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Diffusion coefficients of trivalent rare earth/actinide ions in acid and alkaline aqueous solutions

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Diffusion coefficients of trivalent rare earth/actinide ions in acid and alkaline aqueous solutions

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Abstract. Leaching is one of the key process of rare earth (RE) element recovery. This paper was set out to validate the effectiveness of acid/alkali in RE leaching by measuring the limiting ionic conductivity (λ_o), self-diffusion coefficient (D_i) and overall diffusion coefficient (D_{AB}) to obtain a clear insight on the transport properties of ions and salts in aqueous solution. The calculation diffusivity of D_i which is diffuse individual ions in pure water and D_{AB} diffuse in chemical reagents were determined using Nernst-Haskell equation, applicable for 25ºC. The results of D_i were found to be consistent with experimental data from the literature where most of calculation and experiment data are less than 5% error. The final outcome had managed to confirm that NaOH is best reagent for most RE element leaching, which suits the common practice of the industry.

1. Introduction

Technically, Rare Earth (RE) elements are shown as a series of 15 lanthanide elements, as well as scandium and yttrium, in the periodic table [1]. In the new era of globalization, the industry has a renewed interest in benefiting RE elements as main components in electronics due to the unique physicochemical properties that the elements possess [2]. However, along with its popular demands, the extraction of RE elements from mineral ores remains a major issue. Considering the recent trends in technology, science experts have been urged to explore ways that would be effective to obtain RE elements and overcome the concerns for supply [3-4]. Studying the mechanism of RE extraction will provide important insights to manage the resources in the most cost-effective approach.

Generally, the overall RE processing consists of six important steps including deposit mining, beneficiation, chemical treatment, separation, refining and purification [5]. The pure RE elements exist in complex rocks, known as mineral ores and recovered in the beneficiation process [5-6]. Commercial sources of minerals and the respective elements contain bastnesite (La, Ce) FCO_3, monazite, (Ce, La, Y, Th) PO_4 and xenotime YPO_4 [2, 6]. Central to the subject of extracting pure RE elements is the chemical treatment step, in which RE elements are isolated from the mineral ore. The chemical treatment (or RE extraction) consists of two crucial sequential steps; first is solid liquid extraction (leaching) and liquid-liquid extraction (solvent extraction process). Leaching is the key process to maximize RE extraction and its recovery from ores. As highlighted by several authors, the chemical reagent used for the leaching process is the most essential factor to ensure effective RE recovery [7-8]. Chemical reagents that are strong acid and strong alkali are much favoured [9]. There are several common types of acid/alkali treatment including sulphuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl),

sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3) [10]. Sulfuric acid (H_2SO_4) and caustic soda (NaOH) are mostly used by the industry. Chemical treatment in leaching process may take over to leach the RE elements concentration.

In order to apply hydrometallurgy for RE leaching, it is essential to acquire the thermodynamic aspects and quantities such as enthalpies, entropies, standard partial molar volume, resistivity, thermoelectric power, and thermal conductivity; in a case concerning RE elements, the data for trivalent RE and actinide ions have been studied by several authors [11-12]. What remains scarce is the information on limiting transport properties like limiting ionic conductivity (λ_o), and the self-diffusion coefficient (D_i) [12]. The study by Mauerhofer et al. [12] calculated the λ_o based on Stokes-Einstein law and D_i using Nernst-Einstein relation for trivalent RE and actinide ions dissolved in pure water at 25 ^{o}C and found that the calculation results match the experimental data. It is important to unravel the mechanism of the process by measuring the diffusivity of electrolytes by considering the ionic dissociation of acid/alkali in the medium, relative for the individual lanthanide and actinide ions. To date, the impact of acid/alkali in RE extraction and diffusivity has long become the subject of interest. Current literature successfully tested the effectiveness of reagents in RE diffusivity, many of which using the value of D_i as a method of measure. Surprisingly, most scholars have yet to provide a systematic evaluation of leaching RE using acid/alkali in terms of the mechanism of the process. In other words, most have neglected to extend their scope to include the behaviour of the ionic liquid which could be assessed using the D_{AB} value. This study was designed specifically to understand the transport of RE elements in the leaching medium, as well as substantiate the diffusivity of cations and anions of acid/alkali reagents by determining the overall diffusion coefficient (D_{AB}) as a measure of efficacy for RE leaching. The objective of this paper is to describe RE leaching process with involvement of acid/alkali reagents in terms of the self-diffusion D_i and overall diffusion coefficient D_{AB} by using Nernst-Haskell equation.

