Extractor Type in Liquid Metal-Molten Salt Extraction System

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Two factors, which are important for selecting the extractor type suitable for liquid metal-molten salt system were studied, i.e. the formation and the coalescence processes of liquid metal drop. The drop formation process for liquid metal dispersion in the continuous phase is predictable from semi-empirical correlation reported on aqueous solution-organic solvent systems. The height of droplet bed being accumulated on drop-settling portion is predictable from the coalescence time of single drop on a flat metal interface. The coalescence of metal drop on a clean interface was very fast. The extractor type of liquid metal dispersion in molten salt is considered to be suitable for the pyrochemical extraction process.

KEYWORDS: extractor type, liquid metals, dispersions, molten salts, drop formation, coalescence, metal drops, bismuth, mercury, LiCl-KCl

I. INTRODUCTION

Liquid extraction using liquid metal and molten salt plays an important role in the pyrochemical processing of the nuclear fuel such as the salt fuel in the molten salt reactor. Many works have been performed on the liquid-liquid system which is comprised of aqueous solution and organic solvent (AO). On the contrary, we do not so much as know what type of extractor is suitable for the liquid metal-molten salt system (MS) due to lack of research on the extractor for this system.

The rate determination step in the extraction process is an important factor for selecting the extractor type. The extraction process in liquid metal-molten salt system is fundamentally based on the redox reaction. In case of rare earth extraction, the redox reaction is fast enough to be considered as diffusion controlling. In this case, an extractor type with liquid drop dispersion is to be selected.

The interfacial tension and the density difference between the continuous and dispersed phases are in general much greater in the MS system than in the AO system, the extractor of mixer-settler type being unfeasible due to the peculiar properties of the MS system. The continuous differential contactor type of liquid drop dispersion is suitable for the MS system.

This work is concerned with the behaviors of the liquid metal drops in an extractor of spray type which is a basic type of the differential contactor. Firstly, the formation of liquid metal drop from single nozzle was studied, and the obtained results were compared with the prediction from the semi-empirical equation reported on AO system, because the drop formation is mainly governed by physical properties of the systems. Secondly, the settling process of the liquid metal

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drops was studied, which is a key factor for the realization of the extractor for the MS system. The settling process is sensitively affected by small amounts of impurity involved in the system and the quantitative analysis is very difficult. The coalescence is in general comprised of two processes, i.e., the hydrodynamic process, followed by breaking very thin layer between two phases being coalescing. The impurity mainly affects the latter process, which is essentially determined by the same factor irrespective of the coalescence mode. Therefore, the drop bed height can be estimated with the help of the information on the single drop coalescence mode, in which unknown impurity effect is involved. In this work, the factors governing the single drop coalescence on a flat liquid metal surface was first elucidated. The height of the droplet bed at the settling portion was shown to be predictable from the information on the single drop coalescence process. It is shown that the coalescence of liquid metal drop in the MS system is fast and that the extractor with liquid drop dispersion is feasible in the MS system.

II. EXPERIMENTAL

The density difference and the interfacial tension in the liquid Hg and aqueous solution system (MW) are similar to those in the MS system, and first the MW system was selected as a simulation of the MS system.

Figure 1 shows the experimental set up for studying the Hg drop behavior in aqueous solution. The drops of liquid Hg were formed from single nozzle and fell downward, followed by coalescence at the bottom. The drop diameter was measured by a photograph method using strobo flash light or by weighing the sampled drops. The falling velocity of the drop was measured by the photograph method mentioned above. The coalescence phenomena were recorded by the video scope of high speed and the coalescence time of the drop was measured by reproducing the snapshots every 1/60 s. The experimental temperature was 293 K.

