

trated aqueous solutions of borates [1, 2]. The  $^{11}\text{B}$  nuclear magnetic resonance spectra of sodium, potassium and ammonium polyborates in  $\text{D}_2\text{O}$  solutions, — as a function of concentration and pH value —, provide information of the hydrolysis equilibria. Two NMR signals are observed in the aqueous solutions of the pentaborates  $\text{Na}[\text{B}_5\text{O}_6(\text{OH})_4]$ ,  $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4]$  and  $\text{NH}_4[\text{B}_5\text{O}_6(\text{OH})_4]$ , while only one NMR line is recorded in the solutions of the tetraborates  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4]$  and  $(\text{NH}_4)_2[\text{B}_4\text{O}_5(\text{OH})_4]$ . A solution of  $(\text{NH}_4)_2[\text{B}_4\text{O}_5(\text{OH})_4]$  at pH 7 shows two lines again [3].

The next step was to study the Raman spectra of solid  $\text{H}_3\text{BO}_3$ ,  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ ,  $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$  and of  $\text{Na}[\text{B}(\text{OH})_4]$  as well as of borax in aqueous solutions as a function of concentration and pH, recorded between 300 and  $1500\text{ cm}^{-1}$ .

For comparisons the Raman spectra of solid  $(\text{NH}_4)_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ ,  $\beta\text{-NH}_4[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ ,  $\text{NH}_4[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 0.67\text{H}_2\text{O}$  and  $\text{NH}_4[\text{B}_5\text{O}_6(\text{OH})_4]$  were considered. In solution, all lines in the Raman spectra could be assigned and the degree of depolarization measured. The assigned Raman frequencies can be used for the identification of unknown B—O lines and therefore of unknown borate structures [4].

In the last step the influence of some series of foreign electrolytes in various concentrations of the equilibria of the borate species in a 0.5 M solution was investigated by Raman spectroscopy.

On the one hand, addition of the foreign electrolyte solutions has a dilution effect, so that in many of these systems there exists only the  $[\text{B}(\text{OH})_4]^-/\text{B}(\text{OH})_3$  equilibrium without polyborates. On the other hand, the effect is sometimes a forcing of the equilibrium in favour of the polyborate formation with the triborate ions  $[\text{B}_3\text{O}_3(\text{OH})_4]^-$  and  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$  as predominant species. The tetraborate ion  $[\text{B}_4\text{O}_4(\text{OH})_5]^{2-}$  is present only to a minute extent, while the formation of the pentaborate ion  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$  is repressed the most [5].

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#### A Chemical Interpretation of the Intense Raman Spectra Observed at a Silver Electrode in the Presence of Chloride Ion and Pyridine: Formation of Radicals

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During the past five years, a large number of researchers have been interested in the Raman spectroscopic study of the phenomena involved at a silver electrode immersed in an aqueous chloride solution containing pyridine. We feel that the numerous interpretations proposed (1 to 9 and references therein) to explain the 'giant' intensity enhancement of the Raman spectra observed at the silver electrode solution interface are not convincing.

The aim of this work is to show that the observed phenomenon may be explained by a simple resonance Raman effect due to radical species formed at the silver electrode—solution interface during the oxidation—reduction cycle. In the case of KCl, pyridine solution, the bands observed in Raman and electroreflectance spectroscopy at  $227\text{ cm}^{-1}$  and  $750\text{ nm}$  ( $\Delta\text{R}/\text{R}$ ) are assigned to the presence of  $\text{Cl}_2^-$  radical anions. The band at  $1025\text{ cm}^{-1}$  and the bands at  $1008$  and  $1036\text{ cm}^{-1}$  as well as the shoulder at  $650\text{ nm}$  ( $\Delta\text{R}/\text{R}$ ) are attributed respectively to the formation of pyridinium radical cations and pyridinyl radical anions.

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#### Ligand Effects on Jahn—Teller Distortions. Consistent Force Field Calculations of Cu(II) Complexes

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The structural and electronic properties of Cu(II) complexes with symmetric tridentate facially coordinating ligands have recently been studied with respect to their Jahn—Teller distortions [1]. In such systems the forces opposing the Jahn—Teller distortion are of