Chemical Diffusion Coefficient Calculation of U^{3+} in LiCl-KCl Molten Salt

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Abstract

Self-diffusion coefficient denotes the intrinsic diffusion of elements without the chemical gradient; generally, it is different from the chemical diffusion coefficient that is used in Fick's law. However, the self-diffusion coefficient can be converted to the chemical diffusion coefficient by considering the concentration-dependent activity coefficient of solute. In this study, the multiple time origins method was applied to calculate the self-diffusion coefficient of U^{3+} in LiCl-KCl eutectic salt at different temperatures and concentrations. The chemical diffusion coefficient was obtained based on the calculated results and thermodynamic theory. Calculated results show that self-diffusion coefficient decreases with concentration however chemical diffusion coefficient indicates to change little initially but appears to increase followed by decrease later within the concentration range of 0 to 3 at%.

Keywords: Self-diffusion coefficient, Chemical diffusion coefficient, U^{3+} , LiCl-KCl molten salt, Activity coefficient.

1. Introduction

Pyroprocessing is an advanced electrochemical method for the treatment of used nuclear fuel. Since 1996, more than four metric tons of spent nuclear fuel from EBR-II has been processed by this method at Argonne National Lab to demonstrate its feasibility [1]. The key step of pyroprocessing is the electrorefining of metal fuel, during which noble metal fission products (FPs) and cladding are retained in the anode basket, alkaline metal and rare earth metal FPs remain in the molten salt, and U^{3+} deposits at solid cathode. Finally, Pu and other TRUs will deposit in liquid Cd or a new solid cathode [2]. Compared to PUREX process, pyroprocessing can handle large quantities of "hot" fissile materials due to the electrolyte of molten salt and non-aqueous environment. Also, the equipment is simpler and more compact, thus it may have potential economic benefits and be possible for onsite processing. The most important feature is that pyroprocessing is supposed to be more resistant to proliferation since separated Pu remains mixed with other elements, which gives it an intrinsic barrier for proliferation resistance [3][4]. These advantages make pyroprocessing a more attractive choice for treating used nuclear fuel.

Although there is intrinsic resistance for proliferation, safeguards of materials is still one of the main issues of pyroprocessing. There is no accountability tank in pyroprocessing, which is used to account materials in PUREX [5]. Also, because of the non-uniform distribution of the metallic spent fuel, the initial amount of material put in anode of the electrorefiner may not be known. Thus, it is hard to determine the concentration or amount of the materials, such as U^{3+} and Pu^{3+} , in molten salt during pyroprocessing even though the quantity of materials collected at cathode can be measured, which conflicts with the requirement of material accountancy for safeguards [6].

One of the promising methods to solve this problem is the development of kinetic models of electrorefining [7][8], through which the material flow could be predicted given the initial conditions for running the pyroprocessing. When applying the kinetic model, diffusion coefficients of the solutes in molten salt are indispensable. They directly affect how fast the elements can transport in the solution which may influence the reaction rate at both electrodes. Generally, the diffusion coefficient is expressed by Arrhenius law in dilution

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad \text{Eq. 1}$$

where D_0 is the pre-exponential factor, E_a is the activation energy, and T is the absolute temperature in K. Eq.1 indicates that the diffusion coefficient does not depend on the material concentration in the solution. It should be noted that the equation can only be applied to dilution cases. The diffusion coefficient of species in molten salt could be measured through electrochemical methods, such as cyclic voltammetry (CV), chromopotentiometry (CP), and chronoamperometry (CA). These methods and their associated diffusion coefficients of actinides in LiCl-KCl molten salt for dilution cases have been extensively studied (e.g. [9][10][11][12][13]) and the results are listed in Table 1. Based on the review above, most of the available experimental correlations are obtained for dilution cases where U^{3+} is less than 0.5 at% (~3.0 wt%). However, the concentration of U^{3+} could be up to 10 wt% in a real electrorefiner for processing used nuclear fuel [14]. Therefore, the concentration-dependent diffusion coefficient is necessary to update the data reference.

Considering the limitation of experiment, such as the limited availability of actinides and the intense radiation, simulation method could be treated as a supplement. In fact, it has been successfully applied to calculate the diffusion coefficient of elements in molten salts [15] [16]. However, they stopped at self-diffusion coefficient calculation, which is the diffusivity without chemical gradient. The diffusivity determined from electrochemical experiment is the chemical diffusion coefficient. Generally, self-diffusion coefficient and chemical diffusion coefficient are different [17]. Self-diffusion coefficient cannot compare to the results from experiment or be used in Fick's law to describe the transport of elements with concentration gradient.

