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# SURFACE TENSIONS OF SOME MOLTEN SALTS AND THEIR SURFACE TENSION DRIVEN FLOWS

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Synopsis: The surface tension dependence on temperature of molten NaOH and $Na_3AlF_6$(cryolite) had been measured by the maximum bubble pressure method. It was found that cryolite exhibited negative temperature coefficient of surface tension while NaOH showed positive one in the certain temperature range.

Marangoni convection of both melts were observed directly by hot-thermocouple technique. The results indicated that surface flows occurred from the high temperature zone to the low temperature zone for cryolite while the reverse flow occurred in the molten NaOH. These observations are consistent with the temperature dependence of surface tension.

Key words : temperature dependence of surface tension, NaOH, cryolite, Marangoni convection

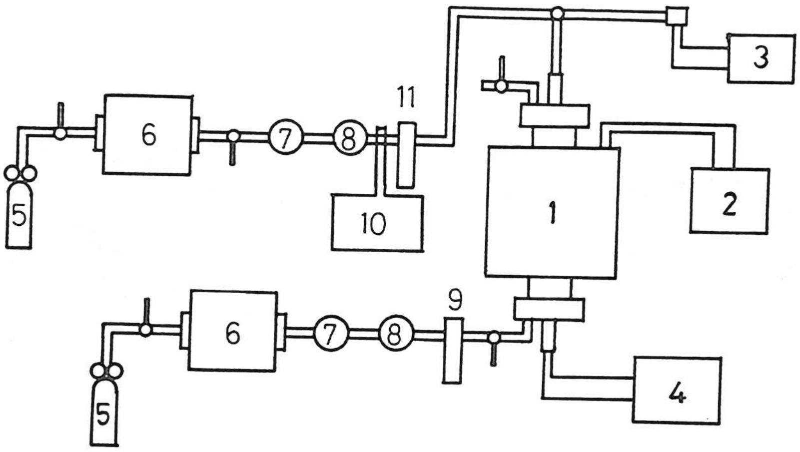
## 1. Introduction

Surface tension gradient at a free surface results in a tangential stress which can induce a motion in the melt. Such a motion, namely Marangoni convection, sometimes takes a important role in materials processing such as iron and steel making[1] and welding process[2]. Schwabe et al[3] showed surface flows in a capillary liquid bridge of sodium nitrate and succeeded to explain the motions qualitatively by the concept of Marangoni convection. Authors have already demonstrated the motion caused by surface tension driven flow in alkali nitrates and some chlorides[4]. In the present paper temperature dependence on surface tension of molten NaOH and cryolite were measured by the maximum bubble pressure method and surface tension driven flows corresponding to the temperature dependence of surface tension were directly observed by hot thermocouple technique.

## 2. Experimental

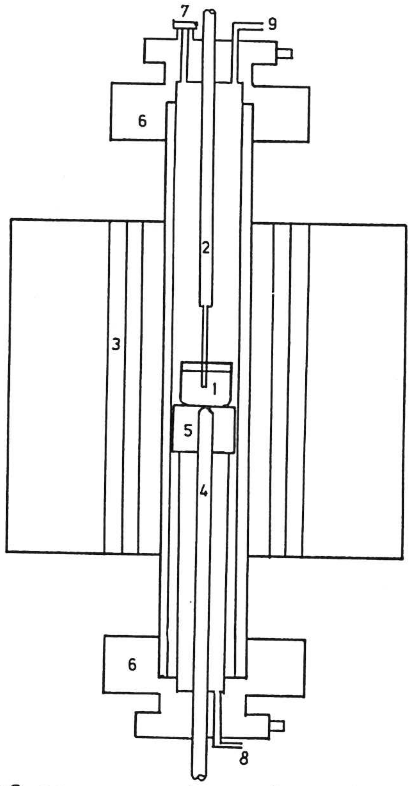
Extra pure grade reagents of NaOH, over 99.9 mass%, and cryolite, 99 mass%, were used in the present experiments.

