
Physicochemical parameters affecting the equilibrium between Tl(I) and Tl(III) in water solutions

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Thallium has two stable oxidation states. Tl(I) is thermodynamically stable, while Tl(III) is more reactive and hydrolyzes in alkaline and neutral solutions. Hydroxyl species of Tl(III) are formed even at low pH (~2), similar to iron hydroxyl species. In contrast to Tl(III), hydrolysis is rather insignificant for Tl(I). Also its complexes with such ligands as carbonates, sulphates and phosphates, are relatively weak ($\log K = 1.0-3.4$). The reduction potential of Tl(III) to Tl(I) is +1.26 V. The reduction rate is affected by pH and the presence of complexing agents. Chlorides lower the reduction potential (+0.77 V), because of forming a complex of $TlCl_4^-$ ($\log K = 18$), also the presence of oxalate ions prevents fast reduction. Even more stable complexes are formed by Tl(III) with large organic ligands such as EDTA ($\log K = 37$) or DTPA ($\log K = 46$), but the strongest inter-complex is formed with DDTC, as precipitation of Tl(III)DDTC from Tl(III)DTPA solution is observed. The reduction of Tl(III) ($\log k = 40$) is much faster than the complexation of Tl(III) ($\log k = 3-9$). Therefore, partial reduction is inevitable, and the equilibria taking place in aqueous solutions containing Tl ions are complex and often difficult to predict, especially in environmental systems.

References

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