Estimation of the Mean Distance of Closest Approach of Actinides and Lanthanides Ions in Aqueous Solutions: Some Experimental and Theoretical Calculations

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Abstract

The estimation of numerical values of the mean distance of closest approach of ions, *a,* of lanthanides and actinides ion salts in aqueous solutions, determined from activity coefficients, as well as from different theoretical approaches, is presented and discussed.

Keywords: Ion size, Lanthanides, Actinides, Mean distance, Solutions, Electrolytes

1. Introduction

Lanthanides ($_{57}$La–$_{71}$Lu) and actinides ($_{90}$Th–$_{103}$Lr),[1–3] part of a unique section of the periodic table, are two families that are related because they are relatively rare when compared to other elements and both result from electrons being added into an f sub-level. Whereas the first ones are abundant in the earth's crust, usually found together in the same ores, in contrast, only two of the actinides, thorium and uranium, occur in nature, being all the others synthesized by nuclear scientists.[1–3]

It is known that all actinides are radioactive and therefore toxic and, consequently, difficult to study. In spite of this, they have been recognized also by tech applications (e.g., thorium is used in the manufacture of high-quality glass and as a catalyst in various industrial processes[4]), as well as components of nuclear energy (e.g., thorium and uranium have potential as nuclear fuel applications).[5]

Also, some lanthanides have been recognized for various applications, such as industrial (e.g., cerium is used in steel manufacturing[6]) and medical ones,[3] such as in antitumor agents, and kidney dialysis medicine. Also, they are often used for their fluorescent properties. Euro-pium compounds, for example, are often used in molecular genetics to mark specific strands of DNA.[7]

Despite many reasons justifying the importance of these elements and their salts and, of course, the needs to study them, the understanding of these complex systems has not yet been well established; consequently, their characterization is very important, as an approach to better understand their structure, and to model them to practical applications. Thus, we need to know accurate data concerning the fundamental thermodynamic and transport properties of solutions containing lanthanide and actinide ions,[8–12] not only for fundamental purposes, but also in order to be used in many technical fields, such as medicinal applications.[3] However, for the interpretation of those data and, more important, for their estimation when no experimental information is available, we need to know parameters such as the "mean distance of closest approach of ions", *a* (å when expressed in Angstroms). Despite considerable work has already been done, (e.g.,[1–7]), much of these data are not available from the literature, mainly due to the complexity involved in their estimation. For example, this parameter, *a,* depends not only on the nature of the electrolyte and its concentration, but also on the nature and concentration of the species present in the solution, which participate in the formation of an ionic atmosphere.

Thus, having in mind its importance on the knowledge of the transport and thermodynamic properties, we propose to extend our studies, already started with alkali and earth alkali metal salts, and heavy metal salts,[13–17] to some lanthanide and actinide salts.

2. Different Methods of Estimation of Parameter *a* from Experimental and Theoretical Methods

2. 1. Estimation of *a* from Experimental Mean Ionic Activity Coefficients

The distance of closest approach, *a*, from the Debye-Hückel theory, regarded as an adjustable parameter in several semi-empirical equations for the activity coefficients, has been estimated for a large number of electrolytes[12] in aqueous solutions using data in[10] and Eq. (1),

$$\ln y_\pm = -\frac{A|Z_1 Z_2|\sqrt{I}}{1 + Ba\sqrt{I}} + bI \qquad (1)$$

where *a* and *b* are considered adjustable constants, Z_1 and Z_2 are the algebraic valences of a cation and of an anion, respectively, $y_\pm$ is the molality-scale mean ionic activity coefficient, and *I* is the molality-scale ionic strength. *A* and *B* are defined as

$$A \equiv \left(2\pi N_A \rho_A\right)^{1/2}\left(\frac{e_0^2}{4\pi\varepsilon_0\varepsilon_{r,A}kT}\right)^{3/2} \qquad (2)$$

$$B \equiv e_0\left(\frac{2N_A\rho_A}{\varepsilon_0\varepsilon_{r,A}kT}\right)^{1/2} \qquad (3)$$

In these equations (which are in SI units), N_A is the Avogadro's constant, k is Boltzmann's constant, e_0 is the proton charge, ε_0 is the permittivity of vacuum, ρ_A is the solvent density, $\varepsilon_{r,A}$ is the solvent dielectric constant and *T* is the absolute temperature. Using the SI values for N_A, k, e_0, and ε_0, and $\varepsilon_{r,A}= 78.38$, $\rho_A= 997.05$ kg/m³ for H_2O at 25 °C and 1 atm, we obtain A = 1.1744 (kg/mol)$^{1/2}$ and B = 3.285 × 10⁹ (kg/mol)$^{1/2}$ m⁻¹.

A computer program has been written for a specific electrolyte, where the values of the activity coefficients and the respective concentrations were introduced. Successive calculations have been made, where *a* varied from 1 × 10⁻¹⁰ m to 20 × 10⁻¹⁰ m (1 to 20 angstroms) with increments of 0.01 × 10⁻¹⁰ m. For a given set of *a* values at each concentration, the program calculates the corresponding set of values for *b*. So, a curve of *b* against *a* is finally found at each concentration. When we extend this calculation to all concentrations for which data were available, the computer program found the best couple of *a*–*b* values that adjusts simultaneously all these concentrations for that specific electrolyte. Table 1 shows the values thus obtained.

