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Surface Tension of Molten LiF-MgF_2, CaF_2 and SrF_2 Binary Systems

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ABSTRACT

Surface tension and density of molten LiF-MgF_2, LiF-CaF_2 and LiF-SrF_2 binary systems were measured by a maximum bubble pressure method. The composition dependence of the surface tension shows the upward curvature in these binary systems. The molar volume of the binary mixtures is represented by a simple additivity. The change in the surface tension with the composition is discussed from the thermodynamic point of view.

1. INTRODUCTION

The authors have investigated the composition dependence of the surface tension in alkaline-halide, carbonate, nitrate and sulfate binary systems from the thermodynamic point of view /1-9/. It has been elucidated from these previous works that these binary systems usually have a downward curvature in the composition dependence of the surface tension, and that they show a large downward curvature particularly in common-anion systems /2-4,7,8/. In these binary systems investigated in the previous work, the ions in the pure components have the same electric charge in cation sites (LiF-KF, Li_2CO_3-K_2CO_3 etc.) or anion sites (LiF-LiCl etc.) When the pure components have a different electric charge in a binary system such as LiF-MgF_2, those binary systems might have different composition dependence from the systems mentioned above. Therefore, it is quite important to accumulate the information on the composition dependence of the surface tension in those systems. In the present work, we have measured the surface tension and the density of molten LiF-MgF_2, LiF-CaF_2 and LiF-SrF_2 binary systems, in which the composition dependence of the physico-chemical properties has not been reported so far, by using a maximum bubble pressure method.

2. EXPERIMENTAL

The experimental apparatus for the maximum bubble pressure method is shown in Fig.1.

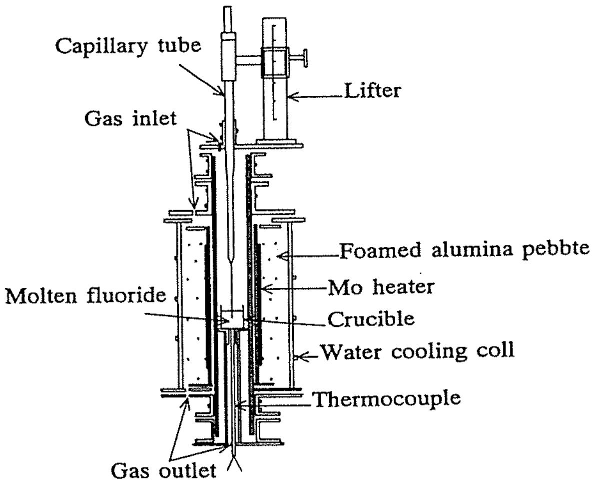

Fig. 1: Experimental Apparatus

After a melt, which is contained in a Pt-20mass%Rh crucible, is kept under Ar gas for a period of more than 1h, a Pt capillary tube (approximately 1.6mmID, 2.5mmOD) is immersed into the melt and bubbles are blown at time intervals of 30sec. Ar gas was used as the bubbling gas and also as the ambient gas. The bubble pressure was measured by a pressure transducer calibrated by a U-tube distilled water-filled manometer and a cathetometer with an accuracy of 0.01mm was used to measure the depth of immersion of the tube.

The surface tension σ was determined from the following Schroedinger's equation /10/.

$$\sigma = \frac{r\cdot H_0\cdot g}{2}\{1-\frac{2}{3}\cdot\frac{r\cdot\rho}{H_0}-\frac{1}{6}\cdot(\frac{r\cdot\rho}{H_0})^2\} \quad ...(1)$$

where H_0 is the maximum bubble pressure at melt surface, which is obtained by extrapolating pressures measured at five points in the melt from 2 to 10 mm in depth, r is the inner radius of the capillary tube, calculated from the value measured at room temperature and the linear expansivity α /11/ as shown in Eq.(2), ρ is the density of the melt, and g is the gravitational constant.

$$\begin{aligned}\alpha(\%) &= \frac{l_T - l_{293}}{l_{293}}\times 100\\ &= 9.122\times10^{-4}(T-293)\\ &+7.467\times10^{-8}(T-293)^2\\ &+7.467\times10^{-11}(T-293)^3\\ &(293< T/K <1900) \end{aligned} \quad (2)$$

The density of the melt is also determined from the differences of the maximum bubble pressures ΔP at two positions separated vertically in the melt by Δh.

