

Hydration thermodynamics and hydrodynamic (Stokes) radius of the lanthanide ions

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Abstract

Biochemical and physiological properties depend on the size of ions and the thermodynamic quantities of ion hydration in numerous states. The diffusion coefficient (D) of lanthanide series ions (Ln^{+3}) in solution ($1.558-1.618 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) as calculated by the Einstein–Smoluchowski relation depended on conductance measurements as electro - analytical measurement. The association constant (K_A) of Ln^{+3} ions ($210.3-215.3 \text{ dm}^3 \text{ mole}^{-1}$) was calculated by using the Shedlovsky method, and the hydrodynamic radius was ($1.515-1.569 \times 10^{-10} \text{ m}$) as calculated by Stokes–Einstein equation. ΔH° , values were obtained from the literature. The thermodynamic functions (ΔG° , ΔS°) were calculated by suitable equations, ΔG° , for ion hydration, had negative values in the range (13.25 - 13.31 kJ/mole), ΔS° also were of negative values, results have been shown in the limit (11.299 - 12.573 kJ/ K. mole).

Key words

Lanthanides,
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الترموديناميك الحرارية المائية وأنصاف الأقطار الهيدرودينامية (ستوكس) لأيونات اللانثانات

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الخلاصة

الصفات البايوكيميائية والفيسيولوجية تعتمد على حجم الايونات ومقادير الديناميكا الحرارية للايون المتمي في المحلول المائي في حالات عديدة. تم حساب معامل الانتشار لايونات اللانثانات ثلاثية حالة التأكسد ($1.558-1.618 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) باستخدام معادلة Einstein–Smoluchowski بالاعتماد على قياسات التوصيلية كطريقة كهرو- تحليلية. تم حاسب ثابت الارتباط للايونات ($210.3-215.3 \text{ dm}^3 \text{ mole}^{-1}$) باستخدام طريقة (Shedlovsky method)، انصاف الاقطار الهيدرودينامية تم حسابها ($1.515-1.569 \times 10^{-10} \text{ m}$) باستخدام معادلة (Stokes–Einstein). قيم ΔH° تم اعتمادها من المصادر العلمية. ثوابت الديناميك الحرارية (ΔG° و ΔS°) حسبت باستخدام المعادلات المناسبة، قيم ΔG° للايونات المتميئة كانت سالبة في مدى (-13.25 kJ/mole) وقيم ΔS° سالبة في حدود (11.299-12.573 kJ/ K. mole).

Introduction

Lanthanides are critical components used in various recent technologies, from batteries of electric cars, wind turbines magnets, security inks, optical glasses, hard disk drives, and lasers [1, 2]. In medicine and nanotechnology the lanthanide has important development in human health like

sensing fluorescent tags, drug delivery, diagnosis cancer, treatment of burn wounds, and bone tissue disease [3-7]. Lanthanides (in full body examine studies) are found in trace amount in numerous organs like bones, kidney, spleen, and liver. In eyes the amount of the lanthanides found to be different in an extensive range. Studies in

biochemistry signed to the greatest significant of lanthanide concentration accrued in many organs vary with different diseases steps progress [8].

The significant biochemical properties of lanthanide series (Ln^{+3}) (Fig. 1) are due to their 4f electrons ($\text{Ln}^{+3} = [\text{Xe}] 4f^{1-14} 5d^1 6s^2$) [1].

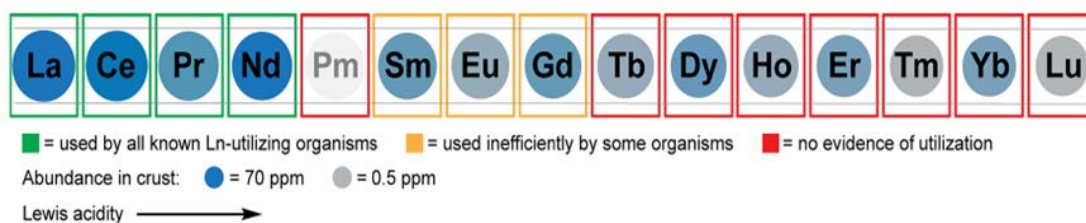


Fig. 1: Some properties of the lanthanide series [1].