2. 2. Estimation of *a* Values from Kielland Data (theoretical approach)

From a table of ionic sizes presented by Kielland,[18] we have estimated values of *a*, as the mean value of the effective radii of the hydrated ionic species of the electrolyte (3rd column in Table 1). The diameters of inorganic ions, hydrated to a different extent, have been calculated by two different methods: from the crystal radius and deformability, accordingly to Bonino's equation for cations,[18] and from the ionic mobilities.[18]

2. 3. Estimation of *a* Values from Marcus Data (theoretical approach)

Using the data of Marcus (that is, interparticle distances, $d_{ion-water}$, of Table XIII of Ref.[19]) two approximations were performed in order to obtain *a* values of several salts in aqueous solution. Firstly, the *a* values were determined as the sum of the ionic radii (R_{ion}) reported by Marcus.[19] The R_{ion} values were obtained as the difference between the mean internuclear distance between a monoatomic ion, or the central atoms of a polyatomic ion, and the oxygen atom of a water molecule in its first hydration shell ($d_{Ion-water}$) and the half of the mean intermolecular distance between two water molecules in the bulk liquid water (the mean radius of a water molecule, $R_{water} = (1.39_3 \pm 0.002) \times 10^{-10}$ m).[19] That is, $R_{ion} = d_{ion-water} - R_{water}$ and $a = R_{cation} + R_{anion}$. These values are summarized in the 4th column in Table 1. In order to account for the effect of the ion hydration shell on the *a* values, a second approximation considering the sum of the $d_{ion-water}$ values reported by Marcus[19] was also done. In this approach the *a* values are determined as $a = d_{cation-water} + d_{anion-water}$. The values found are collected in the 5th column in Table 1.

2. 4. Molecular Modelling Studies

Molecular mechanic (MM) studies are a valuable tool to interpret atom or ion dynamic relations. They are simpler than *ab initio* calculations and yet gave very close results. For that reason they are adequate to evaluate dynamic processes like solvation changes and mean distances of approach between species in solution, involving dozens of molecules with hundreds of electrons, if necessary. Among the MM methods, [20] MM+ is a reference in the area and was used in this study. The results obtained are summarized in the last column in Table 1. They were obtained by considering no water molecules in between anion and cation.

Table 1: Summary of values of the mean distance of closest approach (a/10^{-10} m) for lanthanides and actinides salts in aqueous solutions, estimated from experimental data, ionic radius and other theoretical approaches

Electrolyte	Activity coefficients[a]	Kielland[18]	Marcus[19 b]	Marcus[19c]	Molecular mechanics MM+[d]
$CeCl_3$	–	6.0	3.0	5.7	4.4
$Ce(NO)_3$	–	6.0	2.9	5.7	–
$Ce(SO_4)_3$	–	7.5	–	–	–
$Ce_2(SO_4)_3$	–	6.5	–	–	–
$DyCl_3$	1.7	–	2.8	5.6	4.3
$Dy(ClO_4)_3$	3.7	–	3.4	6.1	–
$Dy(NO_3)_3$	–	–	2.8	5.5	–
$ErBr_3$	–	–	3.0	5.7	4.3
$Er(ClO_4)_3$	2.5	–	3.4	6.1	–
$Er(NO_3)_3$	3.0	–	2.7	5.5	–
$Er_2(SO_4)_3$	–	–	3.4	6.2	–
$EuCl_3$	2.1	–	2.9	5.6	4.6
$Eu(ClO_4)_3$	–	–	3.5	6.2	–
$GdCl_3$	2.0	–	–	–	4.3
$Gd(ClO_4)_3$	3.2	–	–	–	–
$Gd(NO_3)_3$	2.3	–	–	–	–
$HoCl_3$	1.7	–	–	–	4.3
$Ho(ClO_4)_3$	2.1	–	–	–	–
$LaBr_3$	–	6.0	3.1	5.9	4.4
$LaCl_3$		6.0	2.9	5.7	4.4
$La(ClO_4)_3$	–	6.3	3.6	6.2	–
$La(IO_3)_3$	–	6.6	–	–	–
$La(NO_3)_3$	–	6.0	2.9	5.7	–
$La_2(SO_4)_3$	–	6.5	3.6	6.3	–
$LuCl_3$	1.7	–	2.8	5.5	4.3
$Lu(ClO_4)_3$	2.2	–	3.4	6.0	–
$Lu(NO_3)_3$	1.8	–	2.7	5.5	–
$NdBr_3$	–	6.0	–	–	4.3
$NdCl_3$	–	6.0	–	–	4.3
$Nd(ClO_4)_3$	–	6.3	–	–	–
$Nd(NO_3)_3$	–	6.0	–	–	–
$Nd_2(SO_4)_3$	–	6.5	–	–	–
$PrBr_3$	–	6.0	–	–	4.3
$PrCl_3$	–	6.0	–	–	4.4
$Pr(ClO_4)_3$	–	6.3	–	–	–
$Pr(NO_3)_3$	–	6.0	–	–	–
$Pr(SO_4)_3$	–	6.5	–	–	–
$SmCl_3$	–	6.0	–	–	4.3
$Sm(ClO_4)_3$	–	6.3	–	–	–
$Sm(NO_3)_3$	–	6.0	–	–	–
$Sm(SO_4)_3$	–	6.5	–	–	–
$TbCl_3$	2.6	–	–	–	4.3
$Tb(ClO_4)_2$	1.4	4.8	3.2	5.9	–
$Tb(NO_3)_2$	2.3	4.5	–	4.8	–
$TmCl_3$	1.5	–	–	–	4.3
$Tm(ClO_4)_2$	2.5	–	–	–	–
$Tm(NO_3)_2$	2.2	–	–	–	–
$ThCl_4$	–	7.0	–	–	–
$Th(NO_3)_4$	–	7.0	–	–	–
UO_2Cl_2	3.3	–	–	–	–
UO_2F_2	5.2	–	–	–	–
$UO_2(NO_3)_2$	2.4	–	–	–	–
UO_2SO_4	1.7	–	–	–	–

