PHASE DIAGRAM OF LiCl-NaCl-AlCl₃ TERNARY SYSTEM

Yuzuru Sato and Tatsuhiko Ejima
Department of Metallurgy, Faculty of Engineering
Tohoku University, Sendai 980, Japan

ABSTRACT

Phase diagram of LiCl-NaCl-AlCl₃ ternary system has been determined by the use of direct visual observation and DTA methods. Composition ranges studied are 0-100mol% AlCl₃ for LiCl-AlCl₃ and NaCl-AlCl₃ binary systems, and 0-50mol% AlCl₃ for the ternary system.

Chemical compounds LiAlCl₄⁺ and NaAlCl₄⁺ were found in the binary systems and their melting temperatures are 416K and 427K, respectively. The ternary system in the composition range less than 50mol% AlCl₃ shows two liquidus surfaces around LiCl and NaCl, and one boundary line between them. The ternary eutectic composition is considered to be near the eutectic composition of LiAlCl₄⁺-NaAlCl₄⁺ binary system although it could not be found.

It is considered that the ternary system is a reciprocal system of \((\text{Li}^+,\text{Na}^+ | | \text{Cl}^-,\text{AlCl}_4^-)\) in the composition range less than 50mol% AlCl₃. From the slopes of liquidus surfaces of the reciprocal melt, the standard free energy change of the following ion exchange reaction is estimated to be positive.

\[
\text{LiCl}(ℓ) + \text{NaAlCl}_4(ℓ) = \text{NaCl}(ℓ) + \text{LiAlCl}_4(ℓ)
\]

INTRODUCTION

Phase diagrams are essential for the evaluation of thermodynamic properties in the study of molten salts, and also the knowledge of liquidus temperatures is indispensable for the practical use of salts.

LiCl-NaCl-AlCl₃ ternary system is attractive because very stable complex anion is formed in it, and it is well known as the electrolyte of new aluminum smelting process. Phase diagrams of LiCl-AlCl₃ and NaCl-AlCl₃ binary systems were previously reported. In this work, liquidus surface of the ternary system is determined in the composition range less than 50mol% AlCl₃. The thermodynamic properties of the ternary melt are discussed.
EXPERIMENTAL

For the determination of the phase diagram of the ternary system, it is desired that a sample salt is sealed in the container in order to prevent the evaporation or hydrolysis of the sample containing AlCl$_3$.

In this study, the direct observation of the phase change was adopted as a principal method, and DTA as a subsidiary method because the conventional thermal analysis is hard to use for the salts containing AlCl$_3$.

A schematic diagram of the apparatus used for the direct observation is shown in Fig.1. In this method, the sample salt is sealed in a transparent quartz tube under vacuum and heated, and then the appearance of a liquid phase in the solid phase or the disappearance of a solid phase in the liquid-solid coexisting phase was observed directly from the outside of a transparent electric furnace by the use of telescope with low magnification.

The conditions of thermodynamic equilibrium are obtained more easily in this method as compared with conventional thermal analysis, although the present method is also a non-equilibrium method in principle. In this study, the reproducibility was excellent under the conditions that the amount of sample was about 20-30mg and the heating rate was less than 0.1K/min. The reason why the cooling method was not employed is that the reproducibility was poor because the AlCl$_3$ melts have the tendency to super cool.

Figure 2 shows the DTA cell arrangement. DTA cells containing the sample and α-Al$_2$O$_3$ were fed into the holder made of boron nitride which has high thermal conductance and high electrical resistance. The measurement was made in an argon atmosphere.

AlCl$_3$ has an extremely high vapor pressure and strong hygroscopicity. The commercial anhydrous reagent grade AlCl$_3$ contains a fairly large amount of impurities such as HCl, FeCl$_3$ and others, and cannot be used as it is. In this study, a double distillation method shown in Figs.3 and 4 was used for the purification of the commercial reagent grade anhydrous AlCl$_3$. Purification was done by the following procedure. The unpurified AlCl$_3$ on a pyrex boat is placed in the distillation tube shown in Fig.3, and is heated under vacuum at about 390K for one day. Moisture, HCl and other volatile compounds are removed. In this case, the collecting bottle is heated at above 500K. After the heating under vacuum, AlCl$_3$ is heated to about 480K.
while dried argon is passed through as a carrier gas, and AlCl₃ is condensed in the collecting bottle cooled by the water with ice. After the sublimation, the collecting bottle is sealed at both ends. AlCl₃ obtained is white or slightly yellowish powder and still contains small amount of impurities. AlCl₃ powder obtained is sealed in a pyrex tube under vacuum and is melted at about 480K. Then it is cooled slowly in the furnace with the temperature distribution as shown in Fig.4. AlCl₃ condensed at the upper portion of pyrex tube is highly pure and colorless transparent crystal which looks like mica.