In body tissues, electrolytes (ions) are important in a number of functions like neuron activation, body osmotic fluids pressure and muscle contractions. The ability function of lanthanides for numerous biological properties in many biomolecules (ex. in proteins and bone) is replace calcium, without essentially replacing for it role [9, 10]. The toxicity of Ln^{+3} ions can be measured by its amount of aberration from pertinent reference essential ion such as Ca^{+2} [8]. Ln^{+3} salts in water as part of the solution chemistry have varied inferences in many fields such as element tracing,

materials processing and medicine [11]. Many bio-chemical and physiological properties, like effectiveness of a membrane separation process, depend on the size of ions [12]. Ion- water associations in aqueous environment can be termed as $\text{M}^{Z+}(\text{H}_2\text{O})_n$ where (n) is the molecules of water interacting with the ion M^{Z+} by hydrogen bonds (HB) to build a hydration (solvation) shells (Fig. 2), so the effect size is the hydrated radius [13, 14], and this supplies the next independent effects to the thermodynamic quantities of ion hydration.

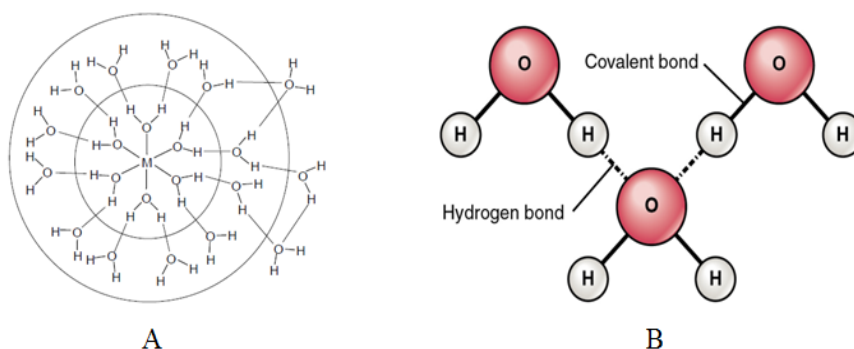


Fig. 2: A- The solvation shells of M^{3+} ion (e.g. M^{3+} of group 3) in water solution [15], B- Hydrogen bonds between water molecules.

The present work reports conductance measurements (Electro-Analytical Measurements), hydrodynamic (Stokes) radius, association constant and, thermodynamics properties for ion hydration of lanthanide ions in water solution at temperature, 298.15 K.

Calculation procedure and results

1. Conductivity, mobility and diffusion coefficient of lanthanide ions in water solution at $T=298.15$ K. The solvation process and ionic hydration of ions play a very significant role in a solution chemistry [16]. The

conductance transport property is important because it provides benefit information about ion association and ion-solvent hydration [17]. At infinite dilution conductance and diffusion properties can be accumulated to velocity, because, the interionic forces which repel transfer of ions disappear in a solution. Ion hydration is the greatest interactions, which is generally used in the chemistry of solutions. The diffusion coefficient (D) of ions in solution can be found by Einstein-Smoluchowski, [18].

$$D = \frac{k_B T}{q} \mu \quad (1)$$

D: ($\text{m}^2 \text{s}^{-1}$), T: Temperature (K), μ : Ion mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$), k_B : Boltzmann

constant (J K^{-1}), q: Charge elementary (Coulomb).

The mobility (μ) of ion hydration in solution can be represented by Eq.(2) [19]:

$$\mu = \frac{\lambda}{zF} \quad (2)$$

λ : Ion molar conductivity ($\text{S m}^2 \text{mol}^{-1}$),
Z: Ion charge number (without units),
F: Faraday constant (Coulomb).

