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Thermodynamic and chemometric modelling of metal cations chemistry in aqueous solution

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By using potentiometric and spectroscopic techniques, such as UV-vis, fluorescence, EPR (Electronic Paramagnetic Resonance) and NMR (Nuclear Magnetic Resonance) spectroscopy, it is possible to characterize the chemistry of metal cations in aqueous solution. The thermodynamic parameters that control the chemical equilibria can be defined by the elaboration of experimental data; then, the speciation distribution diagrams can be plotted. The combination of different techniques allows fortifying the model reliability and to get structural information about the species formed also. The thermodynamic parameters are usually obtained through potentiometric or spectroscopic data elaboration applying a stoichiometric approach based on mass/charge balances and physic-chemical equations [1].

In recent works, chemometry have also been applied to the study of different types of chemical systems, in particular to process spectroscopic data [2-3]. The investigation on two different chemical systems, concerning the complexation capability of kojic acid derivatives towards oxovanadium(IV) and the protonation and complexation capability of tannic acid [4], are reported as examples. The aim was to evaluate the usability of these methods for speciation studies.

The interaction of oxovanadium(IV) with four newly synthetized compounds [5] derived from kojic acid were studied. The ligands are composed of kojate groups linked to each other by an ethylenediamine, a propylenediamine, a butylenediamine or a tris(2-aminoethyl)amine. Potentiometric titrations, UV-vis absorption and EPR spectra were recorded as a function of pH on the systems examined. The experimental data demonstrated the formation of rather stable complexes, and that the coordination of the metal takes place mainly through the intervention of the kojate units. The data were processed with software dedicated to speciation studies [6-7] and with Matlab for chemometric elaboration. Principal Component Analysis - PCA and Multivariate Curve Resolution - Alternating Least Squares - MCR-ALS were applied. MCR-ALS resulted to be rather suitable to interpret the experimental data, in particular to achieve speciation information from EPR data.

As about tannic acid, it is a natural polymers derived from the vegetable kingdom and belonging to the polyphenol family. The protogenic and spectroscopic properties of commercial tannic acid were studied and the role of gallic acid impurities on the acidity and spectroscopic properties of tannic acid solutions was elucidated. The latter task was carried out by the application of MCR-ALS on fluorescence data collected on tannic acid and gallic acid solutions. The same approach was used to investigate the coordination capability of tannic acid towards iron(III). Both MCR-ALS and PARAFAC (Parallel Factor Analysis) were used for the elaboration of spectroscopic data and chemical models were proposed.

The MCR-ALS and PARAFAC techniques turned out to be useful in the interpretation of the spectroscopic data and this chemometric approach could support the study of those real systems that show a not well defined stoichiometry, such as humic acids or natural polymers, but that present peculiar functions able to interact with metal cations.

References

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