Figure 2 is the apparatus for measuring the settling process of Hg drops at the phase boundary. The droplets were generated from a distributor which was consisted of the nozzles (69, 49 or 21 in number and 0.25, 0.5 or 1 mm in diameter). The droplets fell downward through a pipe of 10 mm in diameter and formed a droplet bed at the bottom. The height of the bed was measured by the video scope. The volumetric flow rate of the dispersed phase was measured from the rising velocity of the Hg surface in the tube of 50 mm in diameter on the right-hand side in the figure. The diameter of the drops was measured by the same method as mentioned previously. The experimental temperature was 293 K.
Figure 3 shows the experimental apparatus for investigating the coalescence of a liquid Bi drop in molten salt on a flat Bi interface. Desired amount of LiCl or LiCl-KCl eutectic salt was charged in a quartz tube (30 mm in diameter) which was set in a transparent furnace. The salt was dried by passing Ar gas through it at about 573 K and was then melted. The drop of Bi metal was formed from a nozzle by regulating the flow rate of Bi with the needle valve at the bottom of the Bi reservoir. The nozzle and the reservoir were made of stainless steel (SUS 316). The coalescence phenomena were observed by the same method as in the Hg system. The interfacial tension of the Bi-salt system was measured by drop weight method with the help of this apparatus.

Figure 4 is the apparatus for measuring the droplet bed height in the Bi-salt system. The distributor was made of 9 nozzles of 1 mm in diameter. The droplets formed fell through a quartz tube of 7 mm in diameter and were settled at the bottom. The experimental procedure was almost same as in the Hg drop system. The volumetric flow rate of the dispersed phase was measured from the rising velocity of the top surface of the bed.

Mercury of reagent grade was purified by mixing it with iron alum solution by bubbling air and then passing it through the dilute aqueous solutions of HNO₃ and KOH. Bismuth used was 99.999% in purity. Sucrose solutions (content 0, 10, 20 and 30 %) were used to change the viscosity of the aqueous solution. LiCl and LiCl-KCl of the eutectic composition were used as the salt phase. These salts were of reagent grade.

III. EXPERIMENTAL RESULTS AND DISCUSSION

1. Drop Formation Process and Falling Velocity

Figure 5 shows the diameter of Hg drop, which was generated from the nozzles (0.0351 and 0.0118 cm I.D.), against the Hg velocity through the nozzle $u_N$, together with the features of the drop formation. The solid curves in the figure are the values predicted from the semi-empirical equations for the AO systems\(^{(3)}\)\(^{(5)}\)\(^{(7)}\): The drop diameter is predicted from Eqs. (1)\(^{(7)}\) and (2)\(^{(5)}\).

$$\frac{\pi}{6} d_N^3 = F \left[ \frac{\pi \sigma d_N}{g \Delta \rho} + \frac{5 \pi \mu_c d_N u_N}{d_N^2 g \Delta \rho} - \frac{\pi \rho_d d_N^3 u_N^3}{3 g \Delta \rho} \right]$$

$$+ 4.5 \left[ \frac{\pi \sigma d_N^2 u_N^5 \rho_d \sigma}{4 g \Delta \rho} \right]^{1/3}, \quad (u_N < u_{NJ}) \quad (1)$$

$$d_N \left( \frac{g \Delta \rho}{d_N \sigma} \right)^{1/3} = f \left( \frac{u_N}{u_{NJ, max}} \right), \quad (u_N > u_{NJ}) \quad (2)$$

Here, $f$ is given as an empirical correlation in the chart\(^{(4)}\). The experimental data are well explained by this prediction. The jetting velocity $u_{NJ}$ and the velocity providing maximum jet length $u_{NJ, max}$ are also shown in the figure together with the values predicted.
from the semi-empirical equations for the AO systems(7)(3):

\[ u_{N,\text{pred}} = \left[ 3 \left( 1 - \frac{d_N}{d_p} \right) \frac{\sigma}{\rho_d d_N} \right]^{1/2}, \]

\[ u_{N,\text{max}} = 3.91 \left( \frac{d_1}{d_N} \right)^{1/2} \frac{\sigma / d_f}{1.09 \rho_d + \rho_c} \]

The predicted values agree with the observed ones. From these results, it is concluded that the process of liquid metal formation is well predictable from the equations which have been reported for the AO systems. The process for the MS system is also predictable because the peculiar physical properties of this system are similar to the MW system.

In Fig. 6 the measured falling velocity of Hg drop \( V_p \) is shown comparing with the values predicted by assuming rigid sphere. The falling metal drop behaves like a rigid sphere. The predicted value (solid curve) shows a little higher value than the measured ones in the range of large drop size. This is attributed to slight deformation of the drop to the flat ellipsoid.

