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Journal of Alloys and Compounds 444–445 (2007) 557–560

Journal of ALLOYS AND COMPOUNDS

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Diffusion behavior of actinide and lanthanide elements in molten salt for reductive extraction

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Received 30 June 2006; accepted 26 February 2007
Available online 7 March 2007

Abstract

In support of the development of reductive extraction, the diffusion coefficients of actinide and lanthanide ions in LiCl–KCl eutectic salt were measured by a capillary method. The temperature ranged from 723 to 873 K. The obtained values of the diffusion coefficients are considerably high in the order of 10^{-9} m^2/s and no significant problem is found for the development of reductive extraction. Based on the results, some details are discussed of the diffusion mechanisms of multivalent ions.

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Keywords: Diffusion coefficient; Actinide; Lanthanide; Molten salt; Complex ion

1. Introduction

In recent years, there has been a renewed interest for new nuclear fuel cycles or new nuclear waste management strategies, especially for efficient transmutation of long-lived radionuclides in order to minimize the radiological toxicity of nuclear wastes. Reductive extraction process, which has been developed for reprocessing molten salt reactor fuels, is expected to be more useful for separation and recovery of transuranic elements. Up to date, extensive studies have been performed concerning with the thermodynamics of reductive extraction [1,2]. However, little is still known about the kinetics. Then, for the development of reductive extraction process the rate of extraction of actinide and lanthanide elements in a two-phase system of molten LiCl–KCl eutectic salt and liquid cadmium was measured at 723–873 K in our previous study [3]. The mass transfer coefficients were found to be as high as expected. In some cases, however, it was found that the rate of reductive extraction was possibly affected by the solubility limits of the solute elements in the metal phase.

For comparison, in the present study, the diffusion coefficients of actinide and lanthanide elements were measured as a function of temperature in LiCl–KCl for reductive extraction. The results are useful not only for the development of reductive extraction but also for the improvement of our knowledge on the diffusion mechanisms of multivalent ions.

2. Experimental

Diffusion coefficients were measured by a capillary method [4]. The LiCl–KCl eutectic (Li:K = 59:41 in mole) and $CdCl_2$ were purchased from Anderson Physics Laboratory, rare earth metals and zirconium metal were from Furuuchi Chemical Co., thorium metal was from Reactor Experiments, Inc., and all other reagents were from Nacalai Tesque. The radioactive tracers ^{97}Zr, ^{140}La, ^{143}Ce, ^{152}Sm, ^{152m1}Eu, ^{233}Pa were produced by neutron irradiation of Zr, La, Ce, Sm, Eu and Th metals, respectively. The radioactive tracers and eutectic salt were loaded in an alumina crucible, and were melted at a given temperature. In order to assure a complete dissolution of every solute in the salt phase, $CdCl_2$ was added to the system. The concentration of solute elements was about 0.6 at% for Zr, 0.2 at% for La and Ce, and 0.05 at% for Eu and Sm, respectively. In a similar system, it was found that the radioactive tracers in the salt phase are present as Zr^{4+}, La^{3+}, Ce^{3+}, Eu^{2+} and Pa^{4+} [5]. In the case of Sm, it was expected to be present as Sm^{3+} by considering its redox potential [6]. Using high-purity reagents, all experiments were performed in a glove box with argon atmosphere containing <0.5 ppm of O_2 and <0.2 ppm of H_2O.

In the measurement, a quartz capillary tube of an i.d. of 0.2 or 0.3 mm and a length of about 50 mm sealed from one end was used. The open end

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doi:10.1016/j.jallcom.2007.02.153

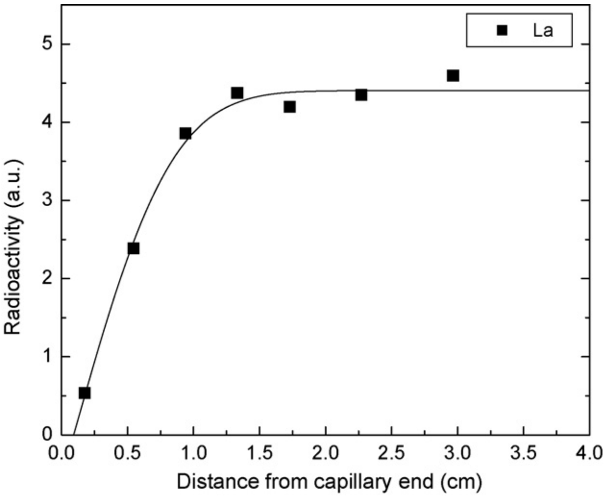

Fig. 1. Radioactivity of La as a function of distance after diffusion at 773 K during 150 min. The curve represents the least-squares fit of the data to Eq. (1).

of the evacuated capillary was immersed into molten LiCl–KCl containing the radioactive tracers in order to allow the liquid to rise up. The capillary filled with the LiCl–KCl was then immersed into a pure LiCl–KCl. The temperature of the system was controlled within ±0.5 K. After a known diffusion time, the capillary was removed, allowed to cool and cut into several sections. The concentration profile of each radioactive tracer was determined by a direct γ-ray spectrometry. No significant differences were observed for the capillaries of 0.2 and 0.3 mm, and it was concluded that thermal convection was not important source of uncertainty.