In the present study, Einstein method was applied to calculate the self-diffusion coefficient of U^{3+} in LiCl-KCl eutectic salt firstly and then the chemical diffusion coefficient was calculated based the relationship between the self-diffusion coefficient, chemical diffusion coefficient and the concentration-dependent activity coefficient.

2. Diffusion Coefficient

For self-diffusion coefficient, there are two different but equivalent methods to calculate it. One is the Green-Kubo method [18], which is based on the velocities of particles. The other is known as the Einstein method [18], which is based on the coordinates of particles. For the Green-Kubo method, it involves the integral of the velocity autocorrelation function. For three dimensions, the self-diffusivity can be expressed as

$$D = \frac{1}{3N} \int_0^\infty \langle \sum_{i=1}^N \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle dt \quad \text{Eq. 2}$$

where N is the number of particles in the system and $\mathbf{v}_i(t)$ is the velocity of particle i at time t . When the simulation time is long enough, the value of the integral should almost be constant. For the Einstein method, the mean square displacement (MSD) is calculated for individual particles for the self-diffusivity, since they are related by

$$MSD(t) = \frac{1}{Nn_t} \langle \sum_{i=1}^{n_t} \sum_{j=1}^N [\mathbf{r}_j(t_i + t) - \mathbf{r}_j(t_i)]^2 \rangle \quad \text{Eq. 3}$$

$$D = \lim_{t \rightarrow \infty} \frac{d(MSD)}{6dt} \quad \text{Eq. 4}$$

where N is the number of particles in the system, n_t is the number of time origins, and $\mathbf{r}_j(t)$ is the coordinate of particle j at time t . After a long time equilibration, the diffusivity can be derived from the slope of MSD. Theoretically, these two methods should give the same results; however, there may be a “long-time” tail to the integral Green-Kubo method that can cause some numerical problems. For this reason, the Einstein method was chosen for the present simulation

Self-diffusion coefficient is the intrinsic diffusion coefficient of the elements in the solution without chemical gradient. It is different from the chemical diffusion coefficient that is used in Fick's law to study the transport of element with concentration gradient [19], but they can be related by [20]

$$D_i^c = D_i^s \left(1 + \frac{d \ln \gamma_i}{d \ln x_i}\right) \quad \text{Eq. 5}$$

where the D_i^c and D_i^s are the chemical diffusivity and self-diffusivity of species i , respectively. γ_i and x_i are the activity coefficient and mole fraction of i , respectively. The concentration-dependent activity coefficient is needed to convert the self-diffusion coefficient to chemical diffusion coefficient. Eq. 5 indicates that the self-diffusion coefficient can represent the chemical diffusion coefficient when the activity coefficient is independent of concentration, which is reasonable for infinite dilute solution.

Considering the expression of Eq. 6, concentration dependent activity coefficient can be derived from excess Gibbs energy, which has been studied at 723 K in previous paper [21].

$$RT \ln \gamma_i = \left(\frac{\partial G^{ex}}{\partial n_i} \right)_{n_{j \neq i}, p, T} \quad \text{Eq. 6}$$

where γ_i and n_i are the activity coefficient and mole number of component i in solution, respectively. G^{ex} is the excess Gibbs energy.

3. Simulation Details

Molecular dynamics (MD) simulation method was used to calculate the self-diffusion coefficient of U^{3+} in LiCl-KCl eutectic salt at temperatures of 723 K and 773 K. It was achieved in the open-source software LAMMPS [22,23]. The interatomic potential used is Tosi-Fumi rigid potential [24,25]. Then potential energy between two charged particles is given by

$$U_{ij} = A_{ij} \exp \left(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} + \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}} \quad \text{Eq. 7}$$

where the r_{ij} is the distance between the particles i, j . A_{ij} , σ_{ij} , ρ_{ij} , C_{ij} , and D_{ij} are parameters. q_i and q_j are the carried charges of ion i and j , respectively. ϵ_0 is the vacuum permittivity. The parameters are shown in Table 2.

