High-Temperature Viscosity Measurement of LiCl-KCl Molten Salts Comprising Actinides and Lanthanides

Jong-Yun Kim,* Sang-Eun Bae, Dae-Hyun Kim, Yong Suk Choi, Jei-Won Yeon, and Kyuseok Song

Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea
*E-mail: kjy@kaeri.re.kr

Pyrochemical process dealing with high-temperature LiCl-KCl molten salts comprising trivalent ions of actinides and lanthanides have been extensively investigated since it has some advantages over the conventional wet chemical processes with respect to the volume reduction of the nuclear wastes, the recycling of spent fuels, the nuclear non-proliferation resistance, *etc*.[1] Physical properties of molten salt such as viscosity, density, solubility, surface tension, solubility, diffusivity, electrical/thermal conductivity, *etc.*, are important for the design and the early fault detection of each unit processes in the pyroprocess.[2] Among them, the viscosities of the high-temperature molten salts should be considered much more carefully when designing the plant as well as handling and transferring the molten fluid containing radioactive actinides and lanthanides from one unit process to the other in the pyroprocess.[3-5] The viscosity is also related to the electrical properties and the structure of the liquids.[5,6] However, there are only viscosity data of pure molten LiCl-KCl eutectic in a limited range of temperatures (890-1080 K).[7,8] Therefore, interpolation and extrapolation are required to determine the viscosity at a specific process condition, for example, at *ca.* 773 K for the transfer of molten salt in the pyroprocess.[4] In addition, there have been no previous reports on the viscosity of LiCl-KCl eutectic containing a wide concentration range of actinides and lanthanides such as uranium (U), neodymium (Nd), cerium (Ce), and lanthanum (La), which are of major interests regarding the recycling of LiCl-KCl molten salts.

There are many experimental techniques in the viscosity measurement of liquids.[9] But, for molten salts with actinides at high temperatures, only limited measurement techniques have been proposed: torsional vibration method, rotational method, and capillary method.[7,10,11] In this study, in-house-designed falling object was used to measure the viscosities of LiCl-KCl eutectic at 773 K in an argon-filled glove box. The speed of the falling object can be measured by using the optical method for the detection of the movement of the falling object in a molten salt. The concept of "apparatus constant",[12] which is useful for characterization of a falling object measurement system, was introduced with a set of viscosity standards for calibration of the falling object.

If an object is falling down in a fluid by its own weight

under gravity, and the frictional force combined with the buoyant force exactly balances the gravitational force, then the viscosity is related by the following Stokes' equation in case that the falling object is perfectly spherical.[9]

$$\mu = \frac{2r^2 g(\rho_A - \rho_B)t}{9L} \tag{1}$$

where μ is the viscosity at the specified temperature (P), ρ_A is the density of the rod (g/cm^3), ρ_B is the solution density (g/cm^3), g is the gravitational acceleration (m/s^2), t is the time of fall (s), L is the distance travelled in the time t (m), r is the radius of the falling sphere (cm). Actually, Stokes' law makes the following assumptions: rigid spherical particle, laminar flow, continuum fluid, free flow without wall effects, constant density of solutions or low Reynolds number flow, steady state flow, homogeneous (uniform in composition) material, and smooth surfaces. If the falling object is not spherical, and there is a wall-effect, the correction factors should be introduced in Eq. (2).[9]

$$\mu = \frac{2r^2 g(\rho_A - \rho_B)t}{9L} \times f \times s \tag{2}$$

$$f = 1 - 2.104\left(\frac{r}{R}\right) + 2.09\left(\frac{r}{R}\right)^3 - 0.95\left(\frac{r}{R}\right)^5 \tag{3}$$

where f given by the Eq. (3) is the Faxen correction factor, which takes into account the effects of viscous drag exerted on the settling sphere by the tube wall with a radius of R, and s is a shape factor. By introduction of a concept of "apparatus constant (K)",[12] Eq. (2) is simplified to Eq. (4), and then such correction factors can be simply integrated into one representative constant.

