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Solubility increase of colloidal zinc hydroxide as revealed by isothermal titration calorimetry

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ABSTRACT

In this study, association between zinc (II) and dipicolylamine was studied by isothermal titration calorimetry. At neutral of weakly alkaline conditions, with zinc (II) in cell and dipicolylamine in syringe, increasing heat release was observed as the titration proceeded. Considering the equilibrium between Zn^{2+} and $Zn(OH)_2$ at these conditions, the increasing heat release is ascribed to the increasing solubilization of colloidal $Zn(OH)_2$ followed by neutralization of OH^- by the buffer. Though quantitative determination of the increase in solubility is not accomplished, to the best of our knowledge, this is the first report about solubility increase of colloidal zinc hydroxide using calorimetric method.

1. Introduction

Association between metal ions and ligands is of fundamental importance for biological and chemical events, including enzyme activity [1], catalysis [2] and super-molecular structure [3]. A variety of methods have been used to study the association, among which isothermal titration calorimetry (ITC) is most attractive not only because of the convenience in manipulation but also because thermodynamic parameters such as association constant, enthalpy, entropy and stoichiometry can be obtained through a single titration [4–8].

Zinc(II)-dipicolylamine is reported to associate with phosphate with moderate affinity and high selectivity, and thus has been extensively employed as phosphate-binding moiety of chemosensors and artificial receptors [9–12]. Nevertheless, association between zinc (II) and dipicolylamine has not been systematically reported, particularly by ITC.

It is known that metal ions such as Zn^{2+} and Fe^{3+} form hydroxide colloids at neutral or alkaline conditions due to the low K_{sp} of the hydroxides [13], and precipitate at high concentration. Thus, in this case, association between metal ions and ligands is complicated, which probably is the reason why ITC study of the association between zinc (II) and ligands is not systematically reported.

In this study, association between zinc (II) and dipicolylamine was studied using ITC. Notably, with zinc (II) in cell and dipicolylamine in syringe, increasing heat release was observed as the titration proceeded. Considering the equilibrium between Zn^{2+} and $Zn(OH)_2$ at neutral aqueous condition, the increase in heat release is ascribed to the solubility increase of colloidal $Zn(OH)_2$ followed by neutralization of OH^- by the buffer.

2. Materials and methods

2.1. Materials

Dipicolylamine was purchased from J&K Scientific. Other reagents were obtained from commercial suppliers and used without further purification, detailed information is provided in Table 1.

2.2. Instrumentation

ITC experiments were performed on VP-ITC equipped with a unit of 1.4322 cm^3 reaction cell and a 0.289 cm^3 syringe. Transmission electron microscopy (TEM) was performed on JEM-2000F. Dynamic light scattering (DLS) measurements were performed using a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-10000AT) at 659 nm wavelength.

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TABLE 1
Sample table.

Chemical name	Mass fraction purity [a]	Source	Purification method
Dipicolylamine	0.95	J&K Scientific	None
Zinc nitrate hexahydrate	0.99	Tianjin Guangfu Fine Chemcial Research Institute	None
Ethylenediaminetetraacetic acid disodium salt dihydrate	0.99	Tianjin Beifang Tianyi Chemical Reagent Co. Ltd	None
2-(N-morpholino)ethanesulfonic acid monohydrate (HEPES)	0.99	Beijing Dingguo Changsheng Biotech CO.LTD	None
4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (MES)	0.99	Beijing Dingguo Changsheng Biotech CO.LTD	None

[a] Given by supplier.

2.3. ITC experiments

For ITC titrations performed at pH > 6.8, 50 mmol · kg^{-1} HEPES buffer was used, for titrations performed at pH < 6.8, 50 mmol · kg^{-1} MES buffer was used. The metal complex and dipicolylamine (or EDTA) were dissolved in same buffer respectively before performing titration. All the titrations were performed at 25.00 °C and atmospheric pressure (in the range of (99.49 to 100.80) kPa), and contained an initial injection of 2 μL followed by 28 injections of 10 μL. The enthalpy of dilution was subtracted from titration data before curve-fitting in Origin. To confirm the reproducibility of the data, at least three independent measurements were performed.

A total of 50 mmol · kg^{-1} HEPES buffer solution (pH = 7.2) was prepared as follows: 2.38 g HEPES (0.01 mol) was dissolved in 180 g double-distilled water; the pH of the solution was then adjusted to 7.2 by adding 5.65 g 1 mol · kg^{-1} NaOH solution, after which 16.52 g double-distilled water was added. The MES buffer solution was prepared in the same way except for a different pH.

The 5 mmol · kg^{-1} dipicolylamine buffer solution was prepared by dissolving 9.96 mg dipicolylamine in 10 g HEPES (or MES) buffer.

The 500 μmol · kg^{-1} $Zn(NO_3)_2$ buffer solution was prepared by dissolving 4.46 mg $Zn(NO_3)_2{\cdot}6H_2O$ in 30 g HEPES (or MES) buffer.

