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Studies on the acid-base properties of the  
AlBr<sub>3</sub>-NaBr melts

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nealing. High current density was obtained from the PSZ fuel cell at 1000°C. The on-off cycle of discharge suggested that  $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$  cathode activity varies with the discharge condition.

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## Studies on the Acid-Base Properties of the $\text{AlBr}_3\text{-NaBr}$ Melts

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Recently, a lot of work has been performed on the acid-base properties of Lewis acidic molten salts. One of the most extensively investigated melt systems is the sodium chloroaluminate melt (175°-220°C) in which the chloride ion activity is dependent upon the composition of the melt. It is well known that unusual higher oxidation state ionic species, such as  $\text{S(IV)}$  (1, 2) or lower oxidation state cluster compounds, such as  $\text{W}_6\text{Cl}_{18}^{4+}$  (3), can be stable in the chloroaluminate melts because of the strong Lewis acidity of these solvents (4-7). These melts are now one of the potential materials for use in low-temperature molten salt batteries (1, 2) or as solvents for organic synthesis (8).

The aluminum bromide-sodium bromide melts also show the variable Lewis acidity. The melting point of pure aluminum bromide is lower than that of aluminum chloride ( $\text{AlBr}_3$ : 97.5°C,  $\text{AlCl}_3$ : 192.4°C), whereas the boiling point of the bromide is higher than that of chloride ( $\text{AlBr}_3$ : 255°C,  $\text{AlCl}_3$ : 187°C) (9). The liquidus temperature of the  $\text{AlBr}_3\text{-NaBr}$  binary system is below 100°C in the 65-85 mole percent  $\text{AlBr}_3$  composition ranges (10), while the liquidus temperature of the  $\text{AlCl}_3\text{-NaCl}$  melts is generally more than 170°C. At 200°C, the vapor pressure of the bromide melt is about a tenth of that in the  $\text{AlCl}_3\text{-NaCl}$  melt (9). Therefore, from a practical point of view, the  $\text{AlBr}_3\text{-NaBr}$  melt seems easier to handle than the  $\text{AlCl}_3\text{-NaCl}$  melt for many chemical processes. These observations are closely related to the fact that the aluminum bromide forms a stable dimer molecule ( $\text{Al}_2\text{Br}_6$ ) not only in the solid state but also in the liquid state.

As described above, some physical properties of the haloaluminate melts are dependent on the halide species. Therefore, the acid-base properties of the melts also may vary with the anion component, even with the same cationic constituent. From these points of view, we investigated the acid-base properties of the  $\text{AlBr}_3\text{-NaBr}$  melts and compared their characteristics with those of the chloroaluminate melts.

In bromide melts, "acid" is defined as a bromide ion acceptor, while the "base" is the bromide ion donor.



The basicity of these melts can be expressed as the  $p\text{Br}^-$  value ( $p\text{Br}^- = -\log a(\text{Br}^-)$ ;  $a(\text{Br}^-)$  means the bromide ion activity). Concerning the acid-base equilibrium in the  $\text{AlBr}_3\text{-NaBr}$  melts, Tremillon *et al.* (11) reported the equilibrium constant of the following chemical reaction, which is dominant in the neutral region of the melt, by a coulometric titration method



In this report, the over-all acid-base equilibria have been taken into account and individual equilibrium constant values evaluated on the basis of the EMF measurements of the following  $\text{Al/Al}$  concentration cell, especially in the acid composition ranges [up to 65 mole percent (m/o)  $\text{AlBr}_3$ ]



where "i" indicates a melt composition.

### Experimental

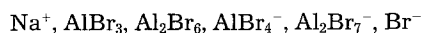
Because of the extreme moisture sensitivity of aluminum bromide, all experiments were done in a glove box. In order to keep the moisture level and the oxygen content to a minimum, argon gas refining and circulating equipment were attached to the glove box. The oxygen content inside the box was maintained below 0.1 volume percent and the dew point was below -70°C. High purity aluminum bromide (Mitsuwa Chemical) was used as received. Sodium bromide (Wako Chemical) had been dried at 160°C in vacuo for 2 days. The electrodes of the concentration cell were made of aluminum wire (99.99%, rare metallic), which were electropolished in 20% aqueous NaOH or cleaned in a 6:1 mixture of  $\text{HNO}_3$  and  $\text{H}_3\text{PO}_4$  at 80°C for 2-3 min. The electrochemical cell used was made of Pyrex

\* Electrochemical Society Active Member.