$$\mu = K \times (\rho_A - \rho_B)t \tag{4}$$

The time of fall (t) could be determined by using the optical transmission method in our present study. One example of the determination of the time fall is shown in Figure 1. The transmittance increased as the quartz rod begins to pass through the beam path, whereas the transmittance decreased back to the initial baseline as the rod passes away from the beam path. The time of fall was defined as the time between onset of rising and falling down to
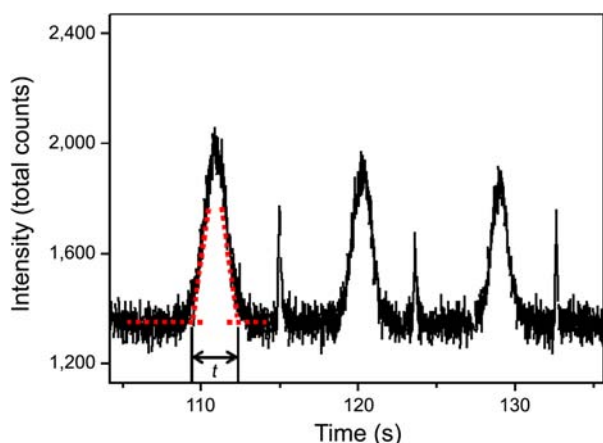
Figure 1. Three successive transmission spectra of molten salts as a representative example for the determination of the time of fall by the transmission intensity changes during the fall of a quartz rod. The arrow indicates the time of fall.
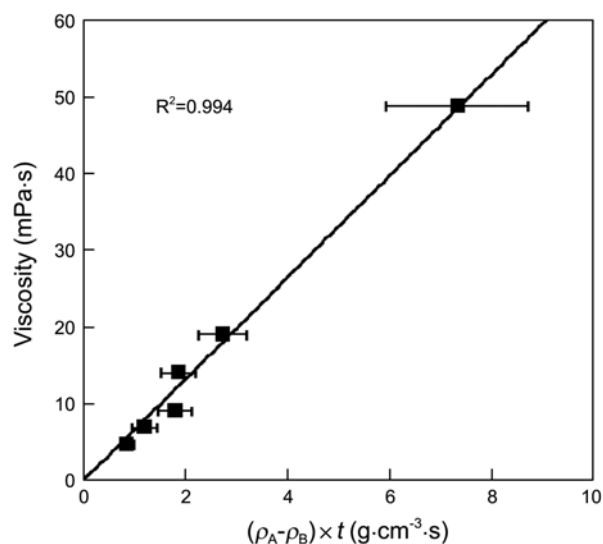

Figure 2. Calibration curve with viscosity standards at 298 K to obtain the "apparatus constant (K)" from the slope of the curve.

the baseline of the transmission spectra.

Firstly, the apparatus constant (K) was derived from the calibration curve obtained by measuring the density of the falling rod (2.1 g·cm^{-3}), the time of fall with six viscosity standard solutions at 298 K as shown in Figure 2 and Table 1. Five replicates of each viscosity standards were used to measure the time of fall and the density. The viscosities of the standard solutions are linearly correlated with ($\rho_A - \rho_B$) × t, and the slope K in the calibration curve was 6.6 ± 0.2 mPa·g^{-1}·cm^3 with R^2 = 0.994.

Then, with the K value obtained from the calibration curve, the viscosities of the molten salt samples were calculated by using the Eq. (4), density, and the time of fall measured for the molten salt samples (11 replicates each) comprising U^{3+}, Nd^{3+}, Ce^{3+}, and La^{3+} ions in a molten LiCl-KCl eutectic. The viscosity of the solute-free pure LiCl-KCl eutectic in Figure 3 was 2.2 ± 0.4 mPa·s. Unfortunately, there are no previous reports on the viscosity data at 773 K
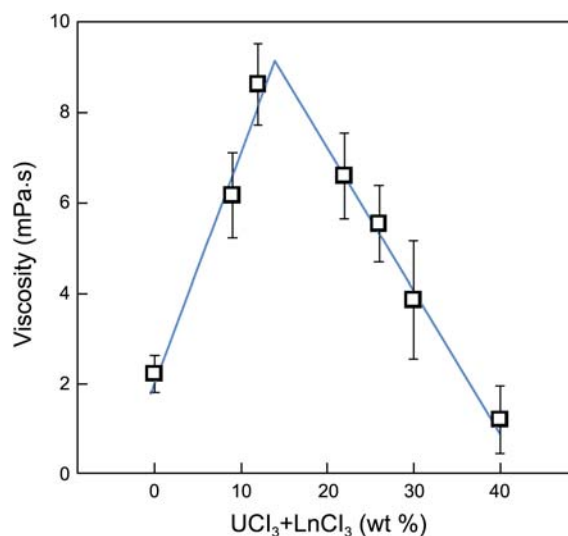

