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THE CONGRUENT MELTING COMPOUNDS IN THE SYSTEM $KCl-SnCl_2$

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The thermal behavior of the powder mixtures of KCl and $SnCl_2$ with various molar ratios was studied by thermal analysis. The reaction between KCl and $SnCl_2$ to form the congruent melting compounds, $KSnCl_3$ and KSn_3Cl_7, occurred at 190 °C and 212 °C, respectively. The existence of these compounds in the system $KCl-SnCl_2$ was indicated in the equilibrium diagram constructed from the data of the DTA heating-curves in agreement with the previous work.

Ch'ih-fa and Morozov have studied the systems formed by alkali metal and ammonium chloride with tin(II) chloride in the melt by thermal and tensimetric analyses and obtained the equilibrium diagrams.[1)] In the diagrams, the existence of the congruent melting compounds is indicated, e.g., in the system $KCl-SnCl_2$, it can be seen that the compounds $KSnCl_3$ and KSn_3Cl_7 exist. These halostannate(II) complexes existing in the systems are very interesting with regard to their structure and bonding.[2-5)] However, they have not been studied extensively so far, because their syntheses were difficult by means of solution chemistry.

In this study, the thermal behavior of the powder mixtures of KCl and $SnCl_2$ with various molar ratios was investigated by the use of a conventional instrument for thermal analysis to examine the existence of the congruent melting compounds in the system $KCl-SnCl_2$ by constructing the phase diagram and to choose the optimum conditions for the congruent melting compounds.

Anhydrous $SnCl_2$ was obtained by drying $SnCl_2 \cdot 2H_2O$ (Super Special Grade, Wako Pure Chemical Ind., Ltd.) in an evacuated glass bottle at 100 °C for two hours. KCl (GR, Wako Pure Chemical Ind., Ltd.) was used without further purification. KCl and $SnCl_2$ were weighed out within $\pm$0.03 wt% for a molar ratio and after the preliminary mixing in an agate mortar, the powder mixture was dry-mixed throughly with an agate vibrating mixer mill under nitrogen for ten minutes.

The TG and DTA heating-curves were recorded simultaneously using a Sinku-riko TGD-5000 RH instrument by heating the sample in flowing nitrogen gas at a rate of 10 °C min^{-1} up to 300 °C. About a 10-mg of powder mixture was placed in a stainless steel cell and standard α-alumina (Sinku-riko Co., Ltd.) was used as reference material. Then the sample melted was cooled rapidly to room temperature and the DTA heating-curve of the once-melted sample was recorded again under the same conditions as before to obtain the equilibrium diagram, because it was not possible to take reliable measurement by the cooling-curve owing to the supercooling as shown in Fig. 1. The data are considered to be accurated within ±2 °C.

The heating-curves of the powder mixtures with various molar ratios of KCl to $SnCl_2$ are shown in Fig. 2. No gravimetric changes were recorded simultaneously in the TG curves. In Fig. 2, an endothermic peak was recorded at the peak maximum temperature about 190 °C in almost overall compositions and one

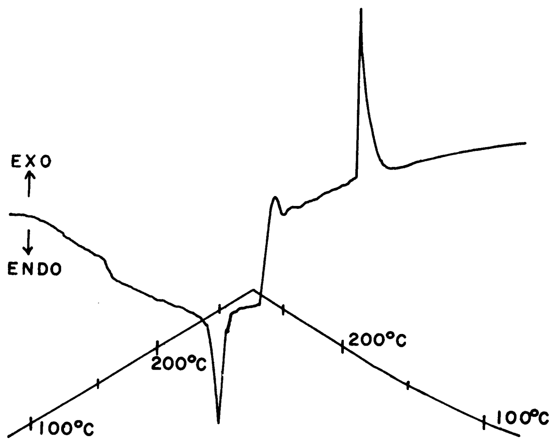

Fig. 1. DTA heating and cooling curves of $SnCl_2$.

