Studies on the acid-base properties of the ZnBr2NaBr molten salt system

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Studies on the Acid-Base Properties of the $ZnBr_2$-NaBr Molten Salt System

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ABSTRACT

The acid-base properties of the $ZnBr_2$-NaBr melts at 623 K were investigated on the basis of the electromotive force measurements of a zinc-zinc concentration cell. The following two chemical equilibria were postulated to describe the acid-base character of the melts

$$ZnBr_2 + Br^- = ZnBr_3^- \quad K_1$$

$$ZnBr_3^- + Br^- = ZnBr_4^{2-} \quad K_2$$

The equilibrium constants K_1 and K_2 were determined to be 5.0×10^2 and 1.0×10^2, respectively, at 623 K. The acidity of $ZnBr_2$-NaBr melts is essentially weaker than that of bromoaluminate melts.

It has been pointed out that some kinds of oxyanions and complex ions which have unusual oxidation states are stable in acidic melts,[1] such as sodium chloroaluminate, because the concentration of "free" halide ion is very low.[2-5] It is possible to obtain some metallic elements by the electroreduction of such unusual ions.[6] Some chalcogen compounds are stable in acidic chloroaluminate melts and have been tested as an active material for a rechargeable battery.[7] Chloroaluminate melts are also potential materials for use as solvents for electro-organic synthesis.[8]

Zinc chloride and bromide are also Lewis acids, but their vapor pressure and reactivity with moisture are substantially lower than those of aluminum chloride and aluminum bromide. Many investigations have been performed on the structure and physical properties of zinc chloride-alkali metal chloride systems.[9-21] However, to date very few studies[15,18] have been reported concerning the fundamental properties of bromide systems. From this point of view,

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EMF measurements of a zinc-zinc concentration cell were performed with $ZnBr_2$-NaBr melts, and the acid-base equilibrium of this system was investigated.

Chemical species in $ZnBr_2$-NaBr melts.—Since chlorides and bromides generally have similar properties, it is helpful to consult the literature on $ZnCl_2$-MCl [M = alkali metal] systems.[9-21]

The polymeric nature or network structure of $ZnCl_2$-MCl melts has long been recognized from their physical properties, such as density,[20] viscosity,[19] and conductivity,[12] and from thermodynamic[9,13,18] and Raman spectroscopic data.[10,14,15,21] Thus, pure $ZnCl_2$ and $ZnCl_2$-rich melts contain $(ZnCl_2)_n$ polymers or aggregates. These species are believed to consist of $ZnCl_4$ tetrahedra sharing corners as in crystalline $ZnCl_2$. After increasing the temperature or after the addition of MCl, the $(ZnCl_2)_n$ polymers dissociate into smaller clusters. The degree of polymerization (the number n) depends on the temperature and composition of the melt. The $(ZnCl_2)_n$ polymers are considered to have peripheral groups, such as $ZnCl_4^{2-}$, $ZnCl_3^-$, and $ZnCl_2$, attached through a chlorine atom. At high $MCl/ZnCl_2$ ratios, zinc chloride tends to form a monomeric complex $ZnCl_4^{2-}$, as evidenced by Raman spectroscopy[10,11,14,15,21] and EMF data of the Zn/Cl_2 cell.[9,13] Other species, such as monomeric $ZnCl_2$,[15] $ZnCl_3^-$ (with a planar configuration),[10,15] and $Zn_2Cl_7^{3-}$,[17] are also suggested. Similar polymers and complex ions are considered in the $ZnBr_2$-MBr systems.[15,18]