$$\rho = \frac{\Delta P}{\Delta h} \quad (3)$$

3. EXPERIMENTAL RESULTS

3.1 Surface Tension

Figures 2-4 show the experimental results of the temperature dependence of the surface tension in molten LiF-MgF$_2$, LiF-CaF$_2$ and LiF-SrF$_2$ binary systems. Figures 5-7 shows the composition dependence of the surface tensions in molten LiF-MgF$_2$, LiF-CaF$_2$ and LiF-SrF$_2$ binary systems. The surface tension of molten pure MgF$_2$, CaF$_2$ and SrF$_2$ are quoted from the values reported by Hara and Ogino/12/. In these figures, the curves indicate the calculated values of the surface tension described later. As can be seen in these figures, the composition dependence of the surface tension of these melts represents the small upward curvatures. In many binary systems of liquid alloys and molten salt mixtures, they usually have the downward curvature in the composition dependence/1-9/. The change in the surface tension with the composition is discussed in the next section.

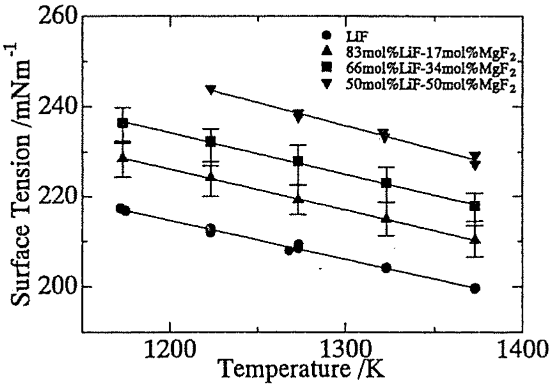

Fig.2: Temperature dependence of surface tension of molten LiF-MgF$_2$.

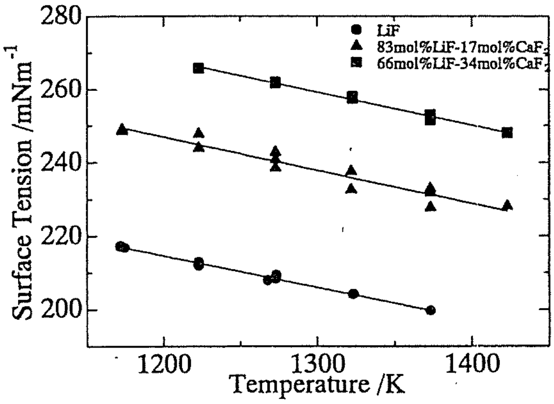

Fig. 3: Temperature dependence of surface tension of molten LiF-CaF$_2$.

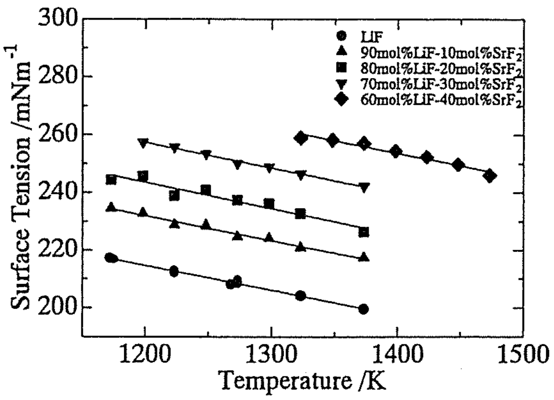

Fig. 4: Temperature dependence of surface tension of molten LiF-SrF$_2$.

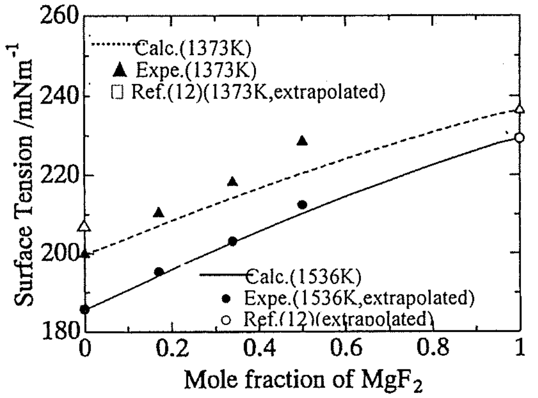

Fig. 5: Composition dependence of surface tension of molten LiF-MgF$_2$ at 1373K and 1536K.