Typically, for the titration 500 mmol · kg^{-1} $Zn(NO_3)_2$ with 5 mmol · kg^{-1} dipicolylamine: dipicolylamine buffer solution were loaded in the cell of the calorimeter. The $Zn(NO_3)_2$ buffer solution was loaded into the syringe, stirring speed was 307 rpm, initial delay was 120 s, the interval between two adjacent injections was 210 s, the titration contained an initial injection of 2 μL followed by 28 injections of 10 μL.

2.4. Standard uncertainties

The standard uncertainty of temperature is 0.006 K. The standard uncertainty of pressure for each sample containing three independent measurements $u_i(p)$ is 0.06 kPa, and combined uncertainty of pressure is 0.75 kPa, which was calculated using the relation $u_c(p) = (u_1(p))^2 + (u_2(p))^2 + (u_3(p))^2 + (u_4(p))^2 + \cdots + (u_i(p))^2$. The standard uncertainty for the buffer concentration is 2.44×10^{-5} mol · kg^{-1}. The standard uncertainty of pH of the buffer is 5.7×10^{-3}. The standard uncertainty of 5 mmol · kg^{-1} dipicolylamine buffer solution is 2.9×10^{-4} mmol · kg^{-1}. The standard uncertainty of 500 μmol/kg $Zn(NO_3)_2$ buffer solution is 0.33 μmol · kg^{-1}. The standard uncertainty of the enthalpy change for each sample containing three independent measurements is 0.06 kJ·(mole of injectant)$^{-1}$, and the combined uncertainty is 0.78 kJ·(mole of injectant)$^{-1}$.

3. Results and discussion

3.1. Titration with $Zn(NO_3)_2$ in the cell and dipicolylamine in the syringe

In ITC experiments, host and guest (metal ion and ligand) were loaded into the cell and syringe respectively, and vice versa. Usually, a higher (more than ten times) concentration is required for the substance loaded into the syringe. In neutral aqueous condition, Zn^{2+} is hydrolyzed and precipitates at higher concentration because of the low solubility of $Zn(OH)_2$. To avoid this, zinc (II) was loaded into the cell, and dipicolylamine was loaded into the syringe. To maintain a stable neutral pH, HEPES buffer was chosen, and the titration was first performed at pH = 7.2. Surprisingly, the titration curve does not display a typical "S" shape always observed in strong associated system, but shows increasing heat release as the titration proceeds (figure 1).

The interesting titration curve motivated us to consider the existence of the colloidal $Zn(OH)_2$. In the system containing equilibrium between free ions and colloidal particles, the association between ligands and metal ions is complicated. In this case, the colloidal particles function as a metal ion reservoir. Upon consumption of the free metal ion, equilibrium shifts from colloidal particles to the free metal ion. On the other hand, according to the Kelvin equation, the solubility of particles is dependent on their size, with smaller particles having a higher equilibrium concentration of free molecules or ions [14,15]. Thus, it is assumed that, as consumption of the free metal ion proceeds, the size of the colloidal particles lessens by releasing free metal ions, and the equilibrium concentration of the free metal ion increases.

The apparent enthalpy change observed in ITC is proposed to be generated mainly from four sources (scheme 1): the first is de-solvation of free Zn^{2+} and dipicolylamine, which is endothermic; the second is association between Zn^{2+} and dipicolylamine, which is exothermic; the third is dissolution and ionization of $Zn(OH)_2$, which is endothermic; the fourth is the neutralization reaction between OH^- and the buffer. Apparently, steps two and four contribute to the overall heat release, and in comparison with the extremely exothermic coordination and neutralization, the endothermic contribution from de-solvation, dissolution and ionization is negligible. Thus, the increased heat release associated with the ITC data indicates increased coordination (step 2) or neutralization (step 4).

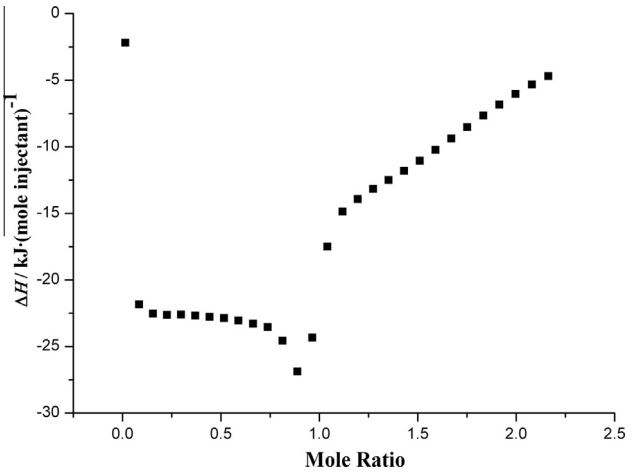

FIGURE 1. ITC data for titration of 5 mmol · kg^{-1} dipicolylamine into 500 μmol · kg^{-1} $Zn(NO_3)_2$ (50 mmol · kg^{-1} HEPES buffer pH = 7.2).