Because it is difficult to take into account all of the possible species, a simplification is attempted in order to describe the acid-base properties of $ZnBr_2$-NaBr melts. Thus we postulate the following chemical constituents (hypothetical species) and the following equilibria among them

$$ZnBr_2 + Br^- = ZnBr_3^- \quad K_1 \qquad [1]$$

$$ZnBr_3^- + Br^- = ZnBr_4^{2-} \quad K_2 \qquad [2]$$

Here, $ZnBr_2$ represents not only the monomeric $ZnBr_2$, but also the $ZnBr_2$ unit in various $(ZnBr_2)_n$ polymers. Similarly, $ZnBr_3^-$ and $ZnBr_4^{2-}$ represent both the simple complexes and peripheral groups attached to $(ZnBr_2)_n$ polymers. The equilibrium constants K_1 and K_2 are defined in terms of mole fractions of these hypothetical species. According to the stoichiometry, the dominant chemical species at various compositions can be estimated as shown in Table I. The border at 50 mole percent (m/o) NaBr corresponds to the equivalent point of Eq. 1, where $[ZnBr_2] = [Br^-]$. The border at 66.7 m/o corresponds to the equivalent point of Eq. 2, where $[ZnBr_3^-] = [Br^-]$.

Acid-base equilibria in the molten $ZnBr_2$-NaBr system.—$ZnBr_2$-NaBr melts are expected to exhibit Lewis acidity and to have a concentration dependent acid-base character. In bromide melts, "acid" is defined as a bromide ion acceptor, while "base" is defined as a bromide ion donor

$$\text{Acid} + Br^- = \text{Base}$$

The basicity of this system is indicated by the use of the pBr^- value. [$pBr^- = -\log a(Br^-)$; $a(Br^-)$ means bromide ion activity.] The bromide ion activity can be determined by EMF measurements of the concentration cell in reference to the activity in a particular melt.

The zinc-zinc concentration cell described below was used for these EMF measurements

$$Zn/ZnBr_2\text{-NaBr (ref.)}//ZnBr_2\text{-NaBr(j)}/Zn \qquad [3]$$

where "j" indicates the melt in the measuring electrode compartment, and "ref." means the reference melt which is saturated with NaBr. The activity changes were deduced from the relationship between EMF values and melt composition (j), then the acid-base equilibrium was discussed.

Experimental

Phase diagram of the $ZnBr_2$-NaBr system.—No phase diagram data of the $ZnBr_2$-NaBr system is available. In order to use this system as a solvent for electrosynthesis, it is necessary to know its liquid range. Therefore, the phase diagram was determined by a simple thermal analysis method.

These experiments were performed in a purified argon atmosphere inside a glove box. Certain amounts of sodium bromide and zinc bromide were put in a high-purity alumina crucible. The crucible was placed in an electric furnace, and the temperature of the furnace was increased until the mixture completely melted. After holding the temperature for several hours, cooling was initiated. The temperature was recorded by using a Chromel-Alumel thermocouple. The phase transition points were detected as an inflection of the cooling curves.

EMF measurement.—Figure 1 shows the schematic diagram of the experimental cell. A NaBr saturated melt was put inside of the β-alumina tube which acts as a diaphragm to separate the reference compartment from the main compartment. Zinc wires (1 mmϕ) of 99.99% purity were used for both electrodes. One was placed in the reference compartment, while the other was placed in the main compartment, as shown in the illustration. The melt composition in the main compartment was adjusted by adding sodium bromide or zinc bromide. Just after the salt addition, argon

Table I. Dominant species in $ZnBr_2$-NaBr melts.

X(NaBr)	0	0.5	0.67	1
Stoichiometric composition	$ZnBr_2$	$NaZnBr_3$	Na_2ZnBr_4	NaBr
Dominant species	$ZnBr_2$ $ZnBr_3^-$		$ZnBr_3^-$ $ZnBr_4^{2-}$	$ZnBr_4^{2-}$ Br^-

