# Interfacial Tension between a Molten Fluoride Mixture and Liquid Bismuth

**Hirotake Moriyama, Kunimitsu Yajima, and Jun Oishi***

*Department of Nuclear Engineering, Kyoto University, Kyoto 606, Japan*

Interfacial tensions between the LiF–KF binary melt and liquid bismuth and between the LiF–BeF$_2$ binary melt and liquid bismuth were measured over a wide range of salt compositions by a modified maximum bubble pressure method. The experimental uncertainties were within 5%. Their interfacial tension isotherms show apparent negative deviation from the linear dependence on salt composition. It was found that the LiF–KF binary melt showed nearly ideal solution behavior in the interfacial tension as well as in the surface tension. On the other hand, the formation of the complex ion BeF$_4$$^{2-}$ would play an important role in the interfacial tension of the LiF–BeF$_2$ binary melt–liquid bismuth system in the same way as in the surface tension.

## Introduction

Molten fluorides are useful nuclear materials, for example, as the coolant and the fuel solvent in the molten salt reactor (MSR) (1). Physical and chemical properties of molten fluorides have been investigated successfully, but little is known of the interfacial tensions between molten fluorides and other immiscible liquids in spite of their importance (2).

We have obtained the surface tension values for binary (3, 4) and ternary (4) melts of fluorides, and now our interest is directed to the interfacial tensions between fluoride melts and liquid bismuth. In the present work, the interfacial tensions between the LiF–KF binary melt and liquid bismuth and between the LiF–BeF$_2$ binary melt and liquid bismuth were measured by a maximum bubble pressure method modified in our laboratory. The former fluoride melt is expected to be a coolant salt of MSR and the latter is a promising candidate for MSR fuel solvent. The obtained data are important in assessing the interfacial properties of those fluoride melts–liquid bismuth systems.

## Experimental Section

*Principle of Measurement*. The experimental techniques of measuring the interfacial tension between two immiscible liquid phases usually require transparent containers for sample liquids, but appropriate materials could not be found because of the highly corrosive properties of molten fluorides. Therefore, the well-known maximum bubble pressure method was adopted with some modifications.

When a capillary is inserted through the upper liquid a into the lower liquid b, the capillary is filled with parts of liquids a and b as shown in Figure 1a. With the rise of gas pressure over the surface of liquid a in the capillary, the interface between liquids a and b in the capillary moves down, and finally all of liquid b is exhausted from the capillary and a small drop of liquid a is formed at the capillary edge. If the excess gas pressure in the capillary at the instant of breaking the drop of liquid a, i.e., the interface between liquids a and b, is known, we may be able to calculate the interfacial tension value from the gas pressure, considering the balance of forces. However, it is very difficult to measure the excess gas pressure in the presence of a large volume of liquid a in the capillary.

We improved the method as follows. When the volume of liquid a in the capillary is sufficiently small, instead of a drop a bubble covered with a thin film of liquid a comes out from the capillary edge as shown in Figure 1b. In this case, both the interface between liquids a and b and the surface of liquid a are broken at the same time and at the same pressure. The maximum excess gas pressure when the bubble is broken can be correlated to the interfacial tension by the following equations, neglecting the weight of the thin film and according to Schrödinger's correction for the deformation of a bubble (5)

$$\gamma_{ab} = \frac{(\rho_b - \rho_a)gh'r'}{2}\left[1 - \frac{2r'}{3h'} - \frac{1}{6}\left(\frac{r'}{h'}\right)^2 - \dots\right] \quad (1)$$

$$h' = \frac{\Delta p - \rho_a g l_a - \rho_b g l_b - \rho_a g h}{(\rho_b - \rho_a)g} \quad (2)$$

$$\gamma_a = \frac{\rho_a g h r}{2}\left[1 - \frac{2r}{3h} - \frac{1}{6}\left(\frac{r}{h}\right)^2 - \dots\right] \quad (3)$$