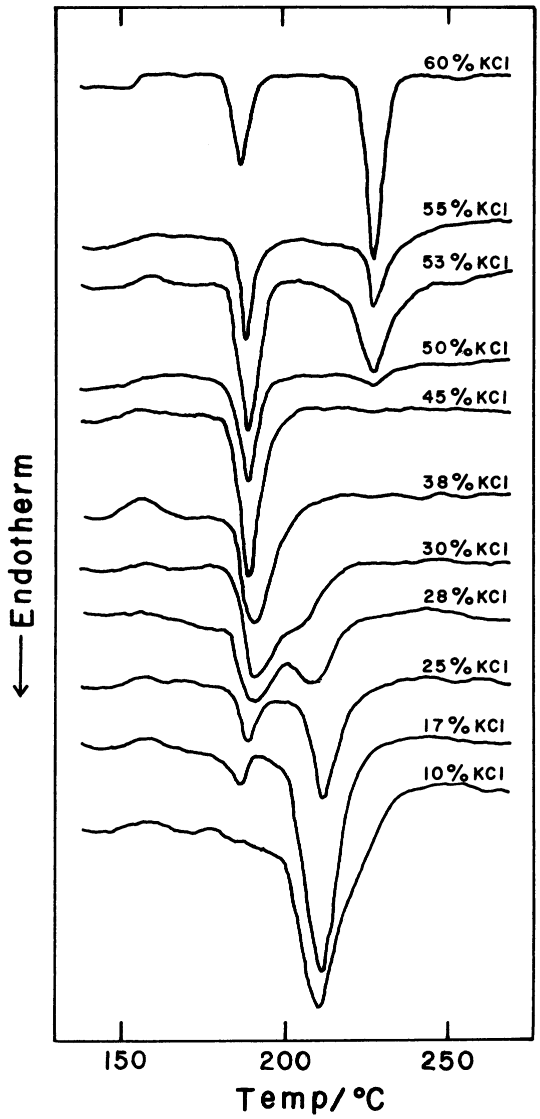

Fig. 2. DTA heating-curves of the powder mixtures of KCl and $SnCl_2$.

more peak recorded at 228 °C in the range of the composition larger than 50 mol% KCl and at 212 °C in the range less than 30 mol% KCl.

The second heating-curves of the once-melted samples are shown in Fig. 3. The equilibrium diagram of the system KCl-$SnCl_2$ constructed from the peak maximum temperatures in the second heating-curves is shown in Fig. 4. The diagram we have obtained agrees generally with that of Ch'ih-fa and Morozov. That is, the existence of two congruent melting compounds, $KSnCl_3$ and KSn_3Cl_7, are clearly indicated in the diagram in agreement with theirs. However, the temperatures we have obtained are somewhat different from the values of Ch'ih-fa and Morozov. In this study, the two compounds melt congruently at 228 °C (225) and 210 °C (218), respectively. The figures in the parentheses are the values of Ch'ih-fa and Morozov. The eutectics lie at 20 mol% KCl, 202 °C (200); 37 mol% KCl, 183 °C (176);

