

Kinetics of Redox switching of Prussian Blue films in $(\text{NH}_4)_2\text{SO}_4$ solutions and Selectivity studies of the films between Ammonium and Potassium Ions Using The Electrochemical Quartz Crystal Microbalance.

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Introduction. The redox process of a Prussian Blue (PB) film involves transfer of a cation as a counter ion and water(1, 2). The fluxes of water and the cation occur in opposite directions and in K_2SO_4 solutions their ratio water/counter ion is ~ -0.5 . Under certain conditions, anion transport also occurs.(3) Here we report water and ion fluxes in $(\text{NH}_4)_2\text{SO}_4$ solution obtained using the Electrochemical Quartz Crystal Microbalance (EQCM) combined with cyclic voltammetry. The fact that solvated radii of K^+ and NH_4^+ are not too different suggested (4) a comparison of their fluxes in the PB switching process would provide information about the nature of these ions in PB that was free of any differences associated with their transport behavior in water. Fluxes were investigated as a function of bathing $(\text{NH}_4)_2\text{SO}_4$ concentration, pH and the potential scan rate.

Results and Discussion Figure 1 show that highest Molar mass values in $(\text{NH}_4)_2\text{SO}_4$ was ~ 7 , while a value about 30 was found in K_2SO_4 solutions (2,5) The latter value corresponds to a water/cation ratio of ~ -0.5 while the former corresponds to a water/cation ratio of ~ -0.6 . Panel A shows that higher molar mass values are found in the more concentrated salt solutions. This result is consistent with a constant free volume situation in PB and a partition process which enriches PB with the cation at higher solution concentrations and thus displaces water from the lattice. Panel B shows that higher scan rates and lower pH conditions lead to lower molar mass values. This result is rationalized by a kinetically controlled transfer of a cation at the higher pH value, and by proton transfer becoming significant at the low pH value.

PB redox switching was also studied in equimolar solution mixture of K_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$. Figure 2 gives the experimental molar masses for this mixture as well as for the pure salt solutions. If we assume that the molar mass in the solution containing both K_2SO_4 and a $(\text{NH}_4)_2\text{SO}_4$ can be represented by a linear combination of the molar masses of pure a K_2SO_4 and a $(\text{NH}_4)_2\text{SO}_4$ solution, these experiments show that the ammonium ion/potassium ion ratio in PB is at least 4 in the mixture.

Redox switching the same PB film sequentially in K_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ solutions several times demonstrated that there was no history effect, i.e., the film did not display any hint of another cation had been used in the previous cycle. However, some of the film was lost by changing solutions, as is also seen if only $(\text{NH}_4)_2\text{SO}_4$ solutions were used, as is seen in Figure 1,

Conclusion

The very favorable partitioning of NH_4^+ as compared to K^+ does not appear to correlate either with their hydrated or ionic radii. Their crystal ionic radii are estimated to be approximately 0.133 nm (K^+) and 0.143 nm (NH_4^+) which would be increased, for their hydrated

ions by ~ 0.14 nm, the average radius of a water molecule.(3). Thus, we suggest that a heterogeneous mixture of ferric potassium ferrocyanide (Prussian Blue) and ferric ammonium ferrocyanide (Milori Blue) formed.

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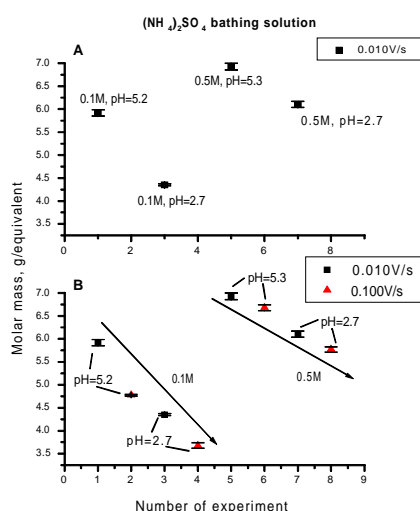


Figure 1. Molar mass dependence on concentration, pH and potential scan rate in 0.1 M and 0.5 M $(\text{NH}_4)_2\text{SO}_4$ bathing solutions at pH = 5.2 and 2.7 (H_2SO_4 added). The potential scan rate for the experiments in Panel A was 0.010 V s^{-1} in Panel B were 0.100 V s^{-1} between -0.2 and 0.5 V.

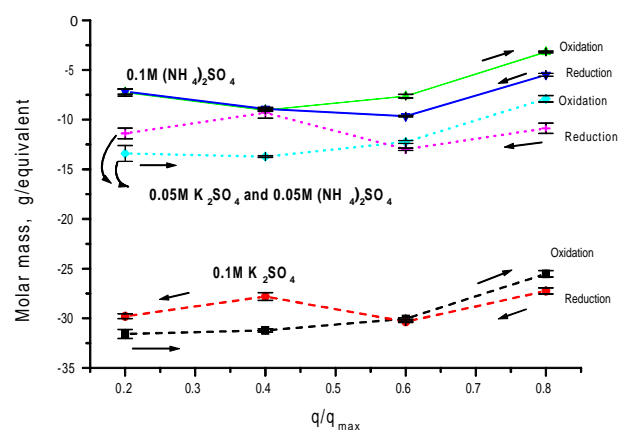


Figure 2 Molar mass vs. q/q_{max} The potential scan rate is 0.010 V s^{-1} . The abscissa represents the fraction of the charge required to oxidize/reduce the film for a particular cycle. This normalizes the results for film loss between redox cycles.