The maximum bubble pressure method was applied to measure the surface tensions of molten salts. This method is good for the measurement of temperature dependence of surface tension. Schematic diagrams of an apparatus of the maximum bubble pressure method and furnace assembly were shown Fig.1 (a) and (b) respectively. Ar gas was used as a carrier gas, which was deoxidized by Mg ribbons and dehydrated by silicagel and $Mg(ClO_4)_2$. Change of pressure when a bubble was detached from a capillary was measured by a digital pressure gauge. Capillary and crucible were made of Pt. The diameter of the capillary was measured through a microscope after the experiments and calibrated using thermal expansion coefficient of Pt. Values of surface tension were calculated by Schrodinger's equation.




(a)

1.furnace 2.furnace controller 3.Digital pressure gauge 4.thermocouple
5.Ar gas 6.Mg getter furnace 7.silicagel 8.$Mg(ClO_4)_2$
9 and 11.flow meter 10.reservoir




(b)

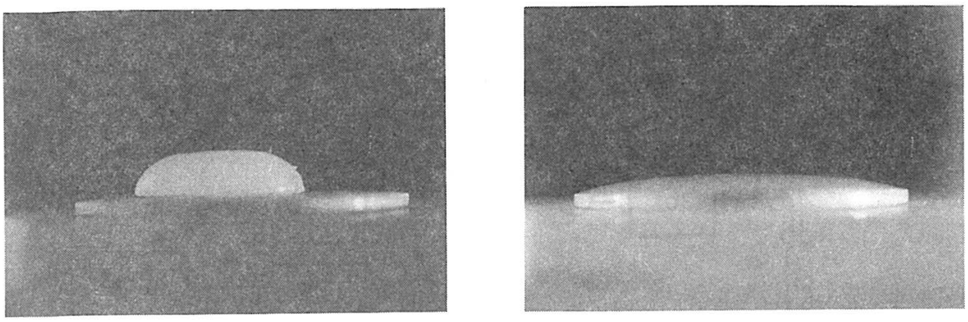
1.molten salt
2.lance
3.heater
4.thermocouple
5.supporter
6.water jacket
7.viewing window
8.gas inlet
9.gas outlet

Fig.1 Schematic diagrams of an apparatus of maximum bubble pressure method (a) and furnace assembly(b).

Direct observations of surface driven flows in a capillary bridge of molten salts were done by hot thermocouple technique[5]. The capillary liquid bridge was maintained by two Pt disks which joined Pt·Rh(10%) - Pt·Rh(30%) thermocouple to the back side. Motions in the liquid bridge were recorded by video through a microscope. Detail of the experimental procedure of the hot thermocouple technique was mentioned in the previous paper[4].

## 3. Temperature dependence of surface tension

Before measuring surface tension, wettabilities of Pt to molten NaOH and cryolite were investigated because materials for capillary should be wet to the liquids measured[6]. A wetting behavior of Pt to molten NaOH, for instance, is shown in Fig.2 (a) at melting point and (b) at 603K.



(a)at melting point (b) at 603K

Fig.2 A wetting behavior of Pt to a NaOH melt at melting temperature(a) and at 603K.

A NaOH melt completely spread on Pt plate in the temperature range of the measurement. Thus Pt was found a suitable material for the capillary to a NaOH melt. A cryolite melt also showed same wetting behavior as a NaOH melt to Pt. Therefore, the inner diameter of the capillary could be used to calculations of surface tensions.

Since cryolite is a main molten salt in Al electrolysis, many results of surface tension measurements have been reported. All data shows negative temperature coefficient of surface tension[6] as same as normal pure liquids. In the present paper a temperature dependence of cryolite was measured in order to confirm the previous data and check the cryolite melt used in the present observation study, because surface tension and its temperature dependence are sometimes affected by a very small amount of minor elements in the melt. It is better to use the cryolite melt confirmed for the direct observation study.

The temperature dependence of surface tension of cryolite melt is shown in Fig.3 with the previous data. One measuring point in Fig.3 was obtained by average of more than ten measurements of maximum pressures at the constant temperature. The present results showed a good agreement with the previous data. The measurement of over 1360K could not be carried out because of the volatilization of the cryolite sample. A temperature coefficient of surface tension of the cryolite melt was calculated by a square root method using data in Fig.3. It was $-1.79 \times 10^{-4}$ N/m·K, which is relatively large value comparing other molten salts.

