

Anomalous Conduction and Behavior of Halide Hydrates Coexisting with Inorganic Powder

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Solid/ liquid coexisting systems have found many applications not only in basic physical chemistry but also in applied chemistry. As systems, called slurries or pastes, have a high solid content and the area of the interface between solid and liquid phases is extremely large, the liquid layer is influenced by the solid phase. Such systems are used frequently and are important in various fields of applied inorganic chemistry, such as batteries, ceramics, metal refining, etc. However little research has been done on the chemical properties for powder/ aqueous electrolyte solution systems that contain liquid phase in less volume fraction than that of solid phase though suspensions and colloidal solutions have been studied extensively. Recently, we have focused the anomalous behavior of the several kinds of the halide hydrate melts, in which the hydration structure is extremely changed by the intensive ionic interaction (1-2). In this paper, we introduce the anomaly of the hydrate in the several measurements of the electrical conductivity and thermochemical properties for the coexisting system consisting of inorganic powder and halide hydrate melts. We discussed the influence of the properties of the solid phase to the melting behavior of the hydrate near the solid.

Inorganic powders used as the solid phases were high-purity α - Al_2O_3 supplied from Showa Denko K. K. The physical aspects of them are shown in Table I. The methods of pretreatment and characterization are the same methods as described elsewhere (1). We used CaCl_2 , and CaBr_2 hydrates as a liquid phase. Each hydrate was prepared from guaranteed reagents. Each concentration of the hydrates is shown in Table II. For each measurement, powder was mixed thoroughly with hydrate melt in an alumina mortar and was immediately molded into a tablet with a diameter of 20 mm under the pressure of 52 MPa for 30 min. After molding, an AC impedance for the paste sample was measured in the frequency range from 5 Hz to 13 MHz from 20 to 60°C in a heating process with a Hewlett-Packard 4192A LF impedance analyzer. The volume fractions of the liquid phase were ranging from 10.9 to 48.0 vol%. The applied voltage for measuring the conductance was 0.6 V. The details of measuring methods and calculations for the electrical conductivity and the activation energy are described in Ref. 1.

Hydrate melts having melting point at ambient temperature show an abrupt change of the conductivity around their temperatures, since the ionic conduction was impeded by the solidification of the hydrate melts below melting point. However, such "normal behaviors" were changed by the coexistence of the powder as the solid phase. According to the temperature dependences of the electrical conductivity of the hydrate melts, the abrupt change is observed for α - Al_2O_3 powder/ $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ coexisting system due to the phase transition (melting) of the hydrates. However the transition point varied toward the lower temperature and the residual relative conduction increased with the decrease of the

hydrate content. The lowering of the transition point is enhanced for α - Al_2O_3 powder/ $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ coexisting system, and at the liquid content range below 20 vol%, the transition point was not observed, as shown in Figure 1. It is suggested that the ionic conduction remained near the solid phase below the melting point, and it depends on the ionic species. The variations of ΔE_a with apparent average thickness (= total volume of liquid phase / total surface area of solid phase) are shown in Fig.2. The value of ΔE_a increased with a decrease of the apparent average thickness in the system containing $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. On the other hand, the minimal point of ΔE_a was observed at ca. 50 nm of the average thickness of the liquid phase for the system containing $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$. It is suggested that the lower value of activation energy was caused by the disordered structure of the CaBr_2 hydrate near the solid surface because of the relatively weaker ionic interaction between cation, Ca^{2+} , and anion, Br^- , was not kept due to the influence of the solid phase.

References

- 1) S. Deki, M. Mizuhata, S. Nakamura, A. Kajinami, and Y. Kanaji, *J. Chem. Soc. Faraday. Trans.*, **89**, 3805 (1993).
- 2) M. Mizuhata, Y. Sumihiro, A. Kajinami, S. Deki, *Studies in Surface Science and Catalysis*, **132**, 255 (2001).

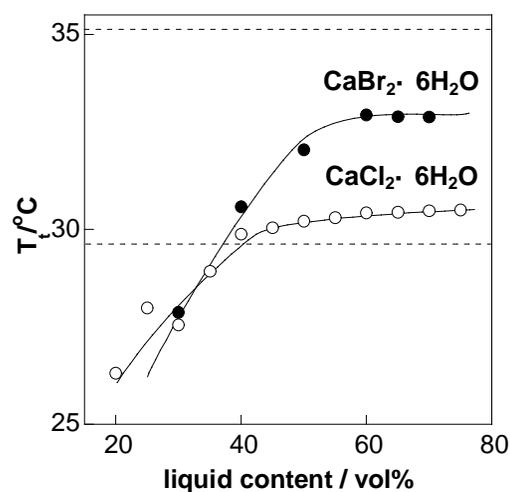


Fig.1. Variation of the transition point of the electrical conductivity for α - Al_2O_3 powder/ CaCl_2 and CaBr_2 hydrate melts coexisting systems. Specific surface area of solid phase: $0.6 \text{ m}^2/\text{g}$.

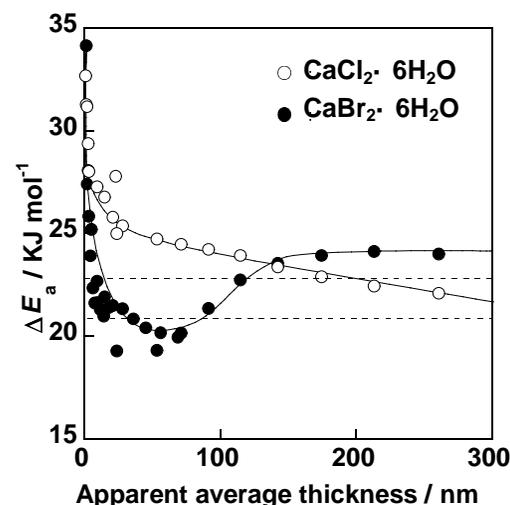


Fig.2. Variations of the activation energy of the electrical conductivity for α - Al_2O_3 powder/ halide hydrate melts coexisting systems. Specific surface area of solid phase: $0.6 \text{ m}^2/\text{g}$.