2. Methodology

Figure 1 shows proposed method for acid/alkaline reagents selectivity of RE leaching proses. The relative effect of acid and alkali as transport reagents to assist diffusion of RE salt was evaluated in this study. The self-diffusion coefficient (D_i) resembles the diffusivity of the lanthanide and actinide ions, while overall diffusion coefficient (D_{AB}) measures the ability of an acid/alkali in contributing to diffusion of the RE ions in the ionic medium. First, the values of D_i were calculated using λ_o data from Spedding et al. [13]. The D_i for individual ion, in a diluted single salt solution at 25°C can be calculated from Nernst-Haskell equation as shown in equation (1) [14-15].

$$D_i = 2.66 \; x \; 10^{-7} \; \frac{\lambda_o}{n_o} \tag{1}$$

where λ_o is the limiting ionic conductance and n_o is the charge of valence of the ion species.

The limiting ionic conductivity (λ_o) represents the magnitude of conductivity caused by per mole ions in a diluted solution at 25 °C [16]. A tabulated data on the value of λ_o for various ions are easily available from Astle and Beyer [17]. Meanwhile, the experimental value of λ_o for RE and actinide ions have long been reported by Spedding et al. [18]. Meanwhile, Mauerhofer et al. [12] studied λ_o and D_i of lanthanide ions in pure water at 25°C. The calculated D_i were then compared with the experimental data from literature data.

After that, the values of D_i were used to calculate the values of D_{AB} which refers to the diffusivity of cation and anion components in an acid/alkali used for leaching. The equation of molecular diffusivity in a diluted solution (D_{AB}) as shown in equation (2) includes the valence of the cation and anion, as well as ionic conductance respective of each cation and anion species. In a case where two or more chemical species are present at different concentrations, inter-diffusion (counter diffusion) must be included to satisfy electro-neutrality [13]:

$$D_{AB} = 8.928 \; X \; 10^{-10} T \frac{\frac{1}{n_+} + \frac{1}{n_-}}{\frac{1}{\lambda_+} + \frac{1}{\lambda_-}} \tag{2}$$

where D_{AB} is the molecular diffusivity in a diluted solution in cm^2/s while n$_+$ and n$_-$ are the valence of cation and anion. λ_+ and λ_- are the limiting ionic conductance for cation and anion, respectively.

The purpose to calculate D_i is to validate λ_0 value, which is obtained from Spedding et al [13]. After validation of the results, λ_0 is employed in D_{AB} calculation where the results and findings are discussed and presented in Section 3.

3. Results & Discussion

3.1. Transport Properties of Self Diffusion Coefficient (D_i)

The experimental values of D_i for trivalent RE and actinide ions were obtained from literatures that had performed an empirical study on RE extraction employing the open-end-capillary tube method [13, 19-20]. The experiment was performed under standard condition at 25ºC and 1 atm. The calculated values for D_i was determined by using equation 1 and the results are demonstrated in figures 1 and 2, while detailed numbers are tabulated in table 1.
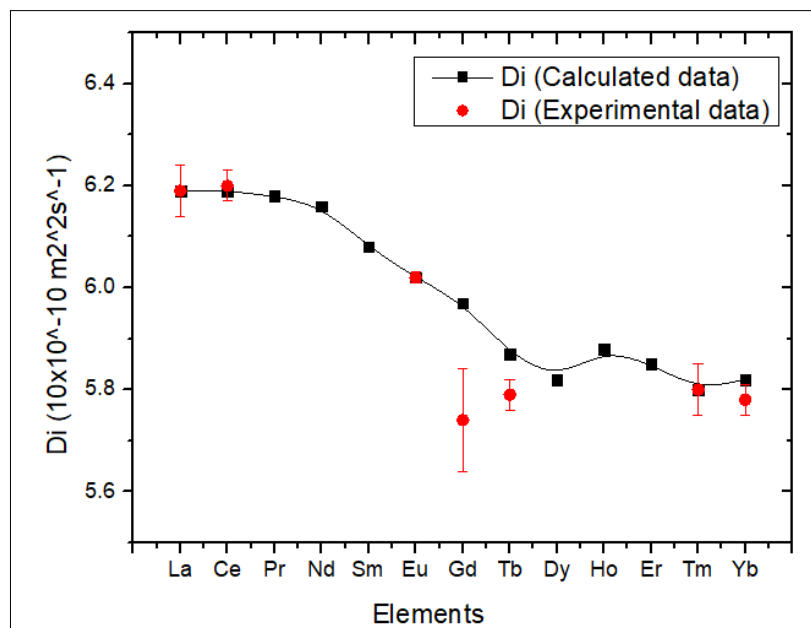

