NECTAR
Network for Equilibria and Chemical Thermodynamics Advanced Research
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WG-1
NECTAR for highly hydrolysable (HHC) and/or low-valence state (LVC) cations

Bartosz Orzeł, Valentyn Dzyhovskyi, Kamila Stokowa-Sołtys, Elżbieta Gumienna-Kontecka
University of Wroclaw, Poland
Přemysl Lubal
Masaryk University, Brno, Czech Republic
Éva A. Enyedy
University of Szeged, Hungary

WG1 - NECTAR for highly hydrolysable (HHC) and/or low-valence state (LVC) cations has prepared the recommendations for working with iron(II) ions in aqueous solution. This work is related to the task of WG1 defining the most appropriate and accurate procedures and experimental approaches for the study of the solution speciation of LVC (e.g., Fe(II), Sn(II), Cu(I)).

The NECTAR recommendations for solution studies with Fe(II) ions

Due to the high susceptibility of Fe(II) ions to oxidation under atmospheric conditions, it is strongly advised to conduct all experiments involving Fe(II) ions in degassed & deoxygenetad solvents and under anaerobic conditions.

- **Deoxygenated solvents**

It is recommended to prepare the solvent one day in advance (by heating ultra-pure (Milli-Q) water in a round-bottom flask for approximately 30 minutes at normal/reduced pressure and then bubbling argon gas through the liquid, and store the solution in a glove box until the next day.

To effectively degas organic solvents, such as methanol or acetonitrile (used for example for mass spectrometry), use a Schlenk line. Ensure a proper setup and connection to a vacuum pump and inert gas source. Purge the entire line with inert gas to eliminate air and moisture. Transfer the solvent to a clean, dry Schlenk flask and connect it securely to the line. Freeze the solvent using liquid nitrogen. Apply vacuum while defrosting to remove dissolved gases and impurities from the solvent. Allow degassing for the appropriate duration, then slowly introduce inert gas to displace the vacuum and prevent re-entry of moisture and oxygen. Repeat the process thrice to ensure thorough degassing. Seal the flask tightly with a rubber septum and store it under inert gas until use.

- **The control of oxygen level in water**

The concentration of the dissolved O_2 in the solution could be determined by several analytical procedures. Instrumental analysis is based on voltametric analysis[1] (measurement of limiting electric current at potentials lower than -0.45 and -1.35 V (vs. NHE) for two waves representing two-electron oxygen reduction):

$$O_2 + 2\,H^+ + 2\,e^- \Leftrightarrow H_2O_2$$

$$H_2O_2 + 2\,H^+ + 2\,e^- \Leftrightarrow 2\,H_2O$$

Another approach is based on the measurement of the luminescence-decay quenching effect of oxygen on Ru(II) complexes of phenonathroline derivatives which is placed on top of optode.[2] Both instrumentations are commercially available, but they require careful calibration of the instrumentation based on knowledge of the oxygen concentration by an analytical independent method.

Another possible approach is the redox titration procedure proposed by Winkler:

$$2\,Mn^{2+}\,(aq) + O_2\,(aq) + 4OH^- \rightarrow 2\,MnO(OH)_2(s)$$

$$MnO(OH)_2(s) + 4\,H^+(aq) \rightarrow Mn^{4+}(aq) + 3\,H_2O(l)$$

Freshly precipitated Mn(II) hydroxide is oxidised by oxygen to Mn(IV) oxo-hydroxide which is dissolved in mineral acid in presence of iodide

$$Mn^{4+}\,(aq) + 3\,I^-(aq) \rightarrow Mn^{2+}(aq) + I_3^-\,(aq)$$

Then iodine formed (as triiodide ion I_3^-) can be titrated by sodium thiosulphate titrant solution of known concentration:

$$2\,S_2O_3^{2-}\,(aq) + I_3^- \rightarrow S_4O_6^{2-}\,(aq) + 3\,I^-\,(aq)$$

Then concentration of dissolved oxygen could be calculated as

$$1 \text{ mole of } O_2 \rightarrow 4 \text{ mole of } S_2O_3^{2-}$$

The solubility of oxygen in water is about 8 mg.L^{-1}, *i.e.* 8 ppm, for normal temperature and normal air pressure. The advantage of this absolute analytical method is that it does not need any calibration, it is very simple and it gives reliable results.

- **Anaerobic conditions in a glove box**

All experiments should be conducted in a glove box filled with an inert gas (e.g. N_2 or Ag). The concentration of oxygen inside the glovebox should be less than 10 ppm, preferably below 0.5 ppm. The concentration of oxygen dissolved in solvents could be estimated by analytical methods discussed above.