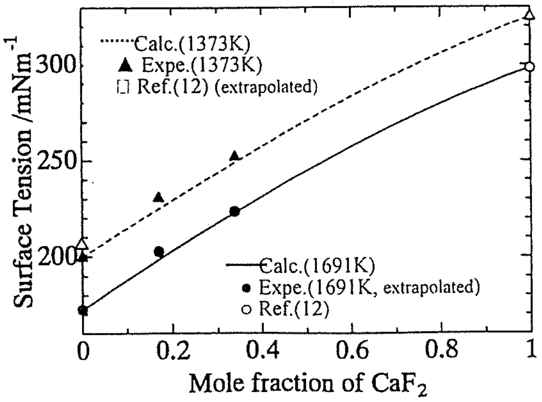

Fig. 6: Composition dependence of surface tension of molten LiF-CaF$_2$ at 1373K and 1691K.

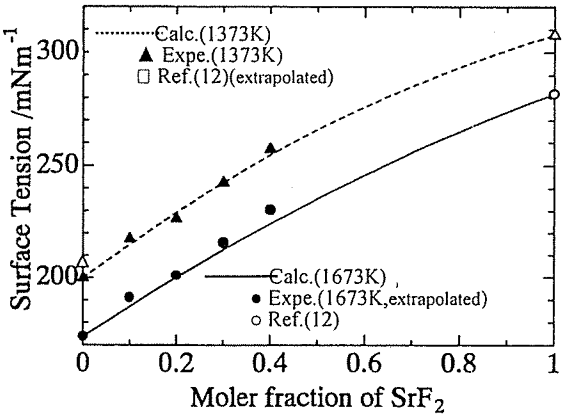

Fig. 7: Composition dependence of surface tension of molten LiF-SrF$_2$ at 1373K and 1673K.

3.2 Density

The densities measured in the present work are shown in Figs. 8-10 for molten LiF-MgF$_2$, LiF-CaF$_2$ and LiF-SrF$_2$ binary systems. The composition dependence of the molar volumes of these melts is shown in Fig. 11. The molar volumes of molten pure MgF$_2$, CaF$_2$ and SrF$_2$ are quoted from the values reported by Hara and Ogino /12/. As shown in Fig. 11, a simple additivity is held for the composition dependence of the molar volume in these binary melts.

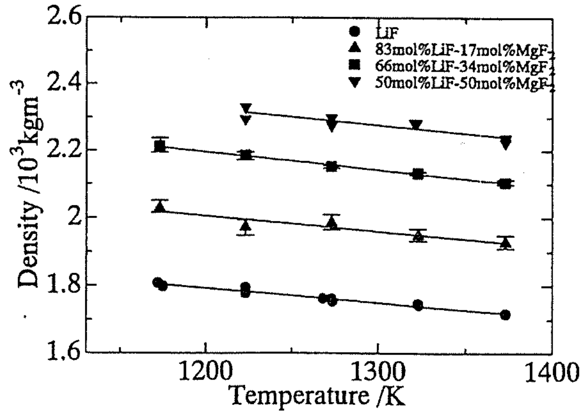

Fig. 8: Temperature dependence of density of molten LiF-MgF$_2$.

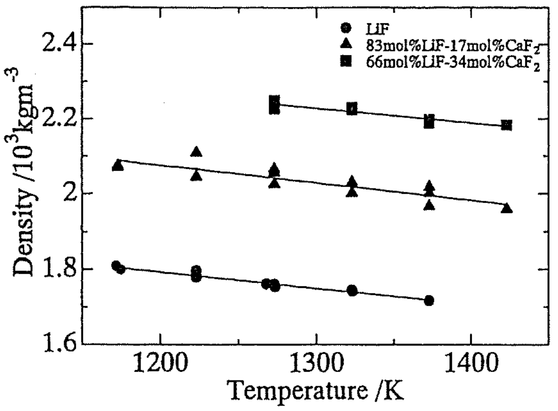

Fig. 9: Temperature dependence of density of molten LiF-CaF_2.