A very few data on surface tension of a NaOH melt can be available[7]. It reported the positive temperature dependence of surface tension of a NaOH melt but it was calculated from only two measuring points. Surface tension of a molten NaOH was measured in the wide temperature range from 630K to 850K. The results is shown in Fig.4. There exists a turning point, 740K, at which the temperature coefficient of the NaOH melt changed from positive to negative. A positive temperature coefficient, $+1.23 \times 10^{-4}$ N/mÑK was obtained from 630K to 740K and a negative one, $-1.72 \times 10^{-4}$ N/m·K, was found over 740K. This behavior could be obtained reversibly and reproducibly. Since a temperature coefficient of a pure melt is normally negative[8], very few examples which have a positive temperature coefficient have been reported[10]. The reason of the above result can not be well explained in the present paper but it is one of the most interesting phenomena on interfacial chemistry.

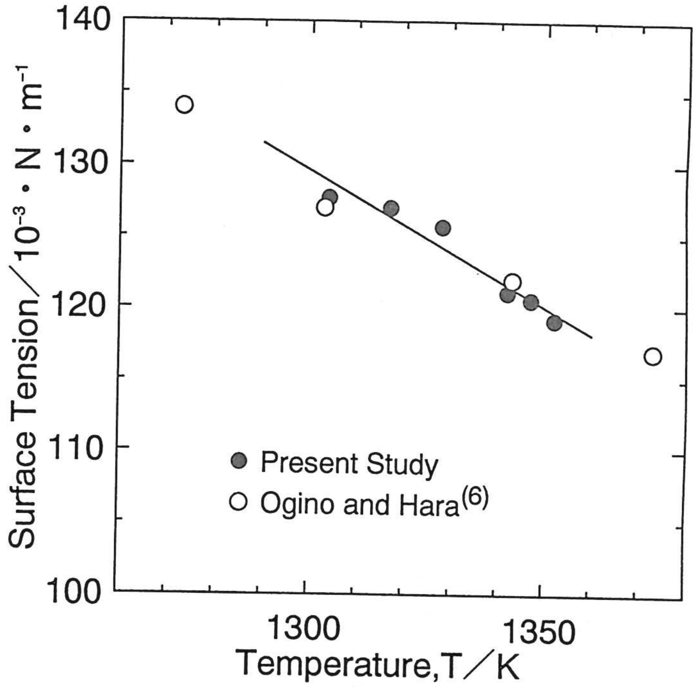



Fig.3 Temperature dependence of surface tension of a cryolite melt.

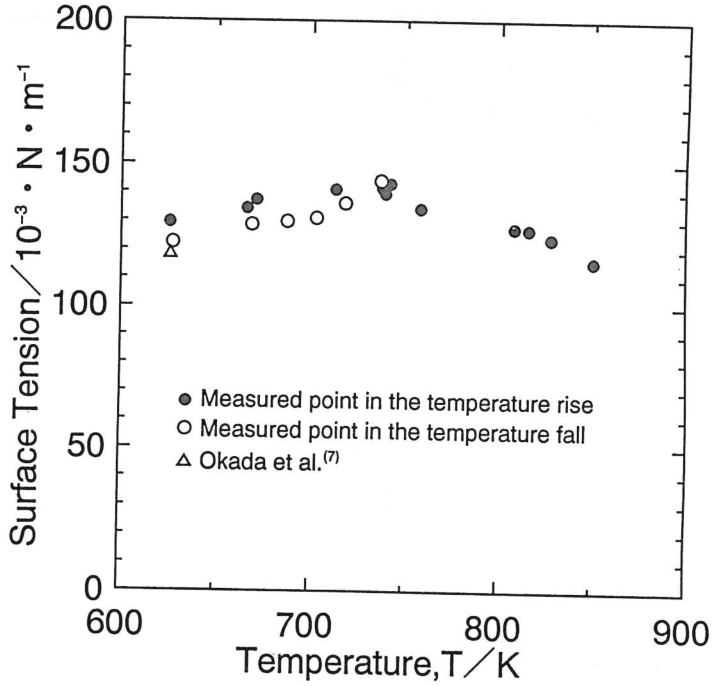



Fig.4 Temperature dependence of a NaOH melt.