- **Preparation of stock solution of Fe(II) ions**

Each time the measurements are taken, prepare a fresh Fe(II) ion stock solution. In this case, dissolve ammonium Fe(II) sulfate (Mohr's salt), the most stable Fe(II) source[3], in a degassed solvent prepared accordingly to the above procedure. It is crucial to note that maintaining an anaerobic environment is essential during the experiment to prevent any color changes in the sample due to the iron oxidation or precipitation of iron hydroxides. Exposure to atmospheric oxygen may cause the sample color to turn yellow, followed by brown-yellow Fe(III) hydroxide precipitation.

It is also possible to prepare the Fe(II) stock solution from fine Fe powder dissolved in a known amount of HCl solution; this procedure should be carried out in absence of air (in flask with Bunsen cap).[4] Then the solution is filtered, stored and used under anaerobic conditions in a laboratory glove box.

- **Determination of Fe(II) ion concentration in stock solution**

During the determination of Fe(II) concentration using spectrophotometric measurements via the complexation with 1,10-phenanthroline ($[Fe(II)(1,10\text{-phenanthroline})_3]^{2+}$),[5,6] several analytical activities should be followed to ensure accurate results:

- Use degassed water for the preparation of the samples.
- Dissolve 1,10-phenanthroline (0.01 M final concentration) in 0.1 M hydrochloric acid solution, sodium acetate (0.1 M final concentration) in water, and Mohr's salt (concentration necessary for research, in our case ~0.05 M final concentration) in a 0.01 M hydrochloric acid solution.
- From the stock solutions, prepare three samples with a 5-fold excess of 1,10-phenanthroline over Fe(II) ions at the desired concentration (in the range of the calibration curve concentrations) and sodium acetate at a concentration of 0.01 M.
- Measure UV-Vis spectra at 350-650 nm wavelength in a 0.1 cm quartz cuvette. Read absorbance at 510 nm. We have determined the value of the molar extinction coefficient (ε) to be 10 806 $M^{-1}cm^{-1}$ (literature value: 10 931 $M^{-1}cm^{-1}$).[7]
- To accurately determine the freshly prepared stock solution's concentration, utilize the calibration curve to convert the absorbance data to Fe(II) ion concentration at the maximum absorbance of 512 nm. The calibration curve can be obtained by preparing samples with varying Fe(II) concentrations (in our case 11 samples ranging from 0.1 to 1.1 mM), analogously as in point three. The plot of absorbance (λ=512 nm) versus concentration of Fe(II) should yield a linear correlation.
- Take the average concentration determined from the three samples.

Absolute analytical methods (e.g., volumetry, coulometry) are preferred since they are simpler and more accurate than relative one, e.g. spectrophotometry . The concentration of Fe(II) ion could be determined directly by the traditional permanganometric titration in presence of sulphuric and/or phosphoric acids to eliminate side reaction of chloride oxidation (formation of gaseous chlorine) without or with ferroin indicator.[8] Another possibility is application of complexometry at pH ~ 2.5 after oxidation of Fe(II) to Fe(III) ion in presence of H_2O_2 or nitric acid using Tiron or Xylenol orange as indicator.[9] Alternatively low concentration of Fe(II) ion could be determined coulometrically in presence of Ce(III) ion as electrocatalyst. The direct coulometric titration of Fe(II) ion is irreversible and therefore impossible, therefore firstly Ce(III) ion is oxidized to Ce(IV) that react immediately with Fe(II) to Fe(III) – indirect coulometric titration.

The relative methods are usually based on measurements by molecular absorption spectroscopy.[11,12] The most suitable procedures are those using the formation of Fe(II) complexes of 1,10-phenanthroline derivatives or Fe(III) complexes of sulphosalicylic acid prepared after oxidation of Fe(II) ion to Fe(III) by H_2O_2.

All procedures could be optimized to determine the concentrations of Fe(II) and Fe(III) ions in solution simultaneously.

- **Equilibrium constants for Fe(II) hydrolysis**

It is crucial to take into account the process of the metal ion hydrolysis when working with Fe(II), especially in solution speciation studies to determine the formation constants of Fe(II) complexes. Fe(II) hydrolytic species are believed to be $[Fe(OH)]^+$, $[Fe(OH)_2]$, and $[Fe(OH)_3]$[11]. The hydrolysis constants of these forms for zero ionic strength are collected in the Periodic Table prepared by the members of the WG1, and can be accessed through the link: https://www.cost-nectar.eu/docs/wg1_pt/FeII.pdf

Various approaches can be used to predict values at different ionic strengths and in different ionic media (e.g., Extended Debye-Hückel, Specific ion Interaction Theory (SIT) and Pitzer models). The final selection criterion should be based on the availability of proper parameters. More at: I. Grenthe, I. Puigdomenech, *Modelling in Aquatic Chemistry*, Paris: OECD, 1997.

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