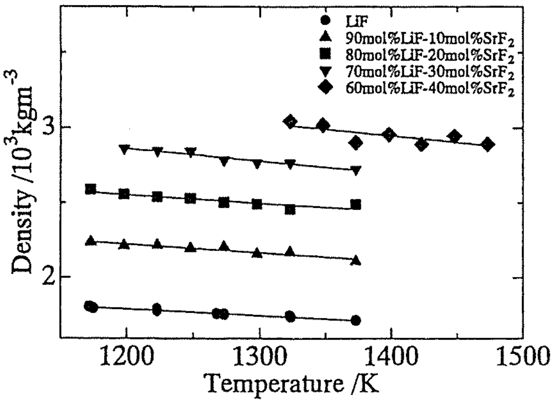

Fig. 10: Temperature dependence of density of molten LiF-SrF_2.

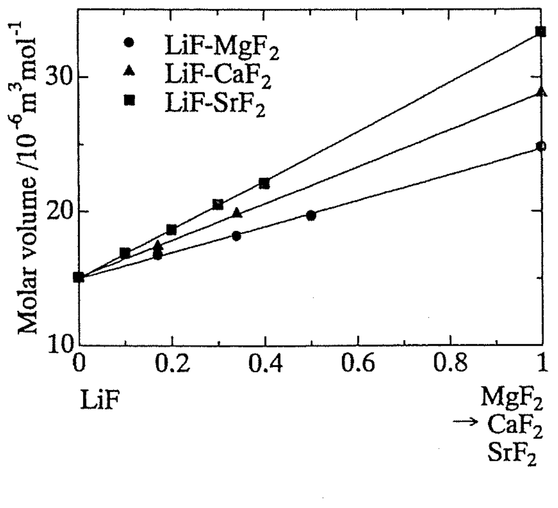

Fig. 11: Composition dependence of molar volumes of molten LiF-based binary systems at 1373K.

4. THERMODYNAMIC EVALUATION OF SURFACE TENSION OF MOLTEN IONIC BINARY SYSTEMS

The authors derived the following equations (4) and (5) /2-8/ to evaluate the surface tension σ of molten ionic mixture in A-B binary system on the basis of Butler's equation /13/, in which a surface is assumed to be an outermost monolayer :

$$\sigma = \sigma_A + \frac{RT}{A_A}\ln\frac{D_A^{Surf}}{D_A^{Bulk}} + \frac{1}{A_A}\{G_A^{E,Surf}(T,N_B^{Surf}) - G_A^{E,Bulk}(T,N_B^{Bulk})\} \tag{4a}$$

$$\sigma = \sigma_B + \frac{RT}{A_B}\ln\frac{D_B^{Surf}}{D_B^{Bulk}} + \frac{1}{A_B}\{G_B^{E,Surf}(T,N_B^{Surf}) - G_B^{E,Bulk}(T,N_B^{Bulk})\} \tag{4b}$$

$$\begin{aligned} &G_X^{Surf}(T,N_X^{Surf}) \\ &= (\frac{Z^{Surf}}{Z^{Bulk}})\frac{1}{\varsigma^4}G_X^{Bulk}(T,N_X^{Surf}) \\ &= 1.1\cdot G_X^{Bulk}(T,N_X^{Surf}) \end{aligned} \tag{5}$$

In the above equations, *R*: the gas constant, *T*: temperature, σ_X:surface tension of pure X (X=A or B), A_X=$N_0^{1/3}V_X^{2/3}$: molar surface area in a monolayer of pure X (N_0 : Avogadro number, V_X : molar volume of pure liquid X.). D_X^P=$d_XN_X^P$ /($d_AN_A^P$+$d_BN_B^P$). (d_X : sum of ionic radii of cation & anion, *P*=*Surf* or *Bulk*) N_X^{Surf} and N_X^{Bulk}: mole fractions of a component X in a surface and a bulk. $G_X^{E,Surf}(T,N_X^{Surf})$ and $G_X^{E,Bulk}(T,N_X^{Bulk})$: partial excess Gibbs energies of X in the surface and the bulk as a function of *T* and N_X^{Surf} or N_X^{Bulk}.

The partial excess Gibbs energies in the bulk can be obtained directly from thermodynamic databases. The excess Gibbs energy in the surface is evaluated from Eq. (5) derived by the present authors /1-9/ on the basis of the idea proposed by Speiser *et al.* /14,15/. In Eq. (5), Z^{Surf} /Z^{Bulk}(=0.94) /1-9/ is the apparent ratio of the coordination number in the surface to that in the bulk. ζ is the ratio of the ionic distance in the surface to that in the bulk. ζ has been evaluated to be 0.97 by Sawada and Nakamura /16/ from their theoretical work on the displacement of ions at the surface for molten alkali-halides. The above equation (5) means that the excess Gibbs energy in the surface of molten ionic mixtures is not determined by only Z^{Surf}/Z^{Bulk}. This occurs because the surface relaxation happens to keep the neutrality of the electric charge in the surface of molten ionic mixtures by changing the ionic distances.