3. Results and discussion

Fig. 1 shows a typical result of the measurements, in which the concentration of a radioactive tracer is plotted against distance from the capillary end. The concentration profile is given by

$$C_x = C_0 \operatorname{erf}\left(\frac{x - x_0}{2\sqrt{Dt}}\right) \qquad (1)$$

where C_x denotes the concentration at a distance x from the open end of the capillary, C_0 the initial concentration, x_0 the fitting parameter to correct zero point, D diffusion coefficient and t is the diffusion time. The diffusion coefficient of each ion was determined by a least-squares fit of the data to Eq. (1).

In Fig. 2, the diffusion coefficients of solute elements in molten LiCl–KCl are plotted as a function of inverse temperature. As shown in this figure, the diffusion coefficient D is well expressed by

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \qquad (2)$$

where D_0 is the pre-exponential factor, E_D the apparent activation energy for diffusion, R the gas constant and T is the absolute temperature. The D_0 and E_D values are obtained by the least-squares fitting method and the results are summarized in Table 1 together with the literature values [6–10]. Fig. 3 shows a comparison of the present results with the literature ones for Sm [6] and U [7] in LiCl–KCl, which have been determined by electrochemical techniques. By considering the experimental uncertainties due to different methods, the present results are found to agree well with the literature ones. It can be seen that the present values of the diffusion coefficients are considerably high in the order of 10^{-9} m^2/s and then that there is no significant problem concerning with the diffusion coefficients in the salt phase for the development of reductive extraction.

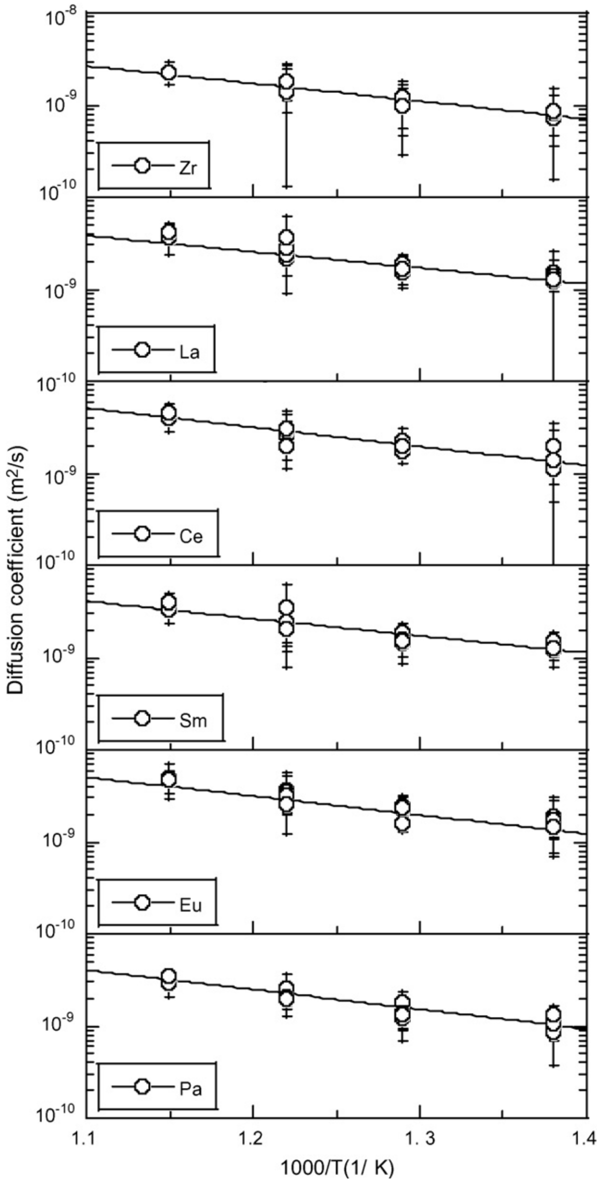

Fig. 2. Arrhenius plots of diffusion coefficients in LiCl–KCl Lines represent the least-squares fits of the data to Eq. (2).