Figure 3. Dependence of total solutes concentration (wt %) on the viscosities of molten KCl-LiCl salts comprising UCl$_3$ and LnCl$_3$ (a mixture of NdCl$_3$, CeCl$_3$, and LaCl$_3$).

for LiCl-KCl eutectic (58 mol % LiCl). Instead, by using the 96 viscosity data over the temperature range of 890-1080 K and the concentration range of 20-80 mol % LiCl reported in Ref. 7, the viscosity value at 773 K for LiCl-KCl eutectic could be obtained by extrapolation of the fifth order of polynomial 2-dimensional surface fit according to the equation $y = A + Bx_1 + Cx_1^2 + Dx_1^3 + Ex_1^4 + Fx_1^5 + B'x_2 + C'x_2^2 + D'x_2^3 + E'x_2^4 + F'x_2^5$ (adjusted R^2 = 0.994). The extrapolation of the fit gave the viscosity value of 2.5 mPa·s, which agrees very well with our measured average viscosity data (2.2 mPa·s). As the total solute concentration increased, the viscosity values of the molten salts showed a maximum near 12 wt % of the total solute concentration as shown in Figure 3. After 12 wt %, viscosity of the molten salts decreased, which might result from the distortion of the solution structure or the formation of the insoluble UCl$_3$, NdCl$_3$, CeCl$_3$, and LaCl$_3$ in solution. The reason for the viscosity decrease at high solute concentrations is beyond the scope of the present study, and more experiments need to be performed. The dependence of the type of trivalent cations such as U^{3+}, Nd^{3+}, Ce^{3+}, and La^{3+} can be concluded only if the viscosities are measured at less than *ca.* 12% of the total solutes since the viscosity decreases above *ca.* 12% of the total solutes. At the moment, regardless of the type of the trivalent cations, the viscosities of molten salts comprising U, Nd, Ce, and La cations appears to depend linearly on the total weight percent of the solutes. However, a more careful experimental design should be preceded at a low solute concentration range to identify the dependence of one particular trivalent cation at a fixed concentration of other cations in a further study.

The aim of our present study was to establish an accurate viscosity measurement system to support the database required for the design and monitor the pyroprocess dealing with high-temperature molten salt under argon atmosphere. Accuracy and precision of the present technique should be

**Table 1.** The time of fall (t) and density (ρ_B) of viscosity standards and molten salt samples

	Viscosity standards			Molten salt samples		
Sample	t^a (s)	ρ_B (g/cm^3)	Sample	t^b (s)	ρ_B (g/cm^3)
S1	0.49	0.92	M0	1.68	1.71
S2	1.71	0.94	M1	1.71	1.87
S3	1.99	0.94	M2	1.99	1.74
S4	2.56	0.95	M3	2.56	2.06
S5	1.22	0.95	M4	2.14	2.06
S6	2.14	0.98	M5	2.74	2.26
			M6	2.14	2.40

[a,b]Average values of 5 and 15 replicate measurements, respectively.

Table 2. Composition of UCl$_3$, NdCl$_3$, CeCl$_3$, and LaCl$_3$ in KCl-LiCl eutectic

Sample	LiCl-KCl (wt %)	UCl$_3$ (wt %)	LnCl$_3^a$ (wt %)
M0	100	0	0
M1	91	9	0
M2	88	6	6
M3	78	10	12
M4	74	9	17
M5	70	20	10
M6	60	20	20

[a]LnCl$_3$ = NdCl$_3$:LaCl$_3$:CeCl$_3$ = 1:1:1 by weight.

further investigated with known viscosity of pure LiCl-KCl samples. Due to the temperature variation along the axis and the effect of convective currents in the high-temperature molten salt reactor, measurement errors are relatively high in the measurement of viscosity of molten salts. Obtaining accurate K is the starting point of the calculation of the viscosity, and therefore accurate viscosity and density data is the key to the final accuracy of the present method.