The surface tension σ of molten ionic mixture can be calculated from Eqs. (4) and (5) as follows:

1) Setting temperature T and composition N_B^{Bulk} of the bulk.
2) Inserting the values for surface tension σ_X and molar volume V_X of pure component at the above temperature in Eqs. (4a) and (4b).
3) Determining excess Gibbs energies in the bulk at the above temperature and composition, and substituting them in Eqs. (4a) and (4b).
4) Then, Eqs.(4a) and (4b) become the simultaneous equations with unknown N_B^{Surf} and σ. These equations are solved for those unknown N_B^{Surf} and σ numerically.

We have applied the above equations (4) and (5) to evaluate the surface tension of alkaline-halides, carbonate, sulfate, nitrate systems, and found that those calculated results agree well with the experimental data /1-9/. In these binary systems, the composition dependence of the surface tension usually shows the downward curvatures /1-9/.

When we assume that the binary system is an ideal solution for a simple case, the above equations (4a) and (4b) become as follows :

$$\sigma = \sigma_A + \frac{RT}{A_A} \ln \frac{D_A^{Surf}}{D_A^{Bulk}} \tag{6a}$$

$$\sigma = \sigma_B + \frac{RT}{A_B} \ln \frac{D_B^{Surf}}{D_B^{Bulk}} \tag{6b}$$

D_A^{Bulk} and D_B^{Bulk} correspond to the bulk composition of the components A and B. Similarly, D_A^{Surf} and D_B^{Surf} correspond to the surface composition of the components A and B. If we have the relations $D_A^{Surf} > D_A^{Bulk}$ and $D_B^{Surf} < D_B^{Bulk}$, the component A segregates in the surface. When the pure component A has almost the same molar volume as that of the component B, we have $A_A \approx A_B$. Then if $\sigma_A < \sigma_B$, we obtain the relations $D_A^{Surf} > D_A^{Bulk}$ and $D_B^{Surf} < D_B^{Bulk}$ in order to have the condition Eq. (6a)=Eq. (6b) /1-9/. In such a case, the composition dependence of the surface tension shows a downward curvature/1-9/. However, if $V_A < V_B$ (in other words, $A_A < A_B$) as well as $\sigma_A < \sigma_B$, the component A does not always segregate in the surface, which means that the composition dependence might show a slight upward curvature in some cases.

The calculated results of the surface tension of molten LiF-MgF_2, LiF-CaF_2 and LiF-SrF_2 binary systems are indicated in Figs. 2-4. Here, we assumed that those binary systems are ideal solutions, in other words, we have used Eqs.(6a) and (6b) because interaction parameters between the components have not been reported in those three binary systems. The calculated results show an upward curvature and they agree well with the present experimental results. In molten LiF-MgF_2, LiF-CaF_2 and LiF-SrF_2 binary systems, molten pure LiF has smaller surface tension than those of molten pure MgF_2, CaF_2 and SrF_2/12/. In addition, molten pure LiF has smaller molar volume than those of the molten pure alkaline-earth fluorines/12/. Therefore, the composition dependence of the surface tension in molten LiF-MgF_2, LiF-CaF_2 and LiF-SrF_2 binary systems stems from that LiF has the smaller surface tension and the smaller molar volume than those of pure MgF_2, CaF_2 and SrF_2 on the basis of the thermodynamic consideration in Eqs.(4)-(6).

5. CONCLUDING REMARKS

We have measured the surface tension and the density of molten LiF-MgF_2, LiF-CaF_2 and LiF-SrF_2 binary systems by using the maximum bubble pressure method. In these binary systems, the surface tension show an upward curvature in the composition dependence, and the molar volume is expressed by a simple additivity. Since LiF has a smaller surface tension and a smaller molar volume than those of pure MgF_2, CaF_2 and SrF_2 in these systems, LiF does not segregate in the surface and they show an upward curvature in the composition dependence of the surface tension, which is different from those in many molten salt mixtures including LiF.

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