2. Coalescence Process of Drop

(1) Drop Bed Height in Hg Drop System

The experimental results of the liquid drop bed height \( H \) are shown in Fig. 7 according to the correlation which was presented for the AO system(3):

\[ \frac{H}{d_p} = 2564 \left( \frac{V \mu_c}{\sigma} \right)^{0.463} \left( \frac{d_p d \rho_f}{\sigma} \right)^{0.863} \left( \frac{\mu_c}{\mu_b} \right)^{0.773}. \]

The results for clean Hg water system locate around the line calculated from Eq. (5). However, the results for Hg-sucrose aqueous solution system are about ten times higher than...
the value calculated from Eq. (5), even though the effects of the changes of the viscosity and the interfacial tension due to the presence of sucrose are taken into account. This result suggests that some peculiar property should be introduced to represent the characteristic of coalescence in the system.

The coalescence process of a drop resting on the flat interface is controlled by the drainage of the continuous phase in a liquid film between the drop and the flat interface, until the film thickness reaches a critical value $h_c$ (see Fig. 8). The coalescence process in the droplet bed also would be controlled by the drainage of the continuous phase in a film between two drops, where the film thinning continues up to a critical thickness $h^*$. These two coalescence processes involve the similar coalescence mechanism. This similarity suggests that the droplet bed height can be related to the peculiar thickness of $h_c$ obtained in the single droplet coalescence.

(2) Single Drop Coalescence Process
Two modes of coalescence were observed in this work. One is the instantaneous coalescence which means the mode for a drop to coalesce as soon as it impacts the flat interface. The other is the rest coalescence, i.e. the coalescence of the drop resting on the flat interface after rebounding as it impacts the interface. The former mode is observed

Fig. 8 Illustration of coalescence processes of drops(2)

Fig. 9 $N/N_0$ vs. $t$

Hg-water: ◦ $d_0=0.146$, ○ $d_0=0.190$, ● $d_0=0.230$
Hg-sucrose soln: △ $d_0=0.189$ (10%), ○ $d_0=0.185$ (20%), ▲ $d_0=0.179$ (30%)
H$_2$O-Benzene: □ $d_0=0.15$
solely for the metal drop system.

First, we consider the rest coalescence process. The fraction of the drops left not to coalesce out of total number of resting drops is shown in Fig. 9 against the time elapsed since the drops were rested on the flat interface. The coalescence rate is low when the viscosity of the continuous phase is high and also when the drop diameter is large. This shows that the coalescence process would be governed by the drainage of the continuous phase in a film between the drop and the flat interface. The coalescence time is determined by the drainage time until the film reaches a peculiar thickness \( h_c \):\

\[
t = (1/32) \left[ \frac{\rho \cdot \sigma^2}{\phi^3} \right] \left( \frac{1}{h_c^2} \right).
\]  

(6)

The rest coalescence process is one of the probability process as described by Vrij(9), and the coalescence time is represented by the half period \( t_{1/2} \), i.e. time elapsed until half of the total drops coalesce. Figure 10 shows the coalescence time \( t_{1/2} \) observed in the experiment for the Hg-aqueous solution systems. In the figure, \( t_{1/2} \) is plotted according to Eq. (6). The drop diameter and the viscosity of the continuous phase were changed for these systems. The result for the Hg-water system obeys Eq. (6), and is located on the same position as for the benzene-water system(4). The peculiar film thickness \( h_c \) is evaluated from Eq. (6), being \( 2 \times 10^{-4} \text{ cm} \). The coalescence time for the Hg-sucrose solution system is larger than that for the clean system mentioned above. The \( t_{1/2} \) must coincide with the line for the clean system if sucrose affects the coalescence process only through the change in viscosity. This suggests that sucrose plays a role in the coalescence process as an impurity. The increase in the coalescence time is interpreted in terms of the decrease in the \( h_c \) value. The resultant \( h_c \) value is \( 1 \times 10^{-4} \text{ cm} \) for the sucrose solution (the sucrose content being 20 to 30%).

The experimental result for the Bi-(LiCl-KCl) eutectic system is also shown in Fig. 10. The coalescence time is much shorter than those for the Hg-aqueous solution system, \( h_c \) being \( 1.3 \times 10^{-3} \text{ cm} \).