where $\gamma_{ab}$ is the interfacial tension between liquids a and b, $\gamma_a$ the surface tension of liquid a, $\Delta p$ the maximum excess gas pressure over the surface of liquid a in the capillary, $l_a$ the depth of liquid a above liquid b in the container, $l_b$ the immersion depth of the capillary edge from the interface in the capillary, $\rho_a$ the density of liquid a, $\rho_b$ the density of liquid b, r the radius of the capillary edge where the inner surface of bubble grows, r' the radius of the capillary edge where the outer surface of the bubble, i.e., the interface, grows, h the height the manometer would read if filled with liquid a whose surface tension is being measured, and g the acceleration due to gravity.

*Procedures*. Experimental apparatus used is much the same as in the previous works (3, 4). All the chemicals used were of reagent grade obtained from Nakarai Chemicals, Ltd. Known amounts of the pertinent fluoride salt and bismuth were put into a stainless steel crucible and dried by evacuating at 200 °C for 1 day in a furnace. The furnace was filled with argon gas purified by passing through molecular sieves and titanium sponges. Then, the temperature was raised above the melting point of the fluoride sample and kept constant by a temperature-controlling device. The lighter fluoride melt lay on the heavier liquid bismuth.

A bubble tube was lowered gradually by a gear-type moving equipment while the argon gas was blown from a stainless steel capillary tip welded at the edge of the bubble tube. The capillary tip has about 1.5 mm outer radius and about 0.2 mm thickness. When the capillary tip came in touch with the free surface of the fluoride melt, a sudden increase of the gas pressure in the bubble tube was observed. The free surface was located by this observation. Similarly, the interface between the fluoride and bismuth phases was also located by observing the pressure increase when the capillary tip reached the interface. The location was determined within 0.05 mm of the moving equipment reading.

When measuring the interfacial tension, as small volume of the fluoride melt as possible was retained in the capillary as described above by controlling the location of the capillary in the salt phase and the pressure in the capillary. After further immersion of the capillary into the bismuth phase, the maximum
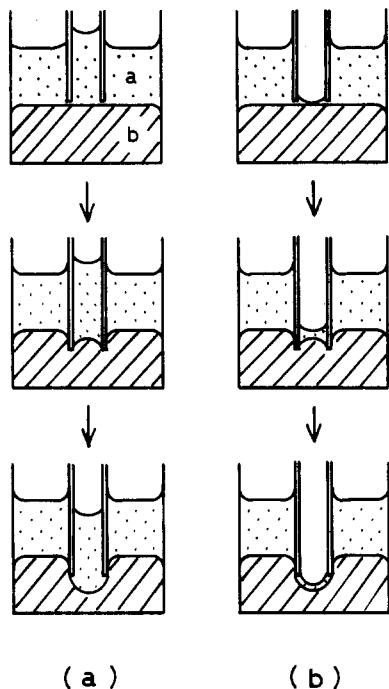
**Figure 1.** Principle of measurement of interfacial tension between two immiscible liquids by a modified maximum bubble pressure method.

**Table I. Interfacial Tension of Some Typical Systems[a]**

| system | | temp ($T$), | interfacial tension, mN/m | |
|---|---|---|---|---|
| a | b | K | present method | lit. |
| $C_6H_6$ | $H_2O$ | ~293 | 35.0 ± 1.8 | 35.7[b] |
| $C_2H_5OH$ | Hg | ~293 | 378.6 ± 3.3 | 381.6[c] |
| KCl | Bi | 1133–1213 | $407.0 - 0.12T(±5\%)$ | $423.0 - 0.12T$[d] |

[a] Surface tension data of Hg and Bi are taken from ref 9 and 10, respectively. Surface tension data of KCl are taken from ref 11. The other data are taken from ref 6. [b] Reference 6, method not shown. [c] Reference 7, pendant drop method. [d] Reference 8, electrocapillary method.

excess gas pressure in the capillary was measured by a manometer filled with dibutyl phthalate within the reading of 0.5 mm.