[a] Eq. (1)[1] c $\leq$ 1.0 M.   [b] $a = R_{cation} + R_{anion}$.   [c] $a = d_{cation-water} + d_{anion-water}$.   [d] $a = d_{cation-anion}$[b20]

3. Results and Discussion

Table 1 summarizes *a* values of 4 cerium salts, 3 dysprosium salts, 4 erbium salts, 2 europium salts, 3 gadolinium salts, 2 holmium salts, 6 lanthanum salts, 3 lutetium lead salts, 5 lutetium salts, 5 praseodymium salts, 4 samarium salts, 3 terbium salts, 3 thulium salts, 2 thorium salts and 4 uranium salts in aqueous solutions, determined from different experimental techniques and/or theoretical approaches. One estimation of this parameter, at least, was done for every electrolyte.

Table 1 shows that the values of *a* obtained by fitting experimental data of activity coefficients (2nd column) are close to those obtained from the sum of ionic radii in solutions of Marcus (or crystal-lattice spacing) or the interatomic distances, $d_{ion-ion}$ (4th column) being, however, smaller than those obtained from molecular mechanic studies (6th column of table 1), and than the sum of the mean ion–water internuclear distances (5th column). In addition, they are smaller than those obtained from Kielland's data (3st column), being the last ones approximately equal to those obtained from the mean ion–water internuclear distances (5th column). This situation was not expected, if we have in mind that all estimations already obtained from these experimental methods (i.e., Kielland's and activity coefficients data), applied to other electrolytes, [13–17] led us to reach, in general, similar values. In the cases of lanthanide and actinides, some effects as ion-ion and hydrodynamic interactions, not taken into account in their estimations, can be responsible for masking the real values of parameter *a* (for example, values even **s**maller than the sum of the ionic radii verified for the electrolyte $DyCl_3$, where $a = 1.7 \times 10^{-10}$ m). On the other words, it is necessary to take into account that these Kielland data result from equations involving ionic mobilities (or phenomenological coefficients) which are rigorously valid only at very high dilution. Under those circumstances, the ion-ion and hydrodynamic interactions[21–25] (not considered in this model) can actually influence the phenomenological coefficients and ionic mobilities and, consequently, lead to obtain non real *a* values.

Also, the estimation of parameter *a* from D–H model (Eq. 1), as an adjustable parameter, presents limitations due to some effects, such as ion–ion and ion–solvent interactions[21–25] also not taken into account. For example, the ion–ion interactions were assumed to be purely coulombic in origin, and short-range noncoulombic forces, such as dispersion forces, have not been considered. These phenomena, not considered in D-H (Eq. 1), together with the others not contemplated by Kielland equations, may be responsible for masking the real values of parameter *a*, leading us to obtain very different values, through the cited methods.

Thus, due to the complexity of the electrolyte solution structure, it would be expected that an intermediate situation ought to be more real. That is, for these salts of lanthanides and actinides showed in Table 1, the real values may be greater than those obtained by fitting experimental data of activity coefficients (or the sum of ionic radii in solutions), and smaller than the ones obtained by fitting experimental data of Kielland (or of the sum of mean ion–water internuclear distances). Thus, they may be estimated by the average of the most suitable values of *a*, and their physical meaning could be interpreted on the basis of the collision of hydrated cations and anions, respectively, and consequently on the compaction of their hydration shells in some extension.

4. Conclusions

It is not possible to accurately know the mean distance of closest approach of ions, *a*, in an electrolyte solution, however desirable that would be. We have found a similar behaviour when studying this parameter involving other ions.

We present here several estimations of *a* using different methods, so that the researcher who needs to use this parameter may have an idea of the possible range of values. All of them could be reasonable compromises to select an adequate *a* value, depending on their applicability to a given real problem. In general, an average value may be the better option, unless there is any specific reason for choosing alternative calculated values.

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6. References

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