It is interesting to discuss some details of the diffusion mechanisms based on the obtained results of multivalent ions. Although a number of the studies have been performed on the diffusion of solute ions in molten salts, there still remain large scatters of the data especially for multivalent ions. In the case of U(III), for example, the values which have been obtained by electrochemical techniques scatter in the order between 10^{-10} and 10^{-9} m^2/s possibly due to the variations in the experimental conditions and the difficulty in precise measurement of the electrode surface area [11]. The present results, which have been obtained by the capillary measurement, are thus expected to be much useful

Table 1
Diffusion coefficients of solute ions in LiCl–KCl eutectic melt

Solute	D_0 ($\times10^{-7}$ m^2/s)	E_D (kJ/mol)	D at 773 K ($\times10^{-9}$ m^2/s)	r (nm) [14]	Temp. range (K)	Ref.
Sm(III)	5.51	40.3	1.23	0.096	673–873	[6]
U(III)	2.29	34.4	1.45	0.103	723–823	[7]
Ag(I)	1.32	24.4	2.98	0.115	670–870	[8]
Au(I)	1.14	26.5	1.85	0.137	670–870	
Fe(II)	1.53	30.2	1.38	0.061	670–870	
Ni(II)	1.56	29.8	1.50	0.069	670–870	
Ag(I)	1.87	32.3	4.22	0.115	647–1019	[9]
Cd(II)	0.94	37.1	1.35	0.095	668–1082	
Pb(II)	3.36	42.9	1.92	0.119	654–1008	
Bi(III)	9.90	36.4	1.63	0.103	637–930	[10]
U(IV)	1.59	37.0	1.04	0.089	693–894	
U(III)	3.20	37.1	0.992	0.103	670–870	
U(IV)	9.71	42.9	1.23	0.089	670–870	
Pu(III)	3.31	36.8	1.08	0.100	650–810	
Pu(IV)	5.91	40.4	1.1	0.086	630–800	
Zr(IV)	3.58 ($10^{-6.45\pm0.25}$)	37.0 ± 3.8	1.13	0.084	723–873	This work
La(III)	6.26 ($10^{-6.20\pm0.27}$)	37.3 ± 4.1	1.87	0.103	723–873	
Ce(III)	8.27 ($10^{-6.08\pm0.29}$)	38.8 ± 4.3	1.97	0.101	723–873	
Sm(III)	4.87 ($10^{-6.31\pm0.28}$)	36.0 ± 4.2	1.80	0.096	723–873	
Eu(II)	6.60 ($10^{-6.18\pm0.21}$)	36.2 ± 3.2	2.37	0.117	723–873	
Pa(IV)	6.60 ($10^{-6.47\pm0.33}$)	34.4 ± 5.0	1.60	0.090	723–873	

for checking the data and for improving our knowledge on the diffusion mechanisms of multivalent ions. It is also important to note that the diffusion coefficients of different multivalent ions have been measured simultaneously in the present study and that the results are more reliable than those measured separately.

In Fig. 4, the E_D values of the present study are plotted as a function of Z^2/r in comparison with those of the literature ones for various solute ions in LiCl–KCl. Since several theories have been proposed for the diffusion coefficients in molten salts [12], the parameter Z^2/r is only temporarily taken for comparison by considering the contributions of solvation energies of multivalent ions [13] and by taking the ionic radii for six coordination [14]. As shown in Fig. 4, most of the E_D values are considerably larger than the activation energy of around 21 kJ/mol for the solvent viscosity [15], although the values for monovalent ions are somewhat smaller than those for multivalent ions. The results are thus consistent with a model in which not only the energy in the Stokes-Einstein equation but also some additional energy are considered for the effect of complex formation of multivalent ions. It is recognised, however, that no apparent dependence of the E_D values on Z^2/r is observed as far as concerned with the present data. It follows that the energies for the effect of complex formation are almost similar for multivalent ions and that