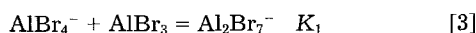
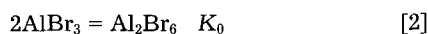
glass. The reference electrode compartment, which was always saturated with NaBr, was separated from the bulk melt either by a beta-alumina tube (NGK spark plug, 15φ) or by a sodium ion selective glass tube (HORIBA). In several experiments, a hand made Pyrex thin film membrane also served as a diaphragm in the concentration cell. The composition of the measuring compartment was changed by adding known amounts of either AlBr<sub>3</sub> or NaBr, and the EMF values of the cell were measured and recorded with a high input impedance digital voltmeter (TAKEDA, TR-6855). A proportional thermoelectronic controller was used to control the melt temperature at 210° ± 2°C. The temperature of the melt was measured by the use of a Chromel-Alumel thermocouple.

### Results and Discussion

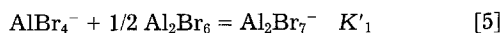
The following chemical species have been reported to exist in the AlBr<sub>3</sub>-NaBr melts, on the basis of Raman spectroscopy (12)



where Na<sup>+</sup> acts only as a current-carrying species and is independent of the acid-base equilibrium in this melt. Thus, the following three chemical equilibria can be set up among the above species

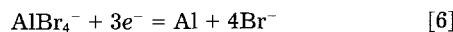


Since no thermodynamic quantity concerning [2] is available, the following chemical equilibrium was considered instead of [2] and [3]



where the equilibrium constant is defined as K'<sub>1</sub>.

The electrode reaction at an aluminum electrode in these melts can be described as



The EMF of the concentration cell is given by

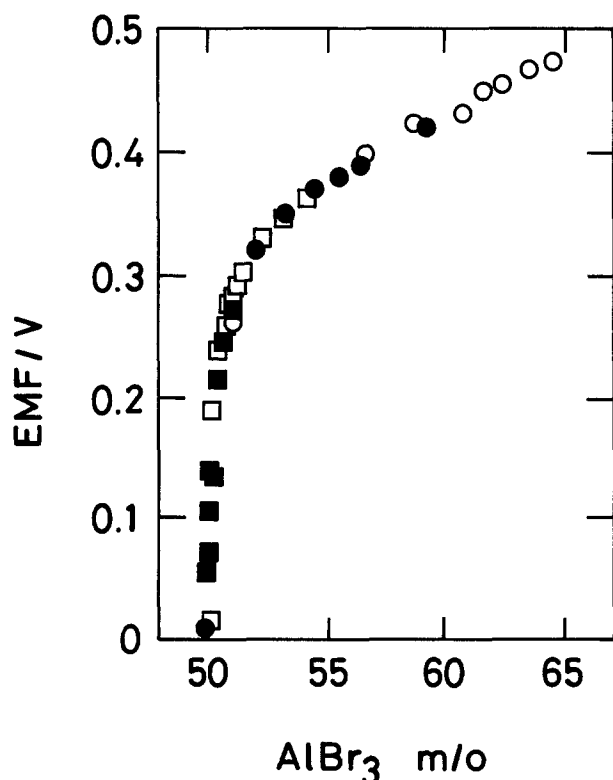


Fig. 1. Relationship between the measured EMF values and melt compositions, ● beta-alumina, ○ Pyrex glass-a, □ Pyrex glass-b, ■ Na<sup>+</sup> ion selective glass.

Table I. Calculated mole fraction values for Br<sup>-</sup>, AlBr<sub>4</sub><sup>-</sup>, Al<sub>2</sub>Br<sub>7</sub><sup>-</sup> in the AlBr<sub>3</sub>-NaBr melt

X(AlBr <sub>3</sub> )	0.497	0.51	0.55
X(Br <sup>-</sup> )	0.01	—	—
X(AlBr <sub>4</sub> <sup>-</sup> )	0.49	0.48	0.39
X(Al <sub>2</sub> Br <sub>7</sub> <sup>-</sup> )	—	0.02	0.11

$$E1 = -\frac{4RT}{3F} \ln \frac{a(\text{Br}^-)_{\text{ref}}}{a(\text{Br}^-)_i} + \frac{RT}{3F} \ln \frac{a(\text{AlBr}_4^-)_i}{a(\text{AlBr}_4^-)_{\text{ref}}} \quad [7]$$

where ref corresponds to the NaBr saturated melt.

