The Aqueous Interaction of Neodymium with Two Omni Existent Biomoieties

– A Mechanistic Understanding by Experiment and Theory

Rama Mohana Rao Dumpala,*,[a] Shikha Sharma,[a] Anil Boda,[b] Neetika Rawat,[a] Sk. Musharaf Ali[b]

[a] Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai, India – 400085

[a] Chemical Engineering Division, Bhabha Atomic Research Centre, Mumbai, India – 400085

(Corresponding Author: rammohan@barc.gov.in, ramamohandumpala@gmail.com; Ph: +91-22-25593928)

2.1. Potentiometric Titrations

All potentiometric titrations are carried out in duplicate at room temperature (298 K) in 1.0 M $NaClO_4$ ionic medium on a Metrohm make auto titrator with Model no. 716 DMS Titrino. The glass electrode electrolyte solution (KCl) was replaced by 1.0 M $NaClO_4$ solution to avoid the formation of sparingly soluble $KClO_4$, which can clog the frit during the titration period. The electrode was calibrated by a strong acid with (0.05 M $HClO_4$) - strong base (0.1 M NaOH) titration to obtain the values of standard electrode potential (E_0), slope and carbonate impurity in alkali by using Glee software.[1] Gran's method of titrating metal ion solution with NaOH was employed to determine the hydrogen ion concentration in the Nd(III) solution used for titration with the ligand solution.[2] The titration of ligand solution (10 mL of 0.05 M of pyrazine-2-carboxylic acid / pyrazine-2,3-dicarboxylic acid) with NaOH and titration of uranyl solution in dilute $HClO_4$ by the ligand solution are done to determine the protonation constants of the ligand and the stability constants of the complexes respectively by using the software Hyperquad.[3]

2.2. Absorption Spectrophotometry

The absorption spectra in the range of 375 to 500 nm with 1 nm resolution were measured for an incremental additions (10 to 50 μL) of half neutralized ligand solution to a fixed metal ion solution (1.50 mL) using a JASCO V530 model spectrophotometer at a temperature of 298 K in 1.0 M

NaClO$_4$ ionic medium. The absorbance is an additive property and in solution, it represents the sum over all the absorbing species present or formed during the complexation process in the solution. In the present studies, in which uranyl forms ML and ML$_2$ complexes with both the ligands, the absorbance measured at each addition of ligand to the metal solution can be represented by below equations

$$A_T = A_M + A_{ML} + A_{ML_2}$$
(1)

$$A_T = \varepsilon_M C_M l + \varepsilon_{ML} C_{ML} l + \varepsilon_{ML_2} C_{ML_2} l$$
(2)

where ε_{MLi} - Molar absorption coefficient of species 'ML$_i$'

C_{MLi} - Concentration of species 'ML$_i$'

l - Path length of the cell

Each addition of ligand generates an equation of the form (2) and an N number of additions of ligand solution to metal results in a matrix of the form A (N, λ). Hyperquad 2006 software programme[3] was used to find the solution of this matrix to determine the species present and their percentage of formation, molar absorptivities along with the respective log β values for all the Uranyl - pyrazine monocarboxylate and Uranyl - pyrazine dicarboxylate complexes formed during the course of titration. All the concentration of the metal and ligand solution employed for the experiments were given in the labels of figures representing the respective complexation studies in the results and discussion section.

2.3. Fluorescence measurements

The measurements were carried out in titration mode on Fluorimeter (Horiba Jobin Yvon Fluorolog 3) equipped with a Xenon lamp as the excitation source. As neodymium emission is in infrared region, the emission detector (GaIn detector) is cooled to Liq. N2 temperature to avoid the thermal noise before taking any emission spectra. Similar to potentiometric and spectrophotometric titrations, 2.0 cm^3 of Nd^{3+} solution was titrated against partially neutralized ligand solution and the emission spectra was recorded for each incremental addition of ligand to metal ion solution. The

solution was excited at 350 nm and the emission was recorded at 800-1350 nm wavelength region arising from $^4F_{3/2} \rightarrow {}^4I_J$ (J= 9/2, 11/2, and 13/2) transitions of Nd^{3+} ion.[4]

2.4. Isothermal titration Calorimetry

All the calorimetric titrations are carried out on a TA made (TAM III model) microcalorimeter in duplicate at 298 K temperature in 1.0 M $NaClO_4$ medium. The instrument consists of a sample and reference cell holders, placed in an oil bath and coupled with thermopiles for temperature sensing. The titration assembly consists of a very fine cannula attached at the end of 0.5 mL microsyringe, driven by Lund motor. The system is calibrated electrically by giving a known amount of external voltage pulse to the sample cell, while the chemical calibration is done by measuring the enthalpy of formation for the reaction of barium with crown-6-ether. The detailed instrumentation and calculation of complex formation enthalpy are given elsewhere.[5]

Complexation Enthalpy by Isothermal Titration Calorimetry

The raw calorimetric data gives the power required to overcome the disturbances caused by complex formation with time, which on integration gives the heat released due to a process (figure 7). The complexation of UO_2^{2+} with both the ligands is studied calorimetrically by titrating half-neutralized ligand solution into a known volume of fixed UO_2^{2+} ion solution. The heat released (Q_T) is measured for each addition of ligand to the metal solution and is comprises of the heat of complexation (Q_C), the heat of protonation (Q_P) and the heat of dilution (Q_D). A separate experiment to measure Q_P and Q_D are carried out by titrating the half-neutralized ligand solution with a known concentration of strong acid ($HClO_4$) and by background electrolyte ($NaClO_4$) solution respectively. The heat of complexation could be arrived by

$$Q_C = Q_T - Q_D - Q_P \qquad (6)$$

The complexation heat for the formation of ML_2 complex only is related to the enthalpy of complex formation by the equation

$$Q_C = (V_{ML} * \Delta H_{ML}) + V_{ML2} * (\Delta H_{ML} + \Delta H_{ML2}) \qquad (7)$$

where ν_{ML} is the number of moles of ML formed for a particular addition of ligand. The above relation generates an "n" number of equations where "n" stands for the number of incremental additions of ligand solution. The complexation enthalpy (ΔH_C) is obtained by non-linear least square analysis of equations generated by the relation (7). The complexation entropies (ΔS_C) could be then deduced by equation (5). The determined ΔH_C along with all other thermodynamic parameters are shown in table 2.

References

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