Limiting conductance of Ln^{3+} ions in water is obtained from literature [20]. The calculation procedure of molar conductivity, λ , mobility, μ , and diffusion coefficient, D, for lanthanide ions in water at temperature 298.15 K are based on references [21-23]. The results are listed in Table 1 and as shown in Figs. 3 and 4.

Table 1: The infinitive molar conductance λ , the mobility μ , and, the coefficient of diffusion D for lanthanide series.

Ion		$\lambda \times 10^{-4}$ $\text{S m}^2 \text{mol}^{-1}$	$\mu \times 10^{-8}$ $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$	$D \times 10^{-9}$ $\text{m}^2 \text{s}^{-1}$
Lanthanum	La^{3+}	196.5	6.79	1.618
Cerium	Ce^{3+}	195.3	6.75	1.608
Praseodymium	Pr^{3+}	194.1	6.71	1.599
Neodymium	Nd^{3+}	192.9	6.66	1.587
Promethium	Pm^{3+}	191.7	6.62	1.577
Samarium	Sm^{3+}	191.7	6.62	1.577
Europium	Eu^{3+}	192.0	6.63	1.580
Gadolinium	Gd^{3+}	189.9	6.56	1.563
Terbium	Tb^{3+}	189.9	6.56	1.563
Dysprosium	Dy^{3+}	189.3	6.54	1.558
Holmium	Ho^{3+}	190.2	6.57	1.565
Erbium	Er^{3+}	190.2	6.57	1.565
Thulium	Tm^{3+}	189.9	6.56	1.563
Ytterbium	Yb^{3+}	190.5	6.58	1.568
Lutetium	Lu^{3+}	190.8	6.59	1.570

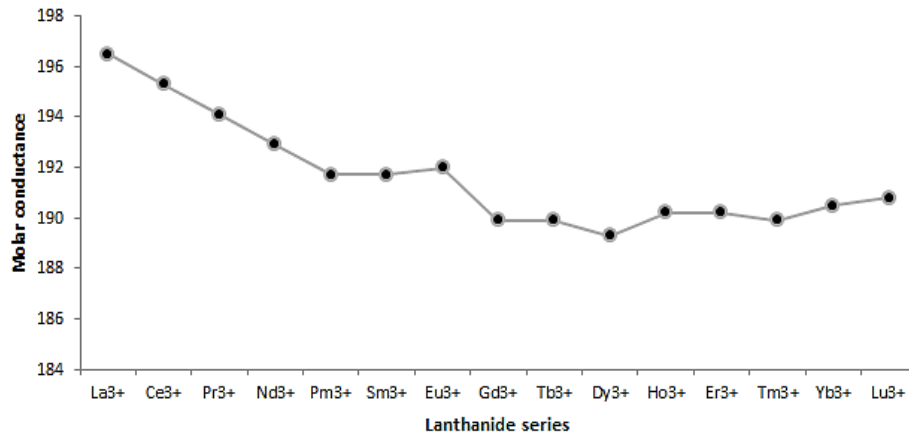


Fig. 3: The infinite molar conductance ($\times 10^{-4} S m^2 mol^{-1}$) of lanthanide series.