Next, we consider the instantaneous coalescence process. This process is a phenomenon peculiar to the metal drop due to high density difference. The number fraction of the Hg drop joining in this coalescence out of the total falling drops was measured by changing the distance between the nozzle tip and the flat interface. The results are shown in Fig. 11. The fraction is correlated with \( \left( \frac{\text{kinetic energy of a drop}}{\phi^2} \right) / (1/h_c) = \frac{\pi}{12} d \rho V^2 \phi h_c \). The term \( 1/h_c \) represents a measure of the barrier energy resistive to coalescence. This shows that the instantaneous coalescence is governed by the two factors: One is the kinetic energy per unit area of the drop surface and the other is \( 1/h_c \), which is related to the energy required for overcoming the barrier to coalescence. The \( h_c \), determined from the rest coalescence plays an im-

\[\text{Fig. 10} \quad \text{Half period of single drop coalescence}\]

\[\text{Fig. 11} \quad \text{Contribution of instantaneous coalescence to overall one}\]
(3) Setting Process of Droplets

The measured heights of the droplet bed $H$ are plotted in Fig. 12 against the superficial velocity of the dispersed phase $V$. The effect of the drop diameter is week, as is clear from the figure. This result shows that the height of the droplet bed is mainly governed by the coalescence of the large drops which have been grown up in the bed. The effect of sucrose is strong. This result is consistent to the small value of $h_c$ in the sucrose solutions.

The settling process at a steady state was illustrated in Fig. 8(b) and was interpreted by Allak et al. as follows: Spherical drops arrive at the top of the bed and arrange themselves to a close pack state as the spherical forms, where the hold up of dispersed phase $\phi_d$ is 0.74. As the spherical drops pass into the bed, they are squeezed together extruding the continuous phase. These drops are deformed to a shape of a dodecahedron. Rate of drops entering droplet bed per unit area is given as $6V/(\pi d_p^3)$, where $V$ is the superficial velocity. The volume of continuous phase attached to each drop equals to $12 \times 0.29d_p^3 \times h/2$, where $0.29d_p^3$ and $h$ are the surface area of a face of dodecahedron and the thin film thickness, respectively. Then, the downward flow rate of continuous phase per unit area at a certain cross-section $Q_c$ is given as

$$Q_c = \frac{6V}{\pi d_p^3} \left(12 \times 0.29d_p^3 \times h/2\right) = \frac{3.32Vh}{d_p}.$$  \hspace{1cm} (7)

The faces of the dodecahedron are flat and the continuous phase is squeezed into the plateau border which forms a drainage net-work through the bed. The upward drainage rate of the continuous phase through the plateau border at the same cross-section $Q'_c$ must be equal to $Q_c$ because of steady state and is derived as

$$Q'_c = \frac{0.0041r_0^4 \Delta \rho g \phi_d}{3 \rho c d_p^2},$$  \hspace{1cm} (8)

where $r_0$ represents the smaller radius of curvature at the plateau border of the face of the dodecahedron and $\phi_d$ is hold up of the dispersed phase at the cross-section. The $r_0$ is determined from the relationship $Q_c = Q'_c$. Pressure difference between drop and the continuous phase $\Delta P$ is given as $\sigma/r_0$ from Laplace equation. The force acting on the thin film between two drops equals to $0.29d_p^3 \Delta P$. Thus, drainage time for thinning from $h$ to $h^*$ is given as

$$\tau = \frac{1}{1.80} \left(\frac{V \mu d_p^3}{\sigma^4 \Delta \rho g \phi_d}\right)^{1/4} \left[\frac{1}{h^{*1.76}} - \frac{1}{h^{1.76}}\right].$$  \hspace{1cm} (9)

with the help of Reynolds' equation, describing the drainage between two parallel rigid disks. When the film thickness of the flat
film of the continuous phase reaches a critical value \( h^*_c \), the coalescence between drops takes place. On coalescence, the \( d_p \), \( h \) and \( r_0 \) change, and the drainage time \( \tau \) is recalculated for the next coalescence step. The coalescence process is repeated until the hold up of the dispersed phase becomes unity.