Figure 1 shows the relationship between the measured EMF values and melt compositions. Near the equimolar composition, there is an abrupt change of the EMF. Table I indicates mole fractions of the various species when K<sub>2</sub> is assumed to be zero. Going from 49.7 to 51.0 m/o AlBr<sub>3</sub>, the mole fraction value of AlBr<sub>4</sub><sup>-</sup> is almost constant, while that of Br<sup>-</sup> sharply decreases. (Above 50 m/o AlBr<sub>3</sub>, the bromide ion concentration is zero in this extreme case.) So, the abrupt change of the EMF values near the equimolar point in Fig. 1 is attributed to the activity changes of Br<sup>-</sup>.

Therefore, in the 49.7-51.0 m/o AlBr<sub>3</sub> region, the second term in Eq. [7] can be neglected and Eq. [7] is replaced by Eq. [8].

$$E2 = -\frac{4RT}{3F} \ln \frac{a(\text{Br}^-)_{\text{ref}}}{a(\text{Br}^-)_i} = -\frac{4RT}{3F} \ln \frac{X(\text{Br}^-)_{\text{ref}}}{X(\text{Br}^-)_i} \quad [8]$$

In the last expression, the activity term *a* is substituted for by the mole fraction, *X*, since the activity values are quite small and activity coefficients are expected to be close to unity.

The K<sub>2</sub> value can be obtained by a curve fitting procedure between the observed EMF values and Eq. [8] by using the data in the neutral region.

In order to obtain a K'<sub>1</sub> value, the data set in the 51.0-65.0 m/o AlBr<sub>3</sub> region was used. In this region, the AlBr<sub>4</sub><sup>-</sup> concentration is relatively high (>0.1 mole fraction), so the activity coefficient of AlBr<sub>4</sub><sup>-</sup>, which is expressed by Eq. [9], was taken into account in the calculation procedure (7)

$$RT \ln (y_N) = W_T(1 - X)^2 \quad [9]$$

where *y<sub>N</sub>* is the activity coefficient, and *W<sub>T</sub>* is the work constant.

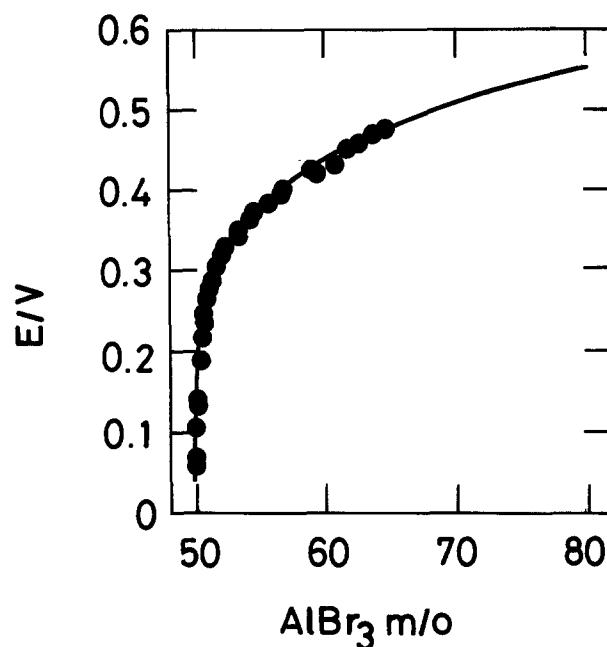


Fig. 2. Comparison of experimental and calculated aluminum electrode potentials in the AlBr<sub>3</sub>-NaBr melt as a function of melt composition. Solid line: the calculated curve; circles: the observed EMF values.