## 4. Direct observations of surface driven flows

Since a surface tension driven flow is caused by a surface tension gradient, temperature gradient was applied to the capillary liquid bridge of the molten salts using hot thermocouple technique.

Photograph of cryolite columnar melt and schematic diagram of stream-lines in the columnar melt are shown in Fig.5. The columnar melt was set horizontally to gravity. Although it is very difficult to realize the direction of the flow from the photograph in Fig.4, the flows on free surface of the melt from high temperature zone(1350K) to low temperature zone(1320K) was observed through a microscope. Then the reverse flow was observed in the core of the columnar melt. This type of flow is caused by surface tension gradient. As shown in Fig.3, surface tension of a cryolite melt at low temperature(1320K) is higher than that at high temperature. The flow at the free surface, therefore, goes from high temperature side to low temperature side due to the surface tension gradient. Same phonomenon was observed in a $NaNO_3$columnar melt[4].

On the other hand, very interesting behavior was observed in the NaOH columnar melt. Photographs of the NaOH columnar melt are shown in Fig.6 with the schematic diagrams of streamlines in the melt when changing the heat patterns. Fig.6(a) shows the streamlines in the melt when a NaOH melt has a positive temperaure dependence of the surface tension. Therefore, the flows from low temperature side to high temperature side were found at the free surface. After heating up the both sides to around 740K at which

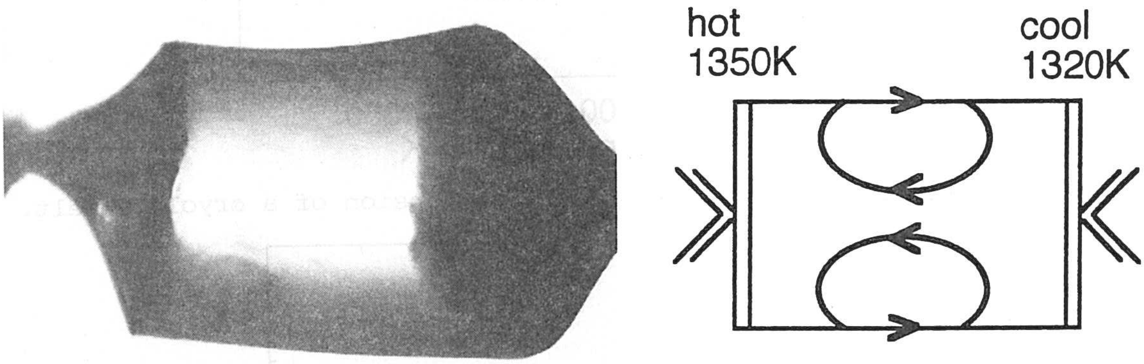
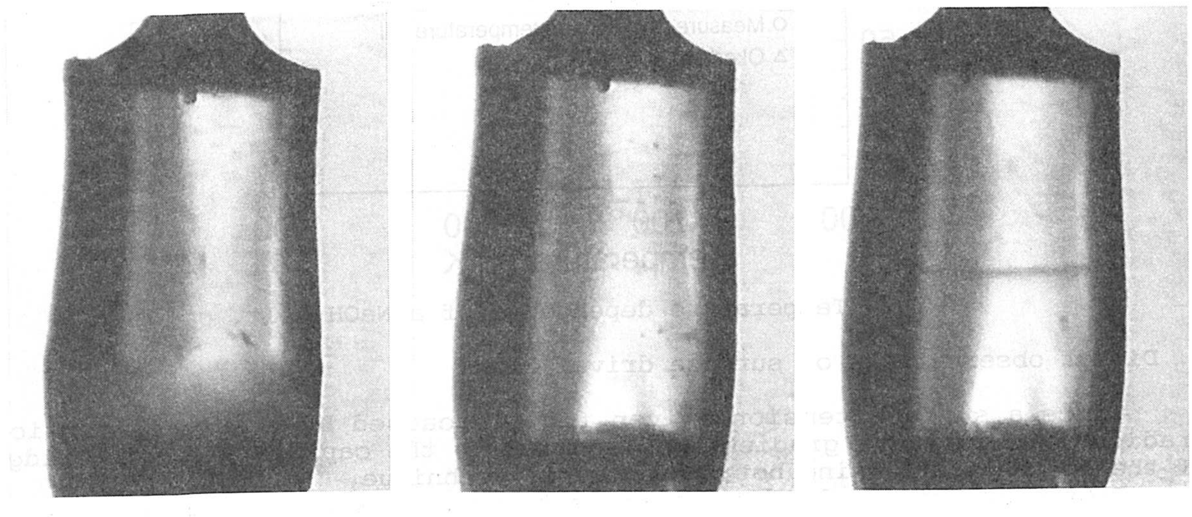