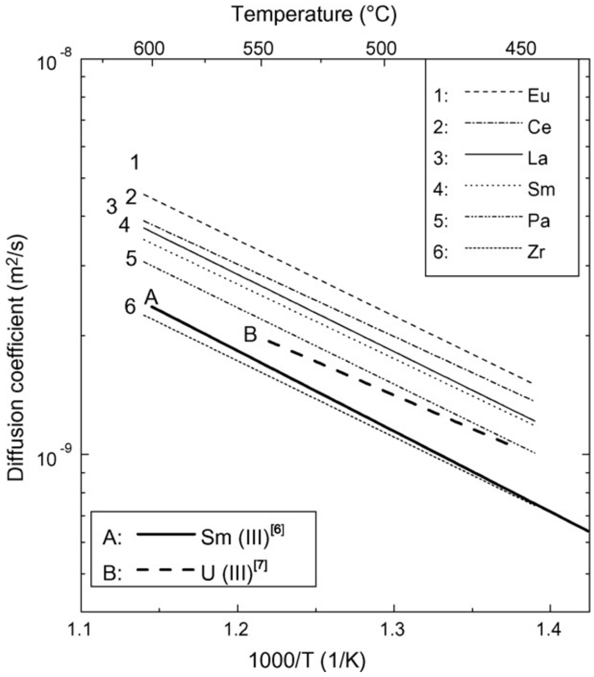

Fig. 3. Comparison of diffusion coefficients in LiCl–KCl.

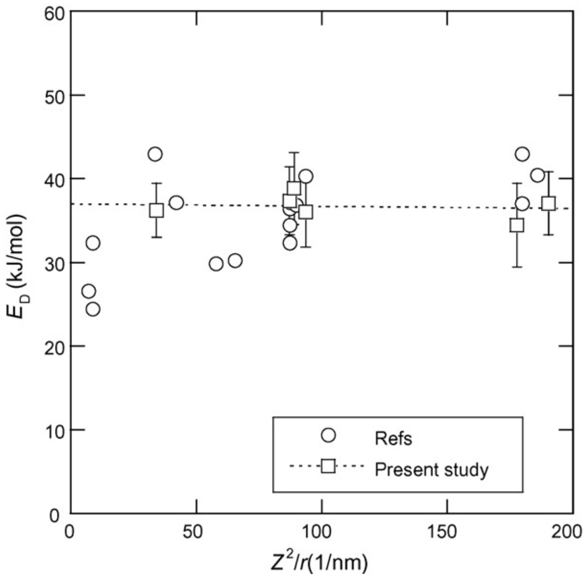

Fig. 4. E_D values of the diffusion coefficients as a function of Z^2/r.

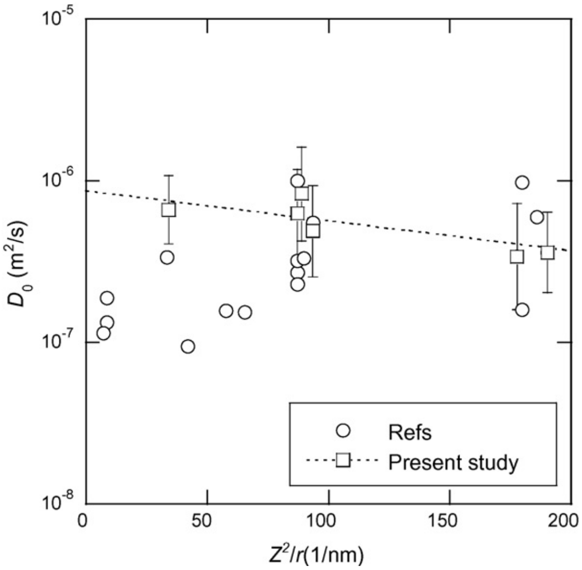

Fig. 5. Diffusion coefficients at 773 K as a function of Z^2/r.

their diffusion is not so directly affected by the solvation energy itself.

Fig. 5 shows the D_0 values as a function of the Z^2/r, which is again temporarily taken for comparison. A similar figure of the D_0 values is also obtained as a function of such a parameter as the ionic potential Z/r. Although the uncertainties are still large for the present data, it can be seen that the D_0 values decrease with the increasing Z^2/r and Z/r values. It is thus inferred that there are some differences due to different multivalent ions in the preexponential term D_0. According to the traditional transition state theory [12], the preexponential term is interpreted as the fundamental frequency with which a particle undergoes migration or makes a jump into an adjacent site. It is thus considered that multivalent ions may diffuse in the form of their complex ions together with the neighbouring ions and that the frequency of such complex ions may decrease with the increasing Z^2/r and Z/r values.

4. Conclusions

The diffusion coefficients of multivalent ions were measured in LiCl–KCl for reductive extraction. The obtained values of the diffusion coefficients were considerably high in the order of 10^{-9} m^2/s and no significant problem was found for the development of reductive extraction. Some details of the diffusion mechanisms of multivalent ions were discussed on the basis of the obtained D_0 and E_D values. It was found that the D_0 values are dependent on the ionic potential while the E_D values are not. Such multivalent ions might be considered to diffuse in their complex forms with chloride ions in LiCl–KCl.

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