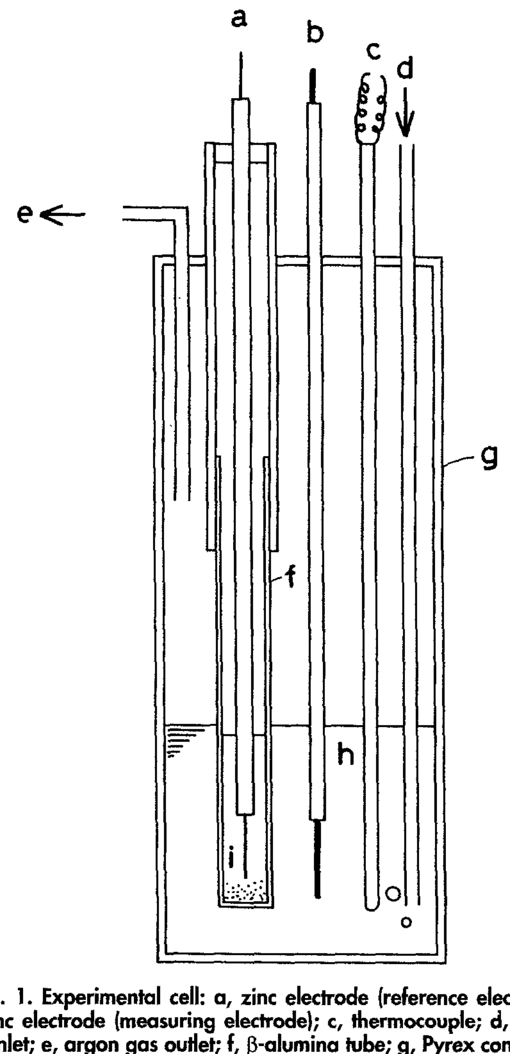

Fig. 1. Experimental cell: a, zinc electrode (reference electrode); b, zinc electrode (measuring electrode); c, thermocouple; d, argon gas inlet; e, argon gas outlet; f, β-alumina tube; g, Pyrex container; h, $ZnBr_2$-NaBr melt; i, $ZnBr_2$-NaBr melt saturated with NaBr.

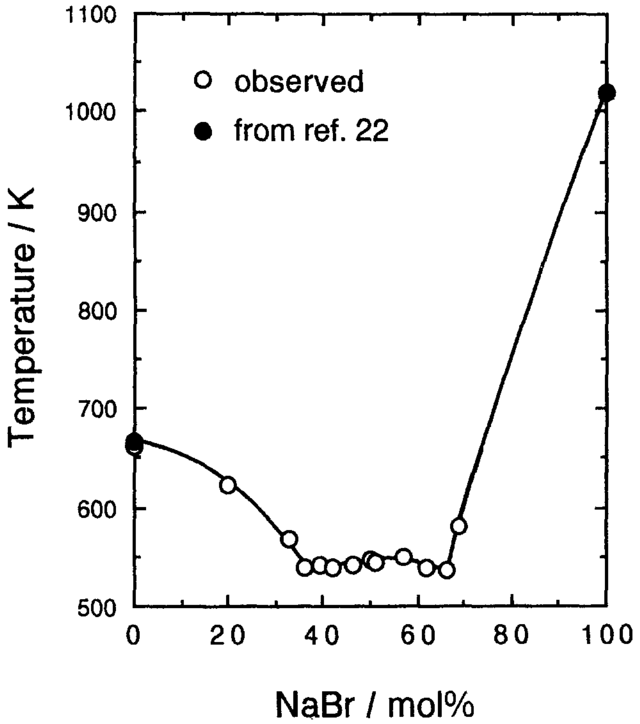

Fig. 2. Phase diagram for the $ZnBr_2$-NaBr system: (○) this work (●) melting point of pure salt.

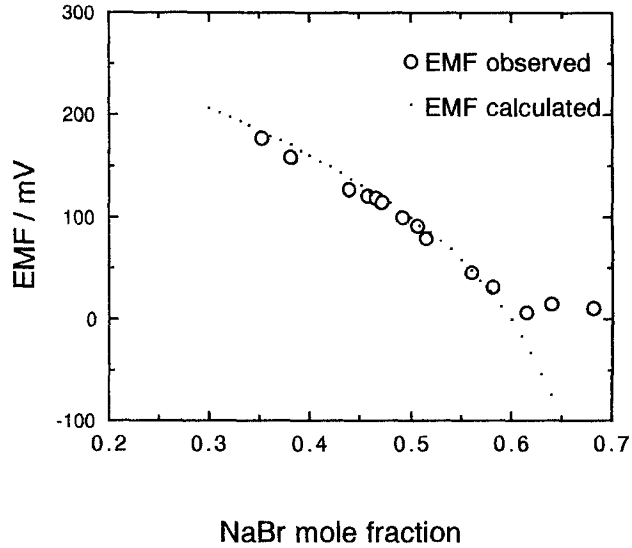

Fig. 3. Relationship between the observed EMF and melt composition; (○) observed EMF, dotted line: calculated curve for $K_1 = 5.0 \times 10^2$, $K_2 = 1.0 \times 10^2$.

gas was bubbled through the melt to ensure complete mixing. All measurements were carried out in the argon atmosphere in a glove box.