Figure 1. Self-diffusion coefficient (D_i) for lanthanide elements. Mean value and standard deviation error of experiment data (circle).
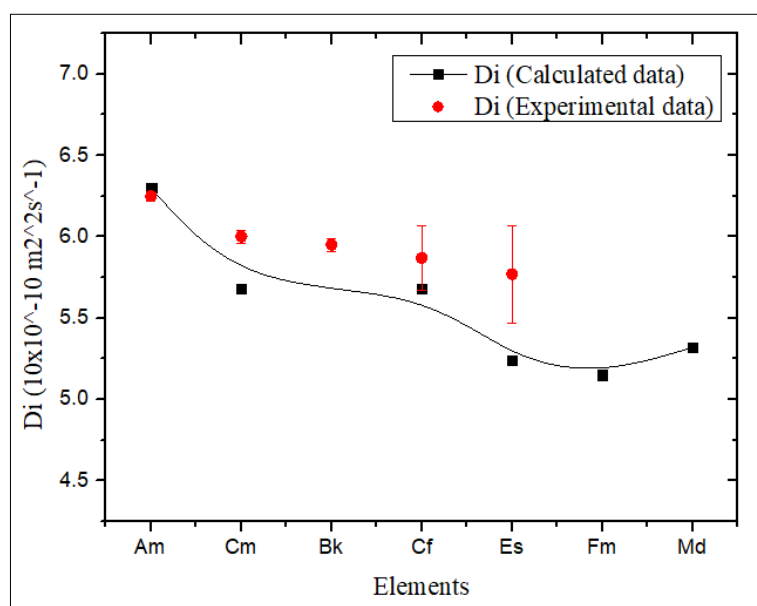
Figure 2. Self-diffusion coefficient (D_i) for actinides elements. Mean value and standard deviation error of experiment data (circle).

The plotted graphs in figures 1 and 2 clearly indicate that D_i is an important predictor of the efficacy of a leaching system. It appears that the results obtained by calculation are positively good agreement with the experimental data except for Gd^{3+} and Tb^{3+}. This high error is due to some experimental error to find λ_0 for both elements. However, this error can be tolerated because only two elements are deviate compare to the other five elements which is positively agreement with experiment data.

On the other hand, the predicted values for C_m, E_a and F_m elements from actinide series were underestimated with minimum errors of less than 10%. Despite the deviation, the trend of plots of the calculated results is consistent with the experimental data. It is rather motivating to find that the projection exhibited in both figures is in fact similar with finding by Mauerhofer et al. [12]. Looking from another perspective, it is somewhat noticeable that the decreasing trend of D_i for both lanthanide and actinide cations may have a correlation with the atomic weight of each individual ions. Literature studies revealed that smaller elements possess lower atomic weight, which eventually affect the value of its D_i.

3.2. Overall Diffusion Coefficient (D_{AB}) in Acid/Alkaline Aqueous Solution

The value of D_{AB} is calculated to define the characteristic of H_2SO_4, HCl, HNO_3, NaOH, or Na_2CO_3 in leaching each of the RE and actinide ions. Nernst-Haskell equation was used to determine the value of overall diffusivity coefficient (D_{AB}) with λ_o obtained from Spedding et al. [16], calculated for standard condition at 25^oC and 1 atm. Currently, the experimental values of D_{AB} for RE and actinide ions are not available in literature except for D_{AB} value $EuCl_3$ as shown in table 1. A satisfactory agreement between the predicted result and the experimental data were observed for element $EuCl_3$ at 25^oC. The D_{AB} value of $EuCl_3$ calculated that the model is in good prediction which is the result similar to experimental data by Ribeiro et al. [21]. However, the others experimental values of D_{AB} are not available. Considering the important of knowledge contribution in RE extraction process, the prediction of D_{AB} values could be useful in preliminary study and as a reference in industrial application.