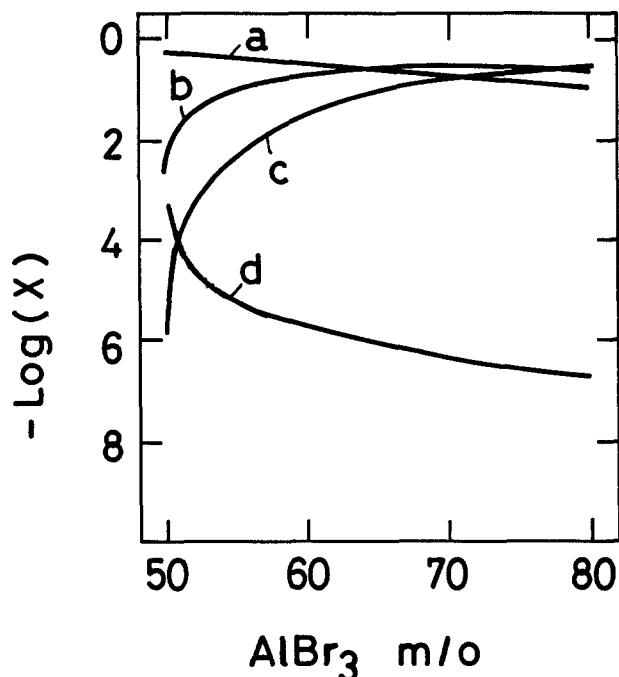


Fig. 3. Activity profiles of the species in the  $\text{AlBr}_3\text{-NaBr}$  melt. Curve a:  $\text{AlBr}_4^-$ , curve b:  $\text{Al}_2\text{Br}_7^-$ , curve c:  $\text{Al}_2\text{Br}_6$ , curve d:  $\text{Br}^-$ .

The mathematical procedure developed by Osteryoung (7) is applied to the calculation of  $K_2$ ,  $K'_1$  and  $W_T$ .

At first, the initial value of  $K_2$  was determined by using the data set in the neutral region. Then the  $K'_1$  value was obtained by using the data set in the acidic region. These iterative procedures were repeated until the least squares fit of Eq. [7] to the experimental data was given. Finally, the following values are obtained

$$K'_1 = 3.5, K_2 = 4.0 \times 10^{-6}, W_T = 1.0 \times 10^3 \text{ J mol}^{-1}$$

The solid line in Fig. 2 shows the calculated curve of the aluminum electrode potential by using the above constant, while the circles indicate the observed EMF values.

As described above, Tremillon *et al.* determined the equilibrium constant of the auto-dissociation of  $\text{AlBr}_4^-$  (11)

$$K = [\text{Al}_2\text{Br}_7^-][\text{Br}^-]; -\log K = 4.40 \pm 0.05$$

(The unit of  $K$  is  $\text{mol}^2 \text{ kg}^{-2}$ .)

This value corresponds to the  $K_2$  value of  $5.0 \times 10^{-6}$  and agrees well with that obtained in this work.  $K_2$  was determined to be  $2.23 \times 10^{-7}$  at  $200^\circ\text{C}$  (7) for the  $\text{AlCl}_3\text{-NaCl}$  melts, which is slightly smaller than that of the bromoaluminate melts. This implies that for the same cationic

constituent the amount of "free" halide is less in the chloroaluminate system than in the bromoaluminate melt.

Figure 3 shows the activity profiles of each chemical species, derived from the  $K'_1$  and  $K_2$  values. The activity values are indicated in units of mole fraction. It is clear from the illustration that the dominant anion species is  $\text{AlBr}_4^-$  below 60 m/o  $\text{AlBr}_3$ . As a whole, the activity profiles are similar to those of the chloroaluminates.

### Summary

The acid-base properties of the  $\text{AlBr}_3\text{-NaBr}$  melts were examined on the basis of the EMF measurements of an aluminum-aluminum concentration cell and the following information was obtained:

1. The  $\text{AlBr}_3\text{-NaBr}$  melts show a composition-dependent Lewis acidity that is similar to that found in the chloroaluminate melts.

2. The equilibrium constants of the two chemical equilibria (Eq. [4] and [5]) that characterize these melts have been determined:  $K'_1 = 3.5$ ,  $K_2 = 4.0 \times 10^{-6}$ .

3. For the same cationic constituent, the amount of "free" halide in the chloroaluminate melt is less than that in the bromoaluminate melt. This implies that the molecular dimer ( $\text{Al}_2\text{Br}_6$ ) is very stable and behaves as a strong Lewis acid in the bromoaluminate melts.

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