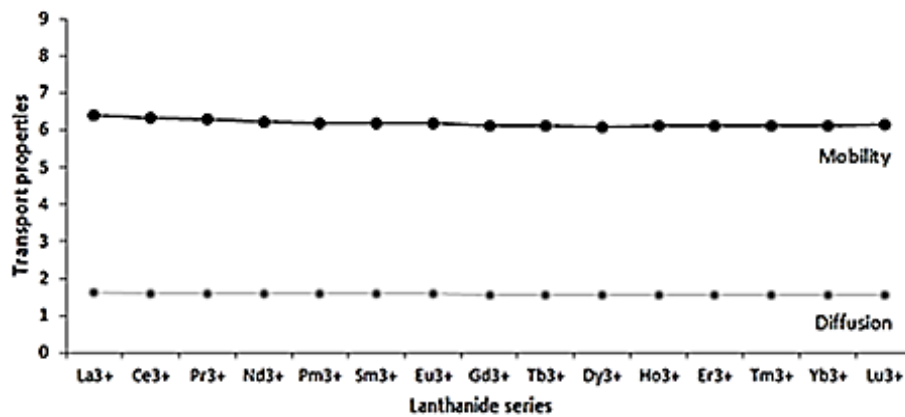


Fig. 4: The mobility ($\times 10^{-8} m^2 V^{-1} s^{-1}$), and diffusion coefficient ($\times 10^{-9} m^2 s^{-1}$) of lanthanide series.

The lanthanide series ions are basically found in the (+3) oxidation state with a number of water molecules surrounding the ion by hydrogen bonds in their aqua complexes in water solution. This affects their transport properties like conductance. From Table 1, it is noticed that the infinite molar conductance of lanthanide series have close values between 196.5×10^{-4} - $189.3 \times 10^{-4} S m^2 mol^{-1}$, with difference at $7 \times 10^{-4} S m^2 mol^{-1}$. This is reflected on the values of mobility and diffusion coefficients for lanthanide series as shown in Figs.3 and 4.

2. Hydrodynamic radius of lanthanide ions in water solution at 298.15 K:

Lanthanides in solutions have coordination number between six

(C.N.6) to twelve (C.N.12). The coordination number nine (C.N.9), Fig.5 [24] is the main observed geometry in solution [8]. Ln^{3+} ions ionic radius decreases through the ions series because the (4f) electrons have slight effect on bonding (lanthanide contraction). Ionic radius for Ln^{3+} series is in the range of $(1.03-0.86 \times 10^{-10} m$ (C.N.6), $1.16-0.98 \times 10^{-10} m$ (C.N.8) and $1.22-1.03 \times 10^{-10} m$ (C.N.9)) for La^{3+} to Lu^{3+} respectively, Pr^{3+} ion is of the same radius as Ca^{2+} (1.12 for C.N.8).

Researches have shown similarities between Ln^{3+} utilization, storage and transport to the widely defined bioinorganic chemistry of Fe^{3+} and Ca^{2+} ions [1, 25].

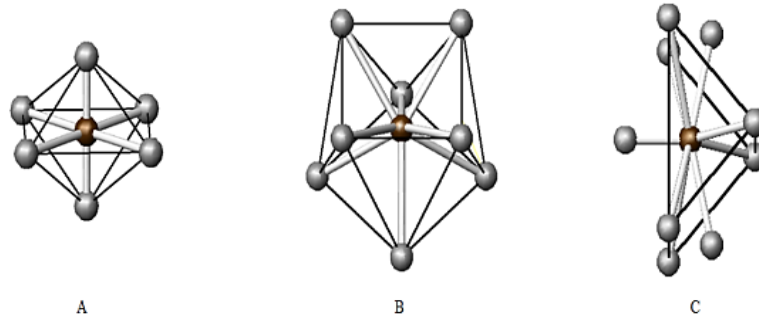


Fig. 5: The geometry structures for A: octahedron, (C.N.6), B: square antiprism, (C.N.8), and C: tricapped trigonal prism, (C.N.9) [24].

In aqueous solutions, HB interactions describe the arrangement of ions with water molecules association [13]. Hydrodynamic (Stokes) radius of a solute is the radius of hard sphere that diffuses at the same ion or solute speed in water solution. The hydrodynamic radius (Stokes radius) for Ln^{3+} diffusing ions can be obtained via Stokes–Einstein equation (Eq. (3)) [26].

$$R = \frac{KT}{6\pi\eta D} \quad (3)$$

R , hydrodynamic radius of the Ln^{3+} ions (m), and η , dynamic viscosity ($\text{g m}^{-1}\text{s}^{-1}$).

