Advanced Materials Research Vol. 324 (2011) pp 170-173
Online available since 2011/Aug/22 at www.scientific.net

doi:10.4028/www.scientific.net/AMR.324.170

Spectrophotometric study of cobalt(II) chlorocomplexes in methanol in the visible domain.

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Key words: spectrophotometry ; stability constant β_j ; cobalt(II) chlorocomplexes; structural modifications $O_h \rightarrow T_d$.

Abstract: Cobalt(II) chlorocomplexes were studied in a polar protic solvent namely methanol at 25°C. The spectrophotometric technique in the visible region was used. The studied equilibrium is: $Co^{2+} + j\ Cl^- \rightleftharpoons CoCl_j^{(j-2)-}$. Formation of three chlorocomplexes and a structural modification ($O_h \rightarrow T_d$) were obtained from recorded spectra analysis. The stability of $CoCl^+$ was studied by the graphical method of Kruh and the overall stability constants were calculated with the SIRKO program based on the least-square method. Different models were tested and the model [1, 2, 3] was retained for which the best values are: $\log \beta_1 = 0.92$, $\log \beta_2 = 1.31$ and $\log \beta_3 = 1.08$.

Introduction

Complexes are involved in several basic processes such as hemoglobin or vitamin B_{12}[1-7], which are respectively iron and cobalt complexes [8,9]. Formation of octahedral and tetrahedral cobalt(II) complexes is known from solid state studies [10]. A detailed study of Cobalt(II), Nickel(II) and Copper(II) chlorocomplexes was carried out in trimethyl phosphate, acetonitrile (AN), dimethyl formamide (DMF) and propylene carbonate (PC) [11, 12]. The present work concerns the structural transformation of the octahedral (O_h) to tetrahedral (T_d) geometry following the formation of successive mononuclear chlorocomplexes between Co^{2+} and Cl^- in an alcoholic medium.
Different characteristic studies have been proposed, calorimetry [13], conductimetric titration [14]…etc. We used exclusively the spectrophotometric absorption in the visible region. The absorption spectra obtained in DMF, dimethyl sulfoxide (DMSO) and PC [15,17], revealed the formation of successive cobalt(II) chlorocomplexes of general formula: $[CoCl_j]^{-(j-2)}$. Studies on Cu(II) and Ni(II) showed the presence of 4 mononuclear complexes in DMSO, DMF and PC, the relationship with the dielectric constant of the solvent has been established [18-19]. The stability constant of cobalt(II) chlorocomplexes was determined in butanol, DMF and AN [20]. Hirose [21] gave an approach to determine βj by combining spectroscopic and titration methods. Results of Co(II) chlorocomplexes in ethanol and propan-2-ol [22] with Schiff bases in different solvents [23] were also given. In water and methanol, the presence of 2 and 4 complex respectively was proved [24, 25]. Some authors have identified only one low intensity complex in aqueous solutions [26, 27]. These studies have been extended in molten inorganic salts as well [28-32].

Experimental

Reagents: Stock solutions were prepared from hexahydrate cobalt(II) chloride ($CoCl_2$, $6H_2O$) and lithium chloride LiCl, subdivided solutions were prepared by dilution. Methanol was used without treatment 99.99%.