2g and the spin multiplicity is a triplet. From the diagram one can observe that there are three spin-allowed *d*-*d* transitions. The first transition, 3A2g to 3T2g, with low energy, is seen in the near IR and is not observed in the visible spectrum (S 3a). The second spin-allowed transition, 3A2g to 3T1g(3F), is seen at 721 nm, and the third one, 3A2g to 3T1g(3P), with high energy, at 393 nm. The weak band at 657 nm corresponds to the spin-forbidden transition 3A2g to 1Eg, which is close to the spin-allowed 3A2g to 3T1g(3F) and ‘borrows’ the intensity by mixing of states. The charge transfer bands presented in the UV regio involve p → d or d → p transitions. The high intensity of these bands is due to the fact that these transitions are both Laporte and spin-allowed.

The electronic spectra of nickel thiocyanate complexes (S 3b), in different solvents show no significant changes in spectrum except that the maximum absorbance values increase for all bands and the band characteristic for 3A2g to 1Eg transition increase comparing to the close 3A2g to 3T1g(3F) spin-allowed transition. The insignificant changes in spectrum lead to the possible maintaining of the octahedral geometry, hence the same spin transitions would be expected.

S. 3. The electronic spectra of a) nickel nitrate and b) nickel thiocyanate complex in different media

In the case of octahedral [Cu(H2O)6](NO3)2 wherein the copper ion has a 2+ oxidation state and *d9* configuration, the transition is from (t2g)6(eg)3 configuration (2Eg state) to the (t2g)5(eg)4 configuration (2T2g state). This could be described as a positive “hole” that moves from eg to the t2g orbital set. This transition can be observed in the experimental spectra at around 800 nm in all solvents (S.4a).

The experimental UV-VIS spectra of copper thiocyanate complex (S.4b), in different solvents show that the band at around 800 nm disappears, while another band appears at 364 nm. This band can be assigned to a ligand to metal charge tranfer transition and the formation of CuSCN, wherein the metal ion was reduced from 2+ to 1+ charge. The formation of copper monothiocyanate is also sustained by the high value of stability constant (213 M-1) compared with that for nickel and cobalt monothiocyanate (~50 M-1).

S. 4 The electronic spectra of a) copper nitrate and b) copper thiocyanate complex in different media

In all octahedral complexes that typify the hydrated metal salts, the absorption band at around 300 nm is due to the π – π\* transition of uncomplexed nitrate counterions.