

Cetylpyridinium chloride as a titrant for potentiometric titration of uranyl ion

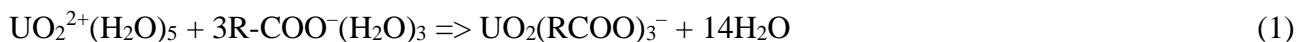
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The possibility of determination of UO_2^{2+} in the form of uranyl benzoate anion by the potentiometric titration technique is presented. Cetylpyridinium-selective electrode have been successfully applied in the potentiometric measurements of uranium and the obtained results showed good performance of this electrode. The cetylpyridinium-selective electrode based on the PVC matrix was plasticized with *o*-nitrophenyl octyl ether and cetylpyridinium tetraphenylborate was used as ionophore. The produced electrode showed good potentiometric characteristics such as low detection limit of cetylpyridinium cation, wide concentration range, and reasonable response time.

We have used DFT calculations for investigation of stability of uranyl carboxylate anions. The main reaction equation (1) considered for this process includes the pentahydrated uranyl cation $\text{UO}_2^{2+}(\text{H}_2\text{O})_5$ and carboxylic acid anion, that for inclusion of solvation effect were hydrated with three water molecules near carboxylic group.



We considered ten residues of aromatic acids and acetate anion as potential ligands for uranyl cation. The aromatic acids studied here are benzoic acid and its *ortho*-, *meta*-, *para*- substituted hydroxy-, amino- and nitro- derivatives. The choosing of these ligands dictated by their availability, stability and investigation of this raw will emphasis the influence of donor and acceptor groups over the binding affinity of RCOO^- with UO_2^{2+} .

Calculation of change in Gibbs free energy in the association reaction gives an information about the uranyl carboxylate anion stability in a water medium. The anions that binds with uranyl cation better than benzoate can be placed in the raw (binding energy, kcal/mol): *p*-aminobenzoate (−35.8) > *p*-hydroxybenzoate (−32.7) = acetate (−32.7) > *m*-aminobenzoate (−30.6) > benzoate (−29.7). These data make mentioned anions as candidates for derivatization of uranyl cation and next determination of complex anion through the titration with cetylpyridinium chloride.

Theoretical calculations indicates that benzoate anion is the right balance between candidates for complexation with uranyl cation: it shows relatively high binding to uranyl with simultaneous high binding of uranyl benzoate to cetylpyridinium and uranyl benzoate is the most lipophilic among all proposed organic anions.

Keywords: uranyl, titration, cetylpyridinium, DFT