Table 1. The experimental data and the calculated results of D_i and D_{AB} for trivalent RE and actinide series ions at standard condition (T=25°C and P =1 atm).

RE Elements (charges)	λ_o[20] 10^{-4} m²S eq⁻¹	D_i (Experimental Data) 10^{-10} m²s⁻¹	D_i (This study) 10^{-10} m²s⁻¹	$\Delta[D_{i(exp)} - D_{i(cal)}]$ %	D_{AB} (This Study) (m²/s) H₂SO₄	HCl	HNO₃	NaOH	Na₂CO₃
Lanthanide									
La (3+)	69.7	6.19 c	6.19	0	8.26E-10	1.29E-09	1.25E-09	1.74E-09	7.47E-10
Ce (3+)	69.8	6.20 a	6.19	0.2	8.27E-10	1.29E-09	1.25E-09	1.74E-09	7.45E-10
Pr (3+)	69.6	-	6.18	-	8.26E-10	1.29E-09	1.25E-09	1.73E-09	7.42E-10
Nd (3+)	69.4	-	6.16	-	8.24E-10	1.29E-09	1.25E-09	1.72E-09	7.40E-10
Pm (3+)	NA	-	NA	-	NA	NA	NA	1.71E-09	7.38E-10
Sm (3+)	68.5	-	6.08	-	8.19E-10	1.28E-09	1.24E-09	1.71E-09	7.38E-10
Eu (3+)	67.8	6.02 a	6.02	0	8.14E-10	1.27E-09	1.23E-09	1.72E-09	7.38E-10
Gd (3+)	67.3	6.04 b	5.97	1.2	8.11E-10	1.27E-09	1.23E-09	1.70E-09	7.34E-10
		5.74 a		4	7.76E-10	1.22E-09	1.18E-09	1.70E-09	7.34E-10
Tb (3+)	66.1	5.79 a	5.87	1.4	8.00E-10	1.25E-09	1.21E-09	1.70E-09	7.33E-10
Dy (3+)	65.6	-	5.82	-	8.04E-10	1.26E-09	1.22E-09	1.70E-09	7.35E-10
Ho (3+)	66.3	-	5.88	-	8.02E-10	1.26E-09	1.22E-09	1.70E-09	7.35E-10
Er (3+)	65.9	-	5.85	-	7.98E-10	1.25E-09	1.21E-09	1.70E-09	7.34E-10
Tm (3+)	65.4	5.80 a	5.8	0	8.00E-10	1.25E-09	1.21E-09	1.70E-09	7.35E-10
Yb (3+)	65.6	5.96 b	5.82	2.7	NA	NA	NA	1.71E-09	7.36E-10
		5.78 a		0.7	7.94E-10	1.24E-09	1.21E-09	1.74E-09	7.00E-10
Lu (3+)	NA	-	NA	-					
Sc (3+)	64.7	-	5.74	-					
Actinide									
Ac (3+)	-	-	-	-	NA	NA	NA	NA	NA
Th (3+)	-	-	-	-	NA	NA	NA	NA	NA
Pa (3+)	-	-	-	-	NA	NA	NA	NA	NA
U (3+)	-	-	-	-	NA	NA	NA	NA	NA
Np (3+)	-	-	-	-	NA	NA	NA	NA	NA
Pu (+3)	-	-	-	-	NA	NA	NA	NA	NA

RE Elements (charges)	λ_o [20] 10^{-4} m^{2}S eq^{-1}	D_i (Experimental Data) 10^{-10} m^{2}s^{-1}	D_i (This study) 10^{-10} m^{2}s^{-1}	$\Delta[D_{i(exp)} - D_{i(cal)}]$ %	D_{AB} (This Study) (m^2/s)				
					H$_2$SO$_4$	HCl	HNO$_3$	NaOH	Na$_2$CO$_3$
Am (+3)	71	6.25	6.3	0.8	1.09E-09	1.31E-09	1.26E-09	1.85E-09	7.78E-10
Cm (+3)	64	6	5.68	5.3	1.01E-09	1.24E-09	1.20E-09	1.72E-09	7.38E-10
Bk (+3)	-	5.95	-	-	NA	NA	NA	NA	NA
Cf (+3)	64	5.87	5.68	3.2	1.01E-09	1.24E-09	1.20E-09	1.72E-09	7.38E-10
Es (3+)	59	5.77	5.24	9.2	9.56E-10	1.18E-09	1.15E-09	1.61E-09	7.07E-10
Fm (3+)	58	-	5.15	-	9.44E-10	1.17E-09	1.14E-09	1.59E-09	7.01E-10
Md (+3)	60	-	5.32	-	9.68E-10	1.19E-09	1.16E-09	1.63E-09	7.13E-10
No (+3)	-	-	-	-	NA	NA	NA	NA	NA
Lr (+3)	-	-	-	-	NA	NA	NA	NA	NA