**Results**

In order to confirm the validity of the present method, the interfacial tension for some typical systems were measured, which had been established by other experimental techniques. The measured values are summarized in Table I together with the published values (6–8). The experimental errors are the standard deviations in several tens of measurements. It is very important to determine the radii $r$ and $r'$ in eq 1 and 3, but the direct measurement of these radii was impossible, especially in the present system. Thus, the following treatment was applied conventionally: the radius $r$ was calibrated by measuring the known surface tension of liquid a, and the radius $r'$ was similarly obtained with liquid b. The agreements between this work and the others are satisfactory within the experimental errors. Therefore the present method was concluded to be useful in the measurement of interfacial tension.

The interfacial tensions between the LiF–KF binary melt and liquid bismuth and between the LiF–BeF$_2$ binary melt and liquid bismuth were measured over a wide range of salt composition. The density of the LiF–KF binary melt was obtained with the density data (12) by assuming the linear composition dependence of molar volume. The density of the LiF–BeF$_2$ binary melt was also taken and interpolated from the literature data
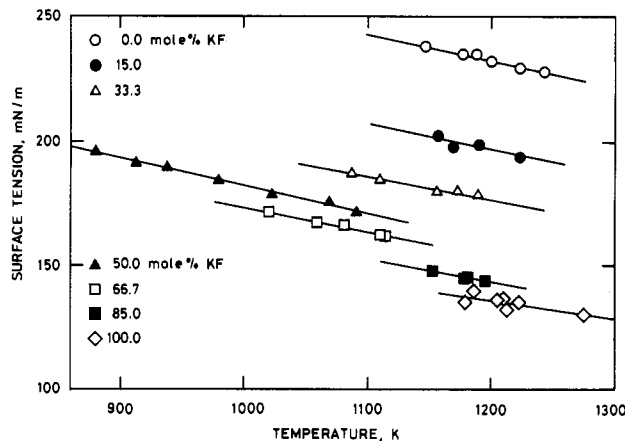


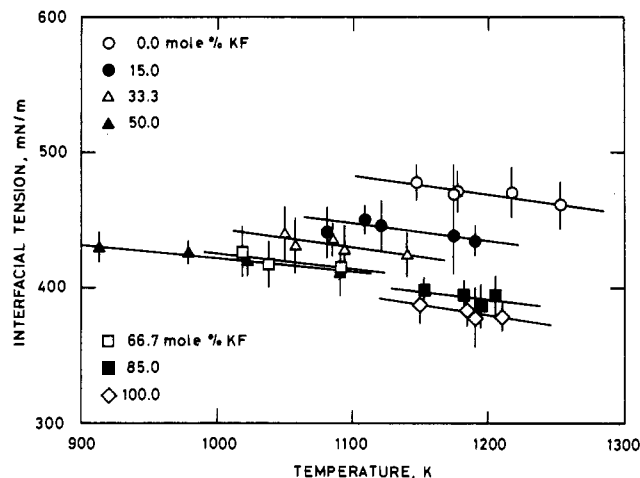**Figure 2.** Surface tension of the LiF–KF binary melt.



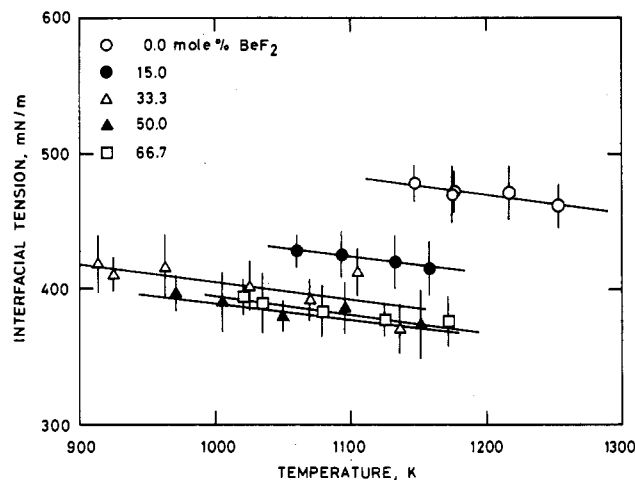**Figure 3.** Interfacial tension between the LiF–KF binary melt and liquid bismuth.