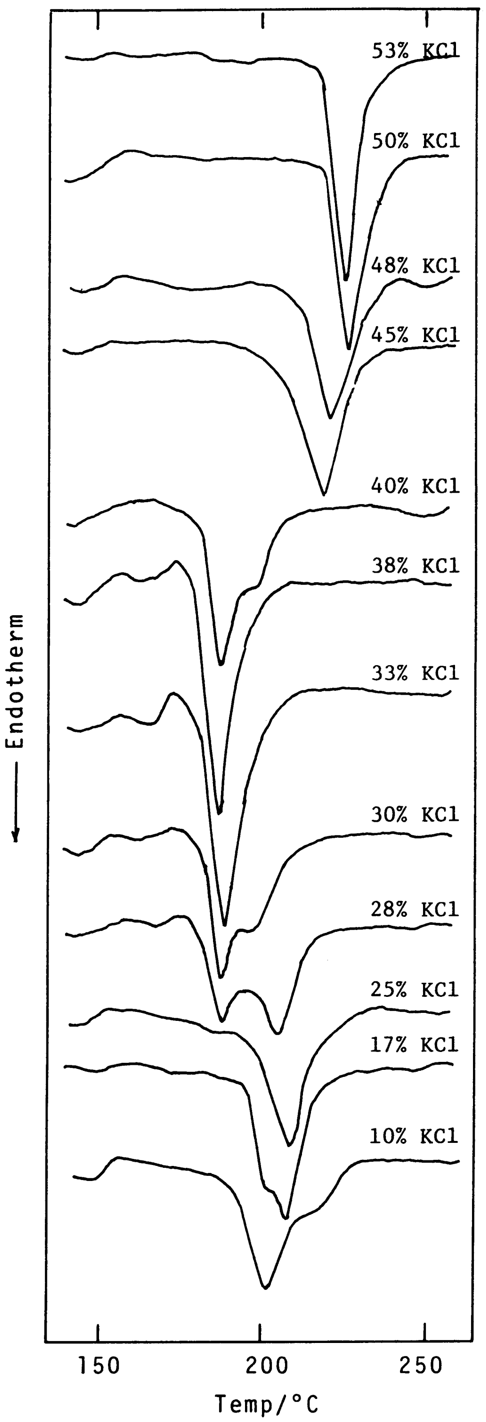

Fig. 3. The second DTA heating -curves of the once-melted samples.

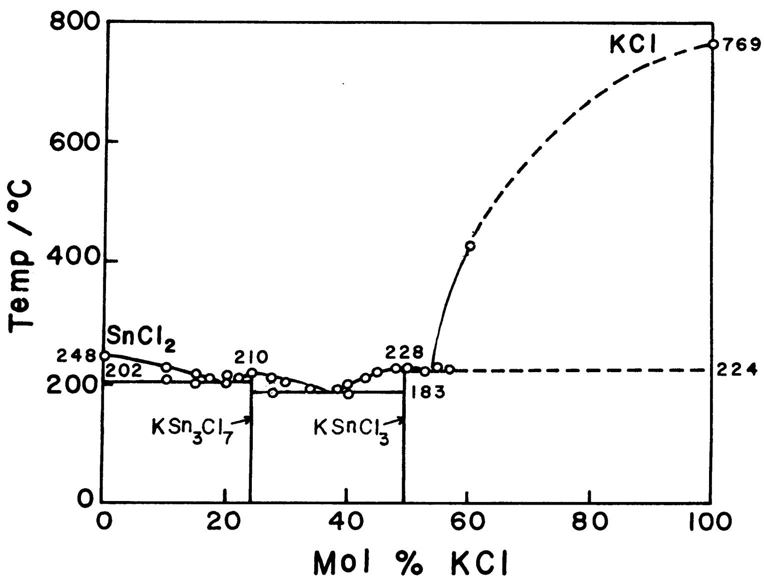

Fig. 4. The equilibrium diagram of the system KCl-$SnCl_2$.

55 mol% KCl, 224 °C (224). The equilibrium diagram could be roughly constructed from the data of the DTA heating-curves by the use of a Sinku-riko TGD-5000 RH instrument.

With reference to the diagram, the reaction at 190 °C in Fig. 1 is an additive reaction to form the compound, $KCl+SnCl_2 \rightarrow KSnCl_3$, and this temperature coincides with the lowest eutectic temperature, so that the reaction to form the compound may not proceed in the solid but in the melt. The reaction at 212 °C is also an additive reaction to form the compound, $KSnCl_3+2SnCl_2 \rightarrow KSn_3Cl_7$, and the reaction at 228 °C is an eutectic reaction, $KSnCl_3+KCl \rightarrow$ liquid.

The characterization of the congruent melting compounds is now in progress.

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