Furthermore, the results from this calculation are exhibited in figures 3 and 4. These results are obtained from table 1 and demonstrated in graph for further understanding. It appears that NaOH (pink bar) exhibits the highest value of D_{AB} for each lanthanide and actinide components compared to the others reagent (refer figure 3). The high quantity of D_{AB} shows the high potential acid/alkaline reagent extract RE elements. These results manage to provide a clear quantitative evidence that NaOH is the best reagent, as per claimed by a great deal of research [22]. NaOH had managed to obtain 90% REE, leached within 5 hours with mass ratio of 1:2–1:4 NaOH/RE [10]. The contribution of NaOH concentration towards the extraction kinetics and alkali consumption for 5 hours of extraction time, increasing the concentration of NaOH by 50% of the initial concentration had rapidly improve time consumption to become 1 hour.
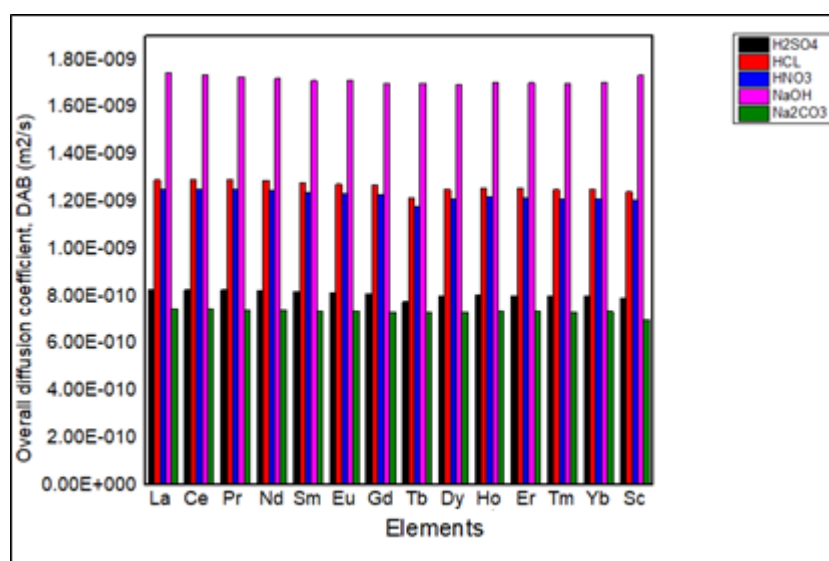

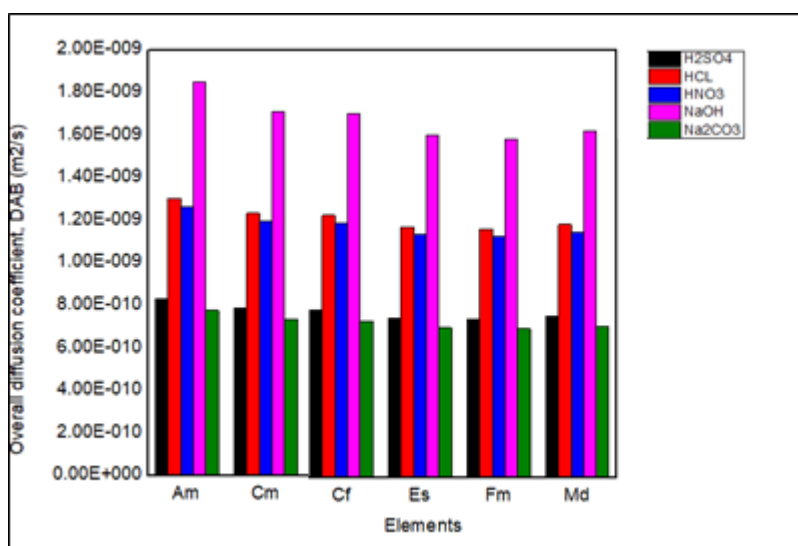**Figure 3**. The values of D_{AB} versus RE elements for different types of leaching reagent.