**Figure 4.** Interfacial tension between the LiF–BeF$_2$ binary melt and liquid bismuth.

**Table II. Surface Tension of LiF–KF Binary Melt**

| composition, mol % | | temp ($T$), | surf. tension,[a] |
|---|---|---|---|
| LiF | KF | K | mN/m |
| 100.0 | 0.0 | 1147–1243 | $357.0 - 0.104T$ |
| 85.0 | 15.0 | 1157–1223 | $320.8 - 0.103T$ |
| 66.7 | 33.3 | 1087–1189 | $291.5 - 0.096T$ |
| 50.0 | 50.0 | 880–1091 | $295.6 - 0.113T$ |
| 33.3 | 66.7 | 1020–1115 | $273.3 - 0.100T$ |
| 15.0 | 85.0 | 1153–1195 | $253.3 - 0.092T$ |
| 0.0 | 100.0 | 1179–1275 | $225.4 - 0.075T$ |

[a] Standard deviations are within 2%.

**Table III. Interfacial Tension between LiF–KF Binary Melt and Liquid Bismuth**

| composition, mol % | | temp ($T$), K | interfacial tension,[a] mN/m |
|---|---|---|---|
| LiF | KF | | |
| 100.0 | 0.0 | 1147–1253 | $630.6 - 0.134T$ |
| 85.0 | 15.0 | 1081–1191 | $594.3 - 0.133T$ |
| 66.7 | 33.3 | 1050–1140 | $580.1 - 0.136T$ |
| 50.0 | 50.0 | 913–1101 | $519.3 - 0.097T$ |
| 33.3 | 66.7 | 1019–1091 | $536.3 - 0.111T$ |
| 15.0 | 85.0 | 1153–1205 | $530.4 - 0.115T$ |
| 0.0 | 100.0 | 1150–1211 | $562.0 - 0.151T$ |

[a] Standard deviations are within 5%.

**Table IV. Interfacial Tension between LiF–BeF$_2$ Binary Melt and Liquid Bismuth**

| composition, mol % | | temp ($T$), K | interfacial tension,[a] mN/m |
|---|---|---|---|
| LiF | BeF$_2$ | | |
| 100.0 | 0.0 | 1147–1253 | $630.6 - 0.134T$ |
| 85.0 | 15.0 | 1060–1158 | $561.5 - 0.125T$ |
| 66.7 | 33.3 | 914–1136 | $531.7 - 0.127T$ |
| 50.0 | 50.0 | 971–1152 | $515.1 - 0.125T$ |
| 33.3 | 66.7 | 1021–1172 | $528.6 - 0.134T$ |

[a] Standard deviations are within 5%.

(*12*). The surface tension of the LiF–KF binary melt was measured by the maximum bubble pressure method in the separate experiment and is shown in Figure 2 and Table II. Some difference was found between our data in Table II and literature data (*11*), especially at the intermediate composition of salt. Our data was temporally adopted in calculating the interfacial tension. The surface tension of the LiF–BeF$_2$ binary melt was taken from our previous work (*3*). Figures 3 and 4 show the interfacial tensions between the LiF–KF binary melt and liquid bismuth and between the LiF–BeF$_2$ binary melt and liquid bismuth, respectively. The linear temperature dependences were found in both systems and are represented by the empirical equations as summarized in Tables III and IV.

**Discussion**

The values of the interfacial tension for the LiF–KF binary melt–liquid bismuth system at 1173 K, which were obtained from the empirical equations in Table III, are plotted against mole percent of KF in the melt in Figure 5. The plots show an apparent negative deviation from the linear dependence on salt composition. Similar negative deviations of the interfacial tension isotherms have been observed in several systems of molten alkali halide mixture and liquid bismuth (*13*, *14*). Figure 5 also shows the surface tension isotherm of the LiF–KF binary melt at the same temperature. It should be noted that the negative deviations of both isotherms in the figure are quite similar to each other.