During the simulation, the pressure and time step were set as 1 bar and 1 fs, respectively. 6,000 ions were used for LiCl-KCl eutectic salt (58% LiCl), and 10, 20 ... 90 UCl_3 were added to the LiCl-KCl molten salt, separately to create solutions with different concentrations (up to around 3 at% of UCl_3). For each case, the NVE ensemble was run firstly for 5,000 steps to bring the system to the desired temperature. Then NPT ensemble was run with 500,000 steps to reach the pressure of 1 bar. Next, NVT ensemble was run with 500,000 steps to do the final equilibration, after which, the trajectory information of U^{3+} was output every 1,000 steps for totally 200,000

steps to calculate the MSD. 100 time origins were used for every MSD calculation and totally 100 values of MSD (at times of 1 ps, 2 ps, 3 ps ... 100 ps) were calculated to fit the self-diffusivity under each concentration.

Since the MSD was fitted into a linear equation with time, such as

$$MSD(t) = A + Bt \quad \text{Eq. 8}$$

where A and B are constant and diffusion coefficient can be derived from B according to Eq. 4, the uncertainty of B was calculated following the method described by Talor [26], which gives one sigma error as

$$\sigma_B = \sigma_{MSD} \sqrt{\frac{N}{\Delta}} \quad \text{Eq. 9}$$

$$\sigma_{MSD} = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (MSD_i - A - Bt_i)^2} \quad \text{Eq. 10}$$

where N is the number of data points, and

$$\Delta = N \sum_{i=1}^N t_i^2 - \left(\sum_{i=1}^N t_i \right)^2 \quad \text{Eq. 11}$$

4. Results and Discussion

Figure 1 shows the self-diffusion coefficient of U^{3+} in LiCl-KCl molten salt at different temperatures and concentrations. It indicates that the self-diffusion coefficient of U^{3+} is a function of both temperature and concentration. It increases with temperature but decreases with concentration.

Following the method in the paper of Zhou [21], the molar excess Gibbs energy of LiCl-KCl- UCl_3 solution with different concentrations of UCl_3 at 773 K can be calculated. The result is shown in Table 3. Fit the molar excess Gibbs energy using Margules model up to seventh order [27], the activity coefficient of UCl_3 can be calculated. The relationship between activity coefficient and concentration at 723 K [21] and 773 K is shown as Figure 2.

Due to the relationship of

$$\frac{d\ln\gamma}{d\ln x} = x \frac{d\ln\gamma}{dx} = \frac{x}{\gamma} \frac{d\gamma}{dx} \quad \text{Eq. 12}$$

$1 + \frac{d\ln\gamma}{d\ln x}$ can be calculated through the fitting curves. Table 4 shows the values of $1 + \frac{d\ln\gamma}{d\ln x}$ at the simulated concentrations, based on which, chemical diffusion coefficient in Eq. 5 can be derived. Figure 3 shows the result of chemical diffusion coefficient at different temperatures and concentrations. The result indicates that the chemical diffusion coefficient is larger with higher temperature. Most importantly, it shows that the chemical diffusivity changes little initially but then has an increase and a decrease with the concentration even though the changes are not that significant. Present work will push us to consider the concentration dependence of the diffusion coefficient and also other thermodynamic properties since previously almost all the researches were conducted in dilute solution and assumed diffusion coefficient is concentration-independent. Table 5 shows the comparison of diffusion coefficient with the literature [10][11][13] at dilute solution and indicates that the result agrees well with existing experimental data.

From the kinetic theory of Einstein relation [28], the self-diffusion coefficient could be expressed by

$$D = \frac{k_B T}{6\pi\eta r} \quad \text{Eq. 13}$$

where k_B is the Boltzmann's constant, η is the dynamic viscosity, and r is the radius of the spherical particle. Eq. 13 explicitly shows that the diffusion coefficient is related to the temperature, and it may increase with the temperature since generally viscosity will become smaller when increasing the temperature [29]. However, the concentration dependence is still implicit.

Kim et al [30] studied the viscosity of LiCl-KCl Molten salts with actinides and lanthanides dissolved at 773 K by an object falling down method. The reported data show that viscosity increases with the concentration up to around 13 wt% even though it starts to decrease after that. The authors believe that it was caused by the distortion of the solution structure or the formation of the insoluble UCl_3 , NdCl_3 , CeCl_3 , and LaCl_3 in solution [30]. The turning point concentration is higher than the maximum one of 11 wt% used in the present simulation. Therefore, the viscosity is expected to increase in this work. With the results in mind, the self-diffusion coefficient D in Eq. 13 may be expected to decrease with higher viscosity, which means higher concentration. It supports the present simulation result of self-diffusivity at least qualitatively.