Sodium bromide (Wako Chemical) and zinc bromide (Wako Chemical) had been dried at 573 K *in vacuo* in two days, separately. The temperature of the melt was controlled by PID electronic instruments at 623 K within ±1 K. The EMF values were recorded by using a high impedance digital voltmeter.

Results and Discussion

Phase diagram of the $ZnBr_2$-NaBr system.—Figure 2 shows the liquidus points thus obtained and the melting points of pure sodium bromide and zinc bromide (NaBr, 1020 K; $ZnBr_2$, 667 K).[22] In this measurement, the inflection at the solidus temperature was not detected, and therefore only the liquidus line is drawn in Fig. 2. In the vicinity of the equimolar point, the liquidus temperature is below 573 K. At 623 K, the liquid ranges expand from 30 to 70 m/o NaBr. Therefore, a temperature of 623 K was chosen for the following experiments.

EMF measurement.—Figure 3 shows the relationship between the observed EMF values and melt compositions. On decreasing the NaBr content in the melt, the EMF values are expected to become constant below 30 m/o, since zinc bromide starts to precipitate at about this composition. Above 70 m/o of NaBr, sodium bromide starts to precipitate, and the observed EMF values approach 0 V.

To simplify the discussion concerning the acid-base equilibria, let us start from A mole of $ZnBr_2$ and 1-A mole of NaBr. On melting the mixture, x moles of $ZnBr_3^-$ and y moles of $ZnBr_4^{2-}$ can be generated. The number of moles (n) of each chemical species in the equilibria can be described as follows

$$n(Na^+) = 1 - A \quad [4]$$

$$n(ZnBr_2) = A - x - y \quad [5]$$

$$n(ZnBr_3^-) = x \quad [6]$$

$$n(ZnBr_4^{2-}) = y \quad [7]$$

$$n(Br^-) = (1 - A) - x - 2y \quad [8]$$

The total number of moles B is given by the equation below

$$B = 2 - A - x - 2y \quad [9]$$

Assuming that the activity is equal to the mole fraction of the species, the equilibrium constants of Eq. 1 and 2 are described by Eq. 10 and 11, respectively

$$K_1 = \frac{B \cdot n(ZnBr_3^-)}{n(Br^-) \cdot n(ZnBr_2)} = \frac{(2 - A - x - 2y) \cdot x}{(1 - A - x - 2y) \cdot (A - x - y)} \quad [10]$$

$$K_2 = \frac{B \cdot n(ZnBr_4^{2-})}{n(Br^-) \cdot n(ZnBr_3^-)} = \frac{(2 - A - x - 2y) \cdot y}{(1 - A - x - 2y) \cdot x} \quad [11]$$

The potential-determining reaction of zinc electrode and the Nernst equation can be described by Eq. 12 and 13, respectively

$$ZnBr_3^- + 2e^- = Zn + 3Br^- \quad [12]$$

$$E = E^\circ - \frac{3RT}{2F} \cdot \ln \frac{n(Br^-)}{B} + \frac{RT}{2F} \cdot \ln \frac{n(ZnBr_3^-)}{B} \quad [13]$$

The EMF values of the concentration cell are expressed as

$$EMF_i = -\frac{3RT}{2F} \cdot \ln \frac{n(Br^-)_i}{B_i} \cdot \frac{B_{ref}}{n(Br^-)_{ref}} + \frac{RT}{2F} \cdot \ln \frac{n(ZnBr_3^-)_i}{B_i} \cdot \frac{B_{ref}}{n(ZnBr_3^-)_{ref}} \quad [14]$$

where "i" and "ref" indicate the ith composition and reference composition, respectively. Equation 14 implicitly assumes that the membrane potential difference across the β-alumina separator is negligible. This approximation may be justified, as in the case of chloroaluminate melts,[2,3,5] because the Na^+ ion is the only charge carrier in the β-alumina separator and the ratio of the Na^+ ion concentrations on both sides of the separator does not differ very much from unity.