Experimental

Viscosity measurement system for the high-temperature molten salt is illustrated in Scheme 1. The furnace attached to dry argon-filled glove box (99.999% Ar, H$_2$O and O$_2 \leq 1$ ppm) has two transparent quartz windows for the spectrophotometric measurements to identify the movement of the falling object inside the quartz tube. Spectrophotometric measurements were carried out with a halogen lamp (DH-2000, Ocean Optics Inc.) as a light source and a CCD detector
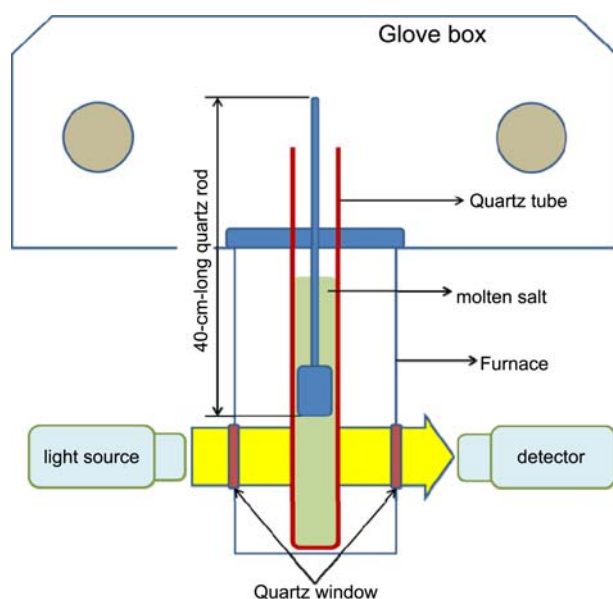
Scheme 1. Schematic diagram of the viscosity measurement system composed of a glove box, a furnace, quartz tube, and a falling quartz rod, and optical transmission measurement system.

(QE65 Pro, Ocean Optics). Temperature of the molten salt in the furnace was controlled at 773 K within ± 2 K using a K type Chromel–Alumel thermocouple wire. Quartz tube (35-cm-long, O.D. = 12 mm, I.D. = 10 mm) was placed into reaction vessel inside the furnace. An in-house-prepared quartz rod used as a falling object was inserted into the quartz tube. The time of fall was determined from the measurement of optical transmittance change during the quartz rod is passing through 11.3-mm beam width.

Anhydrous lithium chloride/potassium chloride (LiCl-KCl) eutectic mixture powder (99.99% purity, 58 mol % LiCl, Sigma-Aldrich, cat. no. 479330) was loaded into the quartz tube and dissolved at 773 K under argon atmosphere in the above-mentioned glove box installed in the post-irradiation test facility in Korea Atomic Energy Research Institute. Uranium trichloride (UCl$_3$) was kindly gifted from Department of Nuclear Fuel Cycle Technology Development (Korea Atomic Energy Research Institute). Neodymium trichloride (NdCl$_3$, 99.99% purity, Alfa Aesar, cat. no. 18680), cerium trichloride (CeCl$_3$, 99.99% purity, Alfa Aesar, cat. no. 35688), and lanthanum trichloride (LaCl$_3$, 99.99% purity, Alfa Aesar, cat. no. 44322) were dissolved together with UCl$_3$ in molten salt media at 773 K. Compositions of UCl$_3$, NdCl$_3$, CeCl$_3$, and LaCl$_3$ in a molten LiCl-KCl eutectic were listed in Table 2.

Silicone fluids (Brookfield Engineering Laboratories, Inc.) were used as viscosity standards with nominal viscosities of 5, 10, and 50 mPa·s. Three more silicone fluids samples with nominal viscosity values of 7.5, 15, and 20 mPa·s were prepared by blending two viscosity standards.

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