For the preparation of LiCl and NaCl, the commercial reagent grade salts were heated at about 600K under vacuum and were melted in a dried HCl atmosphere. After bubbling HCl gas into the melt for one hour, argon was bubbled into the melt for one hour, and then the melt of LiCl or NaCl is solidified under vacuum.

For the determination of chemical composition, the entire sample after measurement is dissolved into distilled water and diluted as required. The analysis was done by the atomic absorption method for Al, and the flame emission method for Li and Na.

RESULTS AND DISCUSSION

Phase diagrams of LiCl-AlCl₃ and NaCl-AlCl₃ binary systems obtained by previous study(1) are shown in Figs.5 and 6, respectively. Figure 7 shows the phase diagram of LiCl-NaCl binary system. In this case, the measurement was done on the liquidus temperatures only. The phase diagram of LiAlCl₄-NaAlCl₄ quasi-binary system having a simple eutectic behavior is shown in Fig.8.

Figure 9 shows the phase diagram of LiCl-NaCl-AlCl₃ ternary system in the composition range less than 50mol% AlCl₃. The points show the liquidus temperature measured, and the isothermal lines are shown. As shown in the figure, the liquidus surface consists of two surfaces around LiCl and NaCl. The dotted line, which connects the eutectic composition of LiCl-NaCl binary system with that of LiAlCl₄-NaAlCl₄ quasi-binary system, corresponds to the boundary line in which two liquidus surfaces around LiCl and NaCl sides intersect each other. Ternary eutectic composition is not seen in this figure, but is considered to be present near the eutectic composition of LiAlCl₄-NaAlCl₄ quasi-binary system.

As shown in Figs.5 and 6, LiCl-AlCl₃ and NaCl-AlCl₃
binary systems evidently have the compounds, LiAlCl\(_4\) and NaAlCl\(_4\). NaAlCl\(_4\) is confirmed to be very stable\(^2\) and LiAlCl\(_4\) is also considered to be stable.

Therefore, LiCl-NaCl-AlCl\(_3\) ternary system is regarded as a reciprocal system of \((\text{Li}^+,\text{Na}^+\mid \text{Cl}^-,\text{AlCl}_4^-)\). The cationic and anionic fractions are given by the following equation (1):

\[
\begin{align*}
\chi_{\text{Li}^+} &= X_{\text{LiCl}}/(1-X_{\text{AlCl}_3}) \\
\chi_{\text{Na}^+} &= X_{\text{NaCl}}/(1-X_{\text{AlCl}_3}) \\
\chi_{\text{Cl}^-} &= (X_{\text{LiCl}}+X_{\text{NaCl}}-X_{\text{AlCl}_3})/(1-X_{\text{AlCl}_3}) \\
\chi_{\text{AlCl}_4^-} &= X_{\text{AlCl}_3}/(1-X_{\text{AlCl}_3})
\end{align*}
\]

where \(\chi\) means the cationic or anionic fraction of ions in the reciprocal system, and \(X\) means the molar fraction of the compound in the ternary system. Phase diagram of the ternary system obtained is redrawn on the basis of the reciprocal diagram, and is shown in Fig. 10.