The results of equation 3 and the ionic radius of Ln^{3+} in different coordination numbers [27, 28] are listed in Table 2, and demonstrated in Fig.6.

Table 2: Ionic and hydrodynamic radiuses of lanthanide series.

Ion	Atomic No.	$r \times 10^{-10} \text{ m}$ C.N. 6 ^[27]	$r \times 10^{-10} \text{ m}$ C.N. 8 ^[27]	$r \times 10^{-10} \text{ m}$ C.N. 9 ^[28]	$r \times 10^{-10} \text{ m}$ Hydrodynamic
La^{3+}	57	1.032	1.160	1.220	1.515
Ce^{3+}	58	1.010	1.143	1.198	1.525
Pr^{3+}	59	0.990	1.126	1.176	1.533
Nd^{3+}	60	0.983	1.109	1.163	1.545
Pm^{3+}	61	0.970	1.090	1.147	1.555
Sm^{3+}	62	0.958	1.079	1.128	1.555
Eu^{3+}	63	0.947	1.066	1.123	1.552
Gd^{3+}	64	0.938	1.053	1.106	1.569
Tb^{3+}	65	0.923	1.040	1.097	1.569
Dy^{3+}	66	0.912	1.027	1.083	1.574
Ho^{3+}	67	0.901	1.015	1.074	1.567
Er^{3+}	68	0.890	1.004	1.062	1.567
Tm^{3+}	69	0.880	0.994	1.050	1.569
Yb^{3+}	70	0.868	0.985	1.040	1.564
Lu^{3+}	71	0.861	0.977	1.030	1.562

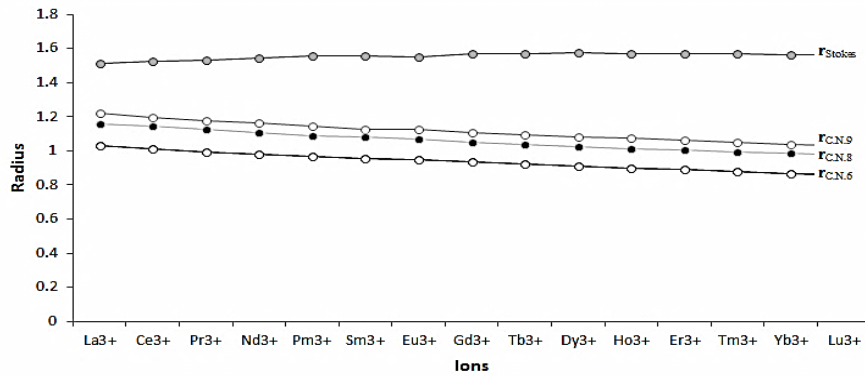


Fig. 6: The hydrodynamic and ionic radiuses ($r \times 10^{-10}$ m) for lanthanide series in different coordination numbers.

The 4f electrons have little effect on lanthanide series ions bonding (the lanthanide contraction), consequently, the values from Table 2 and Fig.6, shows that:

The ionic radius for lanthanide series at different coordination numbers is very closer in values (with a difference 0.17×10^{-10} m, 0.18×10^{-10} m, 0.19×10^{-10} m, in lanthanide series at C.N. 6, 8 and 9 respectability) and decreased as the atomic number increases in series, while the hydrodynamic radii in opposite side rearrangement with narrow differences in value (less than 0.1×10^{-10} m, through the series). The hydrodynamic radii for Gd^{3+} - Lu^{3+} are larger than that for La^{3+} - Eu^{3+} ions. This is relevant to the fact that a smaller ion interacts with larger molecules of water as it transfers via a solution. The hydrodynamic radius depends on the ionic size and the charge of the central ion. Water molecules interacted more with Gd^{3+} - Lu^{3+} , which have charge densities (Z/r) than with La^{3+} - Eu^{3+} of less charge densities. This indicates that Gd^{3+} - Lu^{3+} ions hold more hydration shell from water molecules.