Figure 4. The values of D_{AB} versus actinide series for different types of leaching reagent.

Nonetheless, the industry extracting RE from monazite and bastnaesite are indeed using NaOH, among others [23]. Another significant analysis by Peelman et al. [23] is also in accord with our finding that NaOH is undeniably practical, as they recovered RE elements from bastnaesite with 90% efficiency. It is demonstrated that the bastnaesite was milled with NaOH powder, washed with water to remove the Na compounds, and finally leached with HCl.

In this study, the pattern in figure 3 is identical with figure 4. From these figures show that both RE and actinide series appeared to be affected by H_2SO_4 and HCl in the same manner. A study by researchers had compared these acids while leaching apatite-base ore [24]. It is simulating to discover that our calculation of D_{AB} for HCl is higher than H_2SO_4, which is parallel with the observation of Kim and others [24]. As clearly shown in figures 3 and 4, each ion of the lanthanide and actinide series are undeniably more influenced by HCl than H_2SO_4. Based on the calculated data, we concluded that RE elements are favour to combined with NaOH or HCl. These findings related to the limiting anionic conductivity (λ_-), which is NaOH has high λ_- which is 197.6 [14], thus, increasing the mobility of RE element from its ore. To make the comparison, the limiting anionic conductivity (λ_-) of Cl^-, NO_3^-, SO_4^- and CO_3^- are 76.3, 71.4, 80 and 69.3, respectively [14, 16]. Literature findings say that limiting ionic conductivity (λ_o) and D_{AB} are interrelated, by way that ionic conductivity acts as a driving force which stimulates higher diffusivity rate of RE elements [25].

According to these data, it shows that the Nernst-Haskell equation can be used to validate that D_{AB} is directly influenced by value of λ_-. Thus, it could conceivably be hypothesized that higher D_{AB} suggests better leaching performance as a result of the counter ion effect [25]. This phenomenon can be clearly explained by the ionic diffusion theory [26]. For so many years, diffusion is often considered as a neutral process involving only neutral atoms or molecules. Recent practice in RE leaching has included charged particles to improve the kinetics of the process as the result of electric field induced within the system or even externally imposed [26]. In a case of RE extraction, presence of anions from the acid/alkali attracts cation particles in the mineral ore, thus, explains the higher diffusivity rate.

Consider a salt from RE, for example $LaOH_3$ (a=1, b=3). As the molecule dissolves in water, it separates into 1 La^{3+}, and 3 OH^- in a process known as ionization. The chemical equation as shown in equation (3) simplifies the ionization of particles in water.

$$Aa + Bb \rightarrow aA^{c+} + bB^{c-} \tag{3}$$

Diffusion of Aa and Bb (denotes A and B ions) in the medium may be regarded as molecular or a coupled diffusion of AaBb, wherein 'a' number of cations moving in a homogeneous medium with 'b' number of anions.

5. Conclusions

The objective of this paper is to describe RE leaching with involvement of acid/alkali reagents in terms of the self-diffusion (Di) and overall diffusion coefficient (D_{AB}) by using Nernst-Haskell equation. We can conclude that, along with this calculation and the findings of this research have strengthened the idea that presence of ionic particles from the acid/alkali reagents could increase the leaching rate of RE elements from its ore. The calculated value of D_{AB} using Nernst-Haskell equation established here are comparative with experimental findings from various sources of literature, valid for most of the trivalent RE and actinide ions. However, contrary to expectation, a further work is required to confirm and assess the viability of limiting transport properties for the actinides.

Other than that, these findings provide some support knowledge that a strong alkali such as NaOH has a high D_{AB}, and thus, a better reagent compared to the other reagents. Recent study has successfully applied a mathematical approach to determine D_i and D_{AB} data. An implication of these findings is the possibility to study the thermodynamic properties for unique elements such as the RE elements. Nevertheless, a preliminary work to obtain data for D_{AB} through experiments is emphasized in the future to fill the research gap.

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