The height of the droplet bed is calculated according to the above model with the \( h^*_c \) as a parameter, whose value is shown in Fig. 12. The resultant heights are shown by the curves in the figure. The experimental results for the Hg-aqueous solution system are well explained by the model.

The peculiar film thickness \( h^*_c \) can be related with the \( h_e \) value which was obtained in the single drop experiment (see Fig. 13). Since a linear relationship is obtained, the \( H \) value can be evaluated with the help of the peculiar thickness \( h_e \).

![Fig. 13 Relationship between \( h_e \) and \( h^*_c \)](image)

The \( h_e \) value in the Bi-(LiCl-KCl) eutectic system was obtained previously as \( 1.3 \times 10^{-3} \) cm. The \( h^*_c \) value is estimated from Fig. 13 with the \( h_e \) value, being \( 2.5 \times 10^{-3} \) cm. The dotted curve in Fig. 12 is calculated from the model presented by Allak et al. with the \( h^*_c \). The observed value (also shown in the figure) is very small as expected by the model. From this result, the coalescence process of liquid Bi-molten salt system operated at high temperatures is estimated to be very fast. The operation of the extractor with metal drop dispersion is feasible and is suitable for the pyrochemical extraction process such as the chemical processing of fuel salt in MSR or MSBR.

The \( h_e \) is the most important parameter which governs the drop coalescence phenomena, i.e. the instantaneous and rest coalescences and the settling process of the droplets. It is left to future work to elucidate what factors determine the \( h_e \) value.

**IV. CONCLUSION**

The behaviors of the liquid metal drops in an extractor were studied. The formation process of the metal drops is predictable from the results which have been extensively studied in the aqueous solution-organic solvent systems. Two modes were observed in the coalescence of a falling drop to a flat interface, i.e. the instantaneous and rest coalescences. The rest coalescence process is governed by the drainage of the continuous phase in the thin film between the drop and the interface and also by the rapture of the film. The easiness of the film rapture is described by the critical thickness of the film \( h_e \). The fraction of the drops joining in the instantaneous coalescence is correlated with the kinetic energy of the drop divided by the energy needed for overcoming the barrier to the coalescence, which is related with the value \( 1/h_e \). The critical thickness, which is difficult to evaluate, does not depend on the coalescence modes. The rate of the drop coalescence in an accumulated drop-layer is also predictable with the help of \( h_e \), which is determined from the rest coalescence process of single drop. The coalescence process is very fast in the liquid metal-molten salt system, and the extractor with liquid metal dispersion is suitable for pyrochemical extraction process such as the salt fuel reprocessing of the molten salt reactor or molten salt breeding reactor.

**[NOMENCLATURES]**

- \( d_j \): Diameter of liquid jet (cm)
- \( d_N \): Inner diameter of nozzle (cm)
- \( d_p \): Drop diameter (cm)
- \( F \): Harkins-Brown's correction factor
- \( g \): Acceleration of gravity (cm/s²)
- \( H \): Height of droplet bed (cm)
- \( h \): Film thickness of continuous phase (cm)
- \( h_e \): Critical film thickness for single drop coalescence (cm)
- \( h^*_c \): Critical film thickness for droplet coalescence (cm)
$N$: Number of drops not to coalesce
$N_0$: Total number of drops assessed
$Q_c, Q'_c$: Flow rate of continuous phase (cm/s)
$r_0$: Smaller radius of curvature at plateau border of face of dodecahedron drop (cm)
$t$: Coalescence time (s)
$t_{1/2}$: Half period of coalescence (s)
$u_N$: Velocity through nozzle (cm/s)
$u_{NJ}$: Jet formation velocity through nozzle (cm/s)
$V$: Superficial velocity of dispersed phase (cm/s)
$V_p$: Falling velocity of drop (cm/s)
$\mu_c, \mu_d$: Viscosities of continuous phase and dispersed phase (g/cm·s)
$\rho_c, \rho_d$: Densities of continuous phase and dispersed phase (g/cm$^3$)
$\Delta \rho$: Density difference (g/cm$^3$)
$\sigma$: Interfacial tension (g/s$^2$)
$\tau$: Drainage time (s)
$\phi_d$: Hold up of dispersed phase

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