

Application of Specific Ion Interaction Theory for the Complexation of Dioxovanadium(V) with NTA at Different Ionic Strengths

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Introduction

There is a project on the IUPAC web site about the ionic strength corrections for stability constants using specific ion interaction theory (SIT) which has been completed in 2005, but to our knowledge no reports of the ionic strength dependence of V(V) complexes with NTA has appeared. Therefore in this research, ionic strength effects for NTA complexes with dioxovanadium(V) have been studied in an ionic strength range of (0.1 to 1.0) mol dm⁻³ of NaClO₄ at 25 °C using SIT.

Key Words: SIT; Ionic Strength; NTA; Dioxovanadium(V); Stability Constant

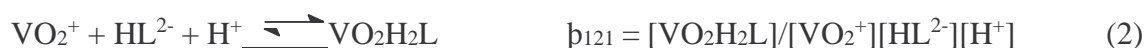
Method

Acidic solutions of dioxovanadium(V) were titrated with basic solutions of NTA at different ionic strengths. The absorbance data in the UV range(245 to 280 nm) and pH=1.00-2.50 were used for minimizing the error function on the basis of Gauss- Newton nonlinear least squares method in Excel 2000 program:

$$U = \sum (A_{\text{exp}} - A_{\text{cal}})^2 \quad (1)$$

Two species (VO₂H₂L and VO₂HL⁻) have been obtained according to curve fitting, which allows us to calculate the values of formation constants. Combination of

formation and dissociation constants gives the values of stability constants at different ionic strengths:



Results and Discussion

The two basic assumptions in the specific ion interaction theory (SIT) are as follows:

(a) The activity coefficient of an ion j of charge z_j in the solution of the ionic strength I may be described by:

$$\log \gamma_j = \frac{-z_j^2 0.509 \sqrt{I}}{1 + 1.5 I} + \sum_k \epsilon(j, k, I) m_k \quad (4)$$

(b) The ion interaction coefficients $s(j, k, I)$ are zero for ions of the same charge sign and for uncharged species.

The following formulas were deduced for the extrapolation to zero ionic strength for $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- respectively according to SIT:

$$\log p_{101} + 4D = \log p_{101}^0 - O_s I \quad (5)$$

$$\log p_{101} + 6D = \log p_{101}^0 - O_s I \quad (6)$$

Conclusions

The linear regressions were done on the basis of Eqs. (5) and (6) and the results are shown in Figure 1. The values of $O_s = 1.5916, 0.6272$, have been obtained for $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- respectively[1]. $s(\text{H}^+, \text{ClO}_4^-) = 0.14$, thus, the following equations are valid[1]:

$$s(\text{VO}_2^+, \text{ClO}_4^-) + s(\text{HL}^{2-}, \text{Na}^+) = -1.7316 \quad (7)$$

$$s(\text{VO}_2\text{HL}^-, \text{Na}^+) - s(\text{VO}_2^+, \text{ClO}_4^-) - s(\text{L}^{3-}, \text{Na}^+) = 0.7672 \quad (8)$$

There is descending pattern for the dioxovanadium(V) complex with NTA according to the SIT model without any maximum or minimum. The results on the basis of extended Debye-Hückel model are shown in Figure 2[2-6]. It seems that we can conclude both of the models apply well for the dioxovanadium(V) complex with NTA.

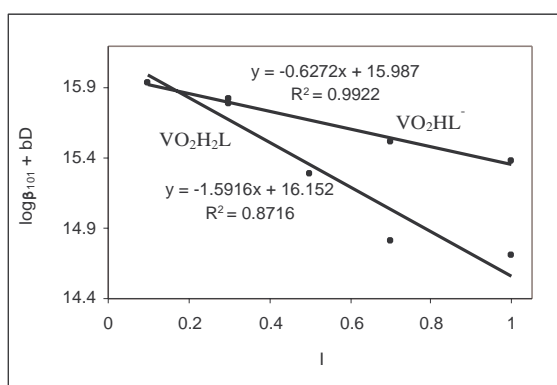


Figure 1. Plot of $\log\beta_{101} + bD$ ($b = 4$ and 6 for $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- respectively) versus I on the basis of SIT model.

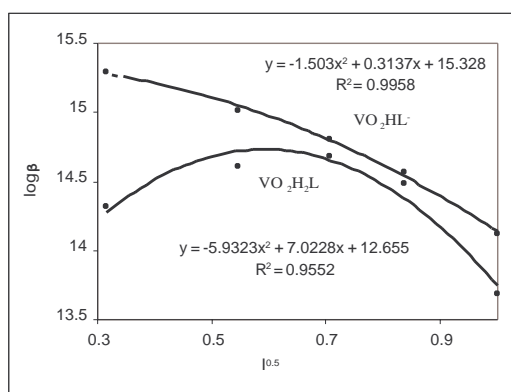


Figure 2. Plot of $\log\beta_{121}$ and $\log\beta_{111}$ versus the square root of ionic strength on the basis of modified Debye-Huckel model.

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