The surface tension of almost all binary mixtures deviates from additivity and has been treated theoretically by several authors (*15–20*). The classical thermodynamic treatment of the surface tension of mixtures due to Gibbs was extended by Butler (*15*), Guggenheim (*16*), Defay and Prigogine (*17*), and Hoar and Melford (*18*) not only for ideal solution but also for regular solution. Especially, the regular solution formulas derived by considering van der Waals interactions have been used with success in calculating the surface tensions of many molecular liquids. It is doubtful, however, to apply these formulas directly to a molten salt mixture, since the effect of ionic interaction is essentially different from that of van der Waals interaction in a molecular liquid. Bertozzi (*19*), on the other hand, advocated another treatment by considering the effect of ionic interaction in a molten salt mixture. It was concluded
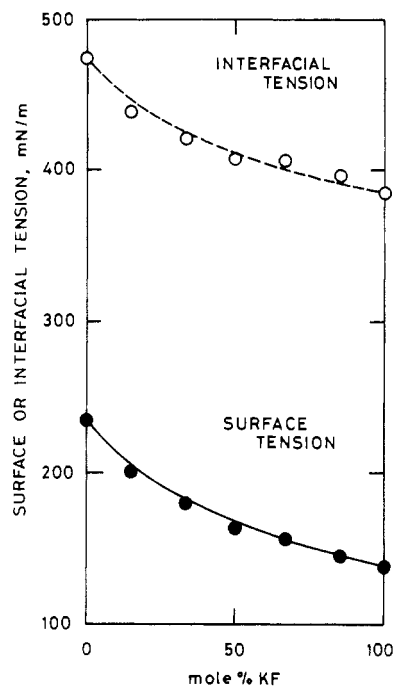


**Figure 5.** Isotherms of interfacial tension between the LiF–KF binary melt and liquid bismuth and surface tension of the LiF–KF melt at 1173 K. Circles show experimental values and curves are drawn from the ideal solution theory. See text.

from his measurement that the observed negative deviations in the surface tension isotherm is mainly due to a change in Coulombic energy in the surface layer. As pointed out by Grjotheim et al. (*20*), however, his semiempirical treatment is yet open to question because of his ignorance of the difference in surface tensions of both components, which is included in most models. Thus, there is found no treatment which is completely satisfactory for molten salt systems. Tentatively, the present results are compared here with one of the thermodynamic treatments for ideal solution.

For the surface tension of ideal binary mixture composed of components 1 and 2, Butler (*15*) introduces