3. Thermodynamic functions of lanthanide ions in water at 298.15 K:

Ion hydration in solution gives benefit quantities of ion-water association like diffusion coefficients and thermodynamic properties [29]. The chemo-physical properties of HB

transmit the intermolecular modifications as a consequence to hydrogen bonds formation in solution. So HB affects the dynamic and thermodynamic properties of solvents [30]. The conductance values of ion hydration at infinitive dilution allow the determination of association and thermodynamic constants.

The attraction between ions and water molecules in ion hydration is measured by association constant (K_A). To calculate the association constant Shedlovsky method is used (Eqs. (4, 5 and 6)) [30].

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_0} + \frac{K_A C A f_{\pm}^2 S(Z)}{\Lambda_0^2} \quad (4)$$

$$-\log f_{\pm} = \frac{A\sqrt{I}}{1+BR\sqrt{I}} \quad (5)$$

$$A = \frac{1.8247 \times 10^6}{(D_1 T)^{3/2}}; \quad B = \frac{0.5209 \times 10^{10}}{\sqrt{D_1 T}}$$

$$S(Z) = \left(\frac{Z}{2} + \sqrt{1 + \left(\frac{Z}{2} \right)^2} \right)^2 \quad (6)$$

$$Z = \left[\frac{S}{\Lambda_0^{3/2}} \right] \sqrt{C A}; \quad S = \alpha \Lambda_0 + \beta$$

$$\beta = \frac{82.501}{\eta \sqrt{D_1 T}}; \quad \alpha = \frac{0.8204 \times 10^6}{(D_1 T)^{3/2}}$$

D_1 : Dielectric constant (without units). The molar conductivities, Λ , of Ln^{3+} ions in solution at Eq. 4 are calculated by Eq. (7) [31].

$$\Lambda = \Lambda^0 - (A + B \Lambda^0) \sqrt{C} \quad (7)$$

Λ^0 : Limiting molar conductivity ($S \text{ m}^2 \text{ mol}^{-1}$), C: solution concentration (mol dm^{-3}), Λ : molar conductivity ($S \text{ m}^2 \text{ mol}^{-1}$), A, and B are constants

that depend on water solvent viscosity, dielectric constant, temperature, and ion charge. Gibbs free energy ΔG° , ("a measure of usable energy in the system") via the association interaction is resulted from Eq.(8) [30].

$$\Delta G^\circ = -RT \ln K_A \quad (8)$$

R ($J K^{-1} mol^{-1}$), constant of gas.

Gibbs-Helmholtz relation (Eq. 9) [30] has been applied to evaluate ΔS° , the change of entropy ("the state function

that gives a measure of disorder or randomness").

The Ln^{+3} ion hydration enthalpies, ΔH° , ("the association heat change when one mole of a compound results from elements") are obtained from literature [29].

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

The data obtained from Eqs. (4, 7, 8 and 9) are listed in Table 3.

Table 3: The molar conductance, the association constants, and, the thermodynamics of lanthanide series.

