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Limiting transport properties of lanthanide and actinide ions in water. Hydration number and hydrolysis phenomena.

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Abstract

We start with the idea that there is no second layer of hydration for trivalent ions La, Ac; Since it is an illogical model that first layer may contains between eight and nine molecules of water, and second layer would have a larger radius and no more than five or closes six water molecules.

In this paper, we present a new simplistic model for estimation of trivalent actinides and lanthanides ions self diffusion coefficients. We take account hydrolysis phenomena. We use Fuoss theory and Bjerrum approach to calculate K_h the thermodynamic hydrolysis constant using Marcus summarized data for different radius. We suppose that ion structure stills the same in solid state (salt) or in aqueous solution, regarding the water molecules surrounding central ions ($M = La^{3+}$, Ac^{3+}). Taking account hydrolysis, experimental self diffusion coefficient D of ion is equal to the sum of two contributions: free and associated ion.

$$D^{\circ} = \alpha D^{\circ}_{free} + (1-\alpha) D^{\circ}_h,$$

$$free = M^{3+} + (H_2O)_n, n=8,9, h = M^{3+} + (H_2O)_n OH^{-}$$

$$with K_h = \frac{[h].[H^+]}{[free]} = 10^{-7} \frac{(1-\alpha)}{\alpha};$$

α is the molar fraction of free La/Ac ions.

At infinite dilution, pH = 7 (Oswald dilution Principle)

In our recent paper, we have verified our simplistic calculus method with experimental data for Lanthanum and Gadolinium (first and middle 4f element series).

Our model will end the discordances results by Spectral and crystallographic methods in solid state or by measurement methods solution...

Key words: Lanthanides , actinides , hydrolysis , hydration shell.

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