Equations 10 and 11 give rise to two simultaneous equations in x_i and y_i. Therefore, both x_i and y_i can be described as functions of K_1, K_2, A_i

$$x_i = f\,(K_1, K_2, A_i)$$

$$y_i = g\,(K_1, K_2, A_i)$$

Substituting appropriate values for K_1 and K_2 yields x_i and y_i for a given value of A_i. The number of moles of each chemical species is calculated by Eq. 4 to 9. Then, the theoretical EMF value is calculated by using Eq. 14 for each melt composition. By changing K_1 and K_2 gradually, the

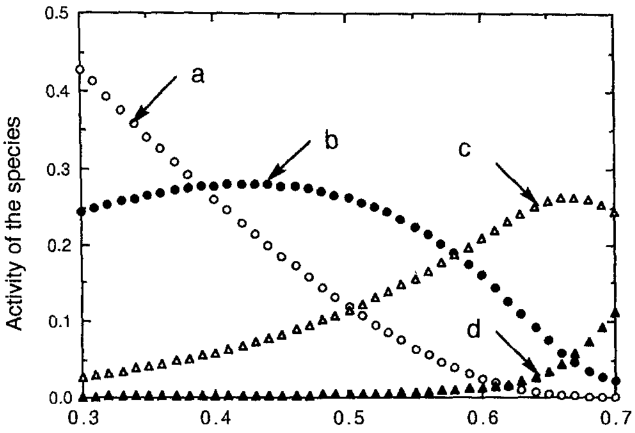

Fig. 4. Activity profiles in the $ZnBr_2$-NaBr melt: (a) $ZnBr_2$, (b) $ZnBr_3^-$, (c) $ZnBr_4^{2-}$, (d) Br^-.

above procedure is repeated until the difference between the observed and calculated EMF attains a minimum. Thus the most probable values of K_1 and K_2 can be obtained. Using this procedure, the values of K_1 and K_2 were determined to be 5.0×10^2 and 1.0×10^2, respectively, at 623 K. The dotted line drawn in Fig. 3 indicates the calculated EMF values.

Figure 4 shows the activity profiles of each of the chemical species derived from the K_1 and K_2 values. The activity is indicated in units of mole fraction. It is clear from the illustration that the activity of bromide ion decreases gradually from 70 to 40 m/o NaBr. In the composition ranges near 50 m/o. $ZnBr_3^-$ is the dominant species, whereas $ZnBr_4^{2-}$ becomes dominant near 67 m/o.

The authors also investigated the acid-base properties of the $AlBr_3$-NaBr melt and evaluated the equilibrium constant K_{Al} of the following reaction to be 2.5×10^5 at 483 K [23]

$$Al_2Br_7^- + Br^- = 2AlBr_4^- \qquad [16]$$

The pBr$^-$ value of 40 m/o NaBr in $AlBr_3$-NaBr melts at 483 K was 5.6, while the value in $ZnBr_2$-NaBr melts at 623 K was 2.9; therefore, it is concluded that the acidity of the $ZnBr_2$-NaBr system is essentially weaker than that of the bromoaluminate melts.

Conclusions

The acid-base properties of the $ZnBr_2$-NaBr melts were examined on the basis of the EMF measurement of a zinc-zinc concentration cell in these melts. The following conclusions were obtained.

1. The equilibrium constants of the reactions shown in Eq. 1 and 2, were calculated to be

$$K_1 = 5.0 \times 10^2 \qquad K_2 = 1.0 \times 10^2$$

2. The $ZnBr_2$-NaBr system is less acidic than the bromoaluminate melt.

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