5. Conclusions

The present paper discussed the difference between self- and chemical-diffusivity, and developed the method to calculate them. The results show that the chemical diffusion coefficient of the U ion in the molten salt does have relationship with concentration. It varies little at low concentration below around 5 wt% but then shows an increase followed by a decrease. The Einstein theory of diffusion coefficient clearly indicates that self-diffusivity should be a function of temperature and viscosity. Investigation of the relationship between viscosity and concentration indicates that the viscosity of the molten salt increases in the concentration range considered in the present calculation, which leads to a smaller self-diffusion coefficient when the solute concentration increases. Therefore, the present calculated results of self-diffusivity are consistent with the Einstein equation.

The present work studied the concentration dependence of diffusivity of U^{3+} in LiCl-KCl comprehensively and may contribute greatly to material concentration measurement in LiCl-KCl molten salt by reversing the electrochemical process generally used to derive the diffusion coefficient given the concentration of UCl_3 in LiCl-KCl molten salt. It is one of crucial parts for the safeguards of pyroprocessing of being aware of the material concentration and distribution.

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Figure 1. Self-diffusion coefficient of U³⁺ in LiCl-KCl with different temperatures and concentrations

Figure 2. Activity coefficient of UCl_3 in LiCl-KCl at 723 K and 773 K [21]

Figure 3. Chemical diffusion coefficient of U^{3+} in molten LiCl-KCl**Table 1.** Diffusion coefficient of U^{3+} from literature

Ref.	D_0 (cm ² /s)	E_a (kJ)	Temperature (K)	Mole fraction (%)
Caligara [10]	1.216×10^{-3}	31.3	673 K - 823 K	0.300
Reddy [11]	0.307	66.4	685 K - 770 K	0.474
Masset [12]	1.37×10^{-4}	24.2	673 K - 823 K	0.340
Kuznetsov [13]	2.29×10^{-3}	32.5	723 K - 823 K	0.221

Table 2 Parameters used for the simulation [31]

pair	A/ eV	$\rho/\text{\AA}$	$\sigma/\text{\AA}$	C/ eV · $\text{\AA}^6$	D/ eV · $\text{\AA}^8$
Cl ⁻ - Cl ⁻	0.174084	0.345863	3.340	132.6892	1245.0685
Cl ⁻ - Li ⁺	0.172894	0.339212	2.570	1.2477	1.5030
Cl ⁻ - K ⁺	0.137381	0.341400	3.190	29.9336	45.4741
Cl ⁻ - U ³⁺	0.705874	0.293983	2.835	58.0403	100.2000
Li ⁺ - Li ⁺	0.260886	0.337051	1.800	0.0478	0.0167
Li ⁺ - K ⁺	0.217637	0.337051	2.420	0.8298	0.5344
Li ⁺ - U ³⁺	0.002241	0.176390	2.065	1.1403	0.5511
K ⁺ - K ⁺	0.190113	0.339212	3.040	15.1519	14.9465
K ⁺ - U ³⁺	6.67E-05	0.176390	2.685	20.7756	15.7982
U ³⁺ - U ³⁺	0.000748	0.176390	2.330	28.4769	16.7000

Table 3. Molar excess Gibbs energy of UCl₃-LiCl-KCl solution with different concentrations of UCl₃ at 773 K (The units are J/mol)

$x_{UCl_3}(\%)$	0	0.4975	0.9901	1.4778	1.9608	2.4390	2.9126
$\bar{G}^{ex}$	0	-223.27	-304.82	-467.85	-554.03	-667.69	-780.40

Table 4. The values of $(1 + \frac{d \ln \gamma}{d \ln x})$ at simulated concentration

$x_{UCl_3}(\%)$	0.332	0.662	0.990	1.32	1.64	1.96	2.28	2.60	2.91
723 K	1.2162	1.4201	1.6121	1.7927	1.9626	2.1220	2.2715	2.4115	2.5445
773 K	1.2141	1.4158	1.6058	1.7844	1.9523	2.1099	2.2575	2.3958	2.5250

Table 5. The chemical diffusion coefficient comparison at dilute solution (the values of this work are the average of the two lines in Figure 3 for each temperature)

	D at 723 K (cm ² /s)	D at 773 K (cm ² /s)
Cligara [10]	6.80E-06	1.03E-05
Reddy [11]	5.52E-06	9.80E-06
Masset [12]	--	3.80E-05
Kuznetsov [13]	1.02E-05	1.45E-05
This work	7.05E-06	1.02E-05

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