Fig.5 Photograph of the cryolite columnar melt and schematic streamlines in the columnar melt.



(a)below M.P. at the bottom Pt plate

(b)around 740 K at both sides

(c) 770K at both sides

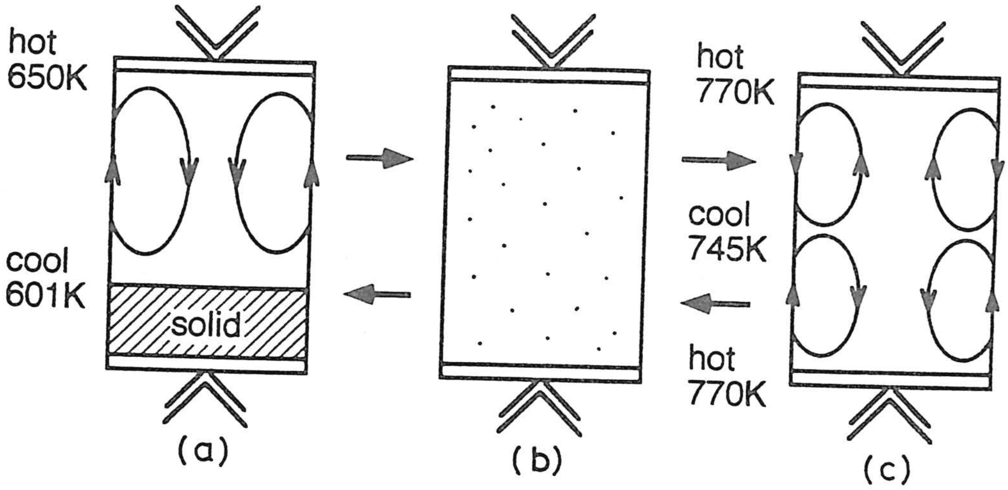



Fig.6 Photographs of the NaOH columnar melt at various heat patterns with schematic diagrams of streamlines in the columnar melt.

temperature dependence changed from positive to negative, there found no motions in the columnar melt as shown in Fig.6(b). Heating up both sides moreover, a low temperature zone occurred at the center of the columnar melt as shown in Fig.6(c). In the temperature range showing the flow patterns of Fig.6(c), the temperature coefficient of the surface tension of NaOH is negative. Then same flow patterns as a cryolite melt were obtained, i.e. free surface flows from high temperature side to low temperature side was observed. And these changes of flow patterns occurred continuously and reversibly. Such motions can be only explained by the Marangoni convection.

All flows observed in the present study demonstrated that surface tension driven flows control mainly total flows of a melt which has a large part of free surface compared to volume.

## 5. Conclusions

Temperature dependence of surface tension of cryolite and NaOH melts were measured. Negative temperature dependence was obtained in a cryolite melt, while a positive one was observed in the temperature range from the melting point to 740K in a NaOH melt. A negative one was obtained above 740K.

The motions of cryolite and NaOH columnar melts observed by hot thermocouple technique were well explained by the concept of the Marangoni convection.

## 6. References

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