Ion	$\lambda_{+} \times 10^{-4}$ $S m^2 mol^{-1}$	K_A $dm^3 mol^{-1}$	ΔG° $kJ mol^{-1}$	ΔH° ^[29] $kJ mol^{-1}$	ΔS° $kJ K^{-1} mol^{-1}$
La ³⁺	179.3	210.3	-13.25	-3395	-11.342
Ce ³⁺	178.1	211.8	-13.27	-3382	-11.299
Pr ³⁺	177.0	211.9	-13.27	-3441	-11.497
Nd ³⁺	175.8	213.5	-13.29	-3429	-11.456
Pm ³⁺	-	-	-	-	-
Sm ³⁺	174.7	213.6	-13.29	-3561	-11.899
Eu ³⁺	175.0	213.2	-13.29	-3612	-12.159
Gd ³⁺	173.0	214.5	-13.30	-3617	-12.087
Tb ³⁺	173.0	214.5	-13.30	-3621	-12.100
Dy ³⁺	172.4	215.3	-13.31	-3614	-12.077
Ho ³⁺	173.3	214.1	-13.30	-3674	-12.278
Er ³⁺	173.3	214.1	-13.30	-3740	-12.499
Tm ³⁺	173.0	214.5	-13.30	3762-	-12.573
Yb ³⁺	173.5	215.2	-13.31	-3721	-12.436
Lu ³⁺	173.8	214.8	-13.30	-3751	-12.536

The results from hydrodynamic radii indicates that the number of water molecules associated with lanthanide series ions are very near (because the charge densities (Z/r) depends on the ionic size (very closer) and the charge of the central ion (equal to +3)), So this affected the thermodynamics association interaction parameters in near values as a results with little differences.

From Table 3 the results show that: The Gibbs free energy ΔG° , for ion hydration has negative values because the association is favored rather than the dissociation in solution. A negative ΔS° , the change of entropy results in a decrease of disorder of ions in water solution, because of increase in the

solvation of Ln^{+3} ions. This can be accumulated to decrease in the freedom degree through forming ion hydration. The hydration enthalpies ΔH° , are of negative values in solution, and this indicates that the interaction between ions with a negative values exothermic processes.

Conclusion

Molar conductivities of Ln^{+3} ions in water solution have been reported at $T = 298.15 K$ according to the limiting molar conductivities. Shedlovsky method was used to calculate the association constant. Stokes–Einstein relation was applied to calculate the hydrodynamic radius.

The lanthanide series ions interact with closer numbers of water molecules surrounding ion via hydrogen bonds in water solution, and this affecting their transport properties, so it was noticed that the infinitive molar conductance of lanthanide series have very close values between 196.5×10^{-4} - 89.3×10^{-4} S m² mol⁻¹. This affected the values of mobility (6.54×10^{-8} m²V⁻¹s⁻¹ – 6.79×10^{-8} m²V⁻¹s⁻¹) and diffusion coefficient (1.558×10^{-9} m² s⁻¹– 1.618×10^{-9} m²s⁻¹) for lanthanide series.

The 4f electrons have very little effect on lanthanide series ions bonding, so the ionic radius of lanthanide series at different coordination numbers were of very close values (with a difference 0.17×10^{-10} m, 0.18×10^{-10} m, 0.19×10^{-10} m, in lanthanide series at C.N. 6, 8 and 9 respectively) and decreased as the atomic number increases through the series. The hydrodynamic radius of Ln⁺³ ions increased as the ionic radius decreases because of the increase in charge densities through the lanthanides series, with little difference in values (less than 0.1×10^{-10} m), via the series. The hydro-dynamic radii of Gd³⁺-Lu³⁺ are larger than that of La³⁺- Eu³⁺ ions. This is relevant to the fact that a small ion interacts with larger molecules of water as it transfers via a solution. The results from hydrodynamic radii indicated that the number of water molecules associated with lanthanide series ions is very near (because the charge densities (Z/r) depends on the ionic size (very closer) and the charge of the central ion (equal to +3)), so this effected on thermodynamics association interaction parameters in near values as a results with little differences. The Ln⁺³ ions hydration enthalpy, ΔH° , was obtained from literature. Gibbs free energy ΔG° and the change of entropy, ΔS° are resulted

from the appropriate equations. ΔG° , for ion hydration has negative values because the association is favored rather than the dissociation in solution. A negative ΔS° , results indicate a decrease in disorder of ions in water solution, because of increase in the solvation of Ln⁺³ ions. ΔH° values were negative in solution, and this refers to exothermic association process.

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