$$\gamma_{12} = \gamma_1 + \frac{RT}{A_1} \ln \frac{x_1'}{x_1}$$

$$= \gamma_2 + \frac{RT}{A_2} \ln \frac{x_2'}{x_2} \qquad (4)$$

where $\gamma_{12}$, $\gamma_1$, and $\gamma_2$ are the surface tensions of binary mixture, pure component 1, and pure component 2, respectively, $A_1$ and $A_2$ are the areas of the components 1 and 2 spread out as a monolayer, respectively, $x_1$ and $x_2$ are the mole fractions of the components 1 and 2 in the bulk of mixture, respectively, $x_1'$ and $x_2'$ and the mole fractions of the components 1 and 2 in the surface layer, respectively, $R$ is the gas constant, and $T$ is the absolute temperature. With this equation and the relation $x_1' + x_2' = 1$, we can determine the values of $x_1'$, $x_2'$, and $\gamma_{12}$ from the known values of $\gamma_1$, $\gamma_2$, $A_1$, $A_2$, $x_1$, $x_2$, $T$, and $R$. The solid curve in Figure 5 shows the calculated value for $\gamma_{12}$ with the available data (*11*). A good agreement has been found between the experimental and calculated isotherms. The success for the surface tension had led us to apply the above equation to the interfacial tension. In this case, the interfacial tension between molten salt mixture and liquid bismuth is used in place of the surface tension in eq 4. A satisfactory agreement between the experimental values and the calculated ones (broken curve) has also been obtained in Figure 5. It can be concluded that the surface tension of the LiF–KF binary melt and the interfacial tension between this
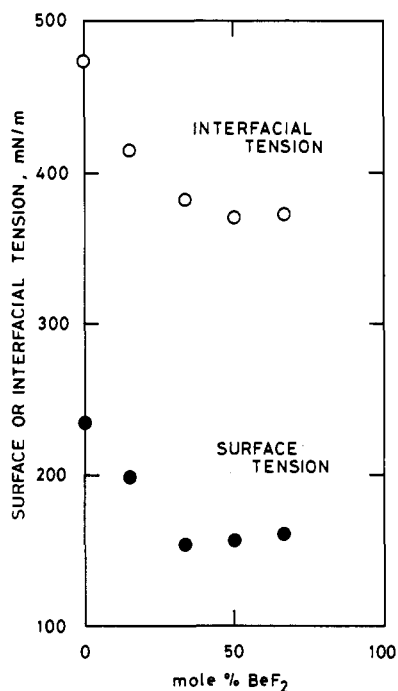
**Figure 6.** Isotherms of interfacial tension between the LiF-BeF$_2$ binary melt and liquid bismuth and surface tension of LiF-BeF$_2$ melt at 1173 K. Circles show experimental values. The surface tension data for the LiF-BeF$_2$ binary melt except for pure LiF are taken from ref 3.

melt and liquid bismuth show behaviors not so different from that of ideal solutions.

Figure 6 shows the interfacial tension isotherm for the LiF-BeF$_2$ binary melt-liquid bismuth system at 1173 K together with the surface tension isotherm of this melt (3). Contrary to the LiF-KF mixture, both isotherms exhibit the presence of minimum values in the studied range of salt composition. This indicates that the ideal solution formulas are not applicable in this case. As previously reported (3), the complex ions BeF$_4^{2-}$ are formed in the surface layer of the LiF-BeF$_2$ binary melt and have a definite influence on the surface tension. The interfacial tension might also be affected similarly by the presence of the complex ions.

Finally, we should note the interactions through the interface between the components in both phases. As is well-known, the interfacial tension $\gamma_{ab}$ between two immiscible liquids a and b is expressed as

$$\gamma_{ab} = \gamma_a + \gamma_b - W_{ab} \qquad (5)$$

where $W_{ab}$ is called the work of adhesion between the phases a and b, and is considered to result from the interactions of the components through the interface. Using this equation, the $W_{ab}$ values for the LiF-KF mixture and the LiF-BeF$_2$ mixture have been obtained to be from 70 to 80 mJ/m$^2$ and from 80 to 110 mJ/m$^2$, respectively. The values of about 100 mJ/m$^2$ have been reported for some systems of molten alkali halide mixture

and liquid bismuth (8, 13, 14). The work of adhesion for the typical systems of molecular liquid and liquid mercury is 100-200 mJ/m$^2$ (21) and is said to result mainly from the dispersion force. Though the values obtained in this study are rather lower, the dispersion force might also take an important role in the work of adhesion for the system of molten fluoride and liquid bismuth.

## Conclusions

A modified maximum bubble pressure method has been successfully applied for the measurement of interfacial tension between the molten salt mixture LiF-KF or LiF-BeF$_2$ and liquid bismuth. Though experimental errors involved are rather high, it is a useful technique for corrosive systems such as molten fluorides.

In the case of the LiF-KF mixture, surface tension and interfacial tension isotherms are described with fair accuracy by the ideal solution formulas. In the case of the LiF-BeF$_2$ mixture, on the other hand, both isotherms seem to be influenced by the formation of complex ions.

## Acknowledgment

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