The thermodynamic properties of a reciprocal system are discussed. At first, the activities of components were calculated for LiCl-LiAlCl\(_4\) and NaCl-NaAlCl\(_4\) quasi-binary systems. In these quasi-binary systems, the activity of LiCl or NaCl in the melt can be obtained by the equation (2) except the composition near to LiAlCl\(_4\) or NaAlCl\(_4\), because the liquidus line from LiCl or NaCl reaches to the composition near to LiAlCl\(_4\) or NaAlCl\(_4\), respectively, and they do not have solid solubility.

\[
R \ln a_{\text{MC1}} = \int_{T_f}^{T} \frac{\Delta H_f}{T^2} \, dT
\]

where M means Li or Na, \(a_{\text{MC1}}\) is the activity of MC1 in the melt, \(T\) and \(T_f\) are the temperatures of liquidus and fusion of MC1, \(R\) is the gas constant, \(\Delta H_f\) is the heat of fusion of pure MC1. Heats of fusion used were taken from JANAF table\(^3\) for LiCl and Dawson's data\(^4\) for NaCl.

Activites of LiCl and NaCl obtained at their melting temperatures are shown in Figs. 11 and 12. The activities of LiAlCl\(_4\) and NaAlCl\(_4\) were determined by the use of Gibbs-Duhem's equation and are shown in the figures. The activities of LiCl and NaCl show considerably positive deviation from Raoult's law, and the deviations are more remarkable for LiCl-LiAlCl\(_4\) quasi-binary system. By considering the previously reported result on KCl-AlCl\(_3\) binary system\(^5\) as well as the present results, the following remarks can be made. The mixing of Cl\(^-\) and AlCl\(_4^-\) anions
increase the instability of the melt, and the instability decreases with increasing the size of cation.

Thermodynamic properties of a reciprocal melt, for example, \( (A^+, B^+ | Y^-; Z^-) \) are characterized by the standard free energy change of ion exchange reaction \((6)\) expressed by the equation \((3)\).

\[
AY(\ell) + BZ(\ell) = AZ(\ell) + BY(\ell)
\]

The standard free energy change is related closely to the coulombic force between the ions. If the radii of \(A^+\) and \(Y^-\) are smaller than that of \(B^+\) and \(Z^-\), respectively, the ion pairs of \(AY\) and \(BZ\) are stable generally and the standard free energy change of equation \((3)\) is positive.

On the other hand, equation \((4)\) gives the relation between the liquidus temperature of the reciprocal system and the activity of the compound, \(AY\) in the melt which equilibrates with pure solid of \(AY\).

\[
R \ln a_{AY} = R \ln \gamma_{AY} = \frac{T \Delta H_f}{T_f} \ln \frac{\gamma_{AY}}{T} \frac{T_f}{T^2} \quad \text{(4)}
\]

where \(\gamma_{AY}\) is the activity coefficient of \(AY\) in the melt.

As shown in Fig. 10, the liquidus surface around \(NaCl\) decreases monotonically toward the direction of \(LiAlCl_4\), but the liquidus surface around \(LiCl\) maintains a high temperature toward the direction of \(NaAlCl_4\). This means that the activity of \(LiCl\) in the melt is high, and the standard free energy change of equation \((5)\) is positive. This result agrees with the prediction mentioned above. This indicates that the combination of \(LiCl\) and \(NaAlCl_4\) (smaller and larger cation-anion pairs) is more stable than the combination of \(LiAlCl_4\) and \(NaCl\).

\[
LiCl(\ell) + NaAlCl_4(\ell) = LiAlCl_4(\ell) + NaCl(\ell)
\]

It is considered that this tendency becomes stronger as the difference between the cationic sizes increases. For example, two liquid region is found in the ternary system of \(LiCl-KCl-AlCl_3\) in the composition range less than 50mol% \(AlCl_3\) as reported by Grothe et al. \((7)\), this system has larger difference between the cationic sizes.

CONCLUSION

Phase diagram of \(LiCl-NaCl-AlCl_3\) ternary system was determined by the use of direct visual observation and DTA methods. In the composition range less than 50mol% \(AlCl_3\), the ternary system has two liquidus surfaces around \(LiCl\) and \(NaCl\), and they intersect on the line which
connects the eutectic composition of LiCl-NaCl binary system with that of LiAlCl4-NaAlCl4 quasi-binary system. The liquidus surfaces drop steeply as the content of AlCl3 approaches 50mol%. The ternary eutectic composition is considered to be near the eutectic composition of LiAlCl4-NaAlCl4 quasi-binary system.

By considering that the ternary system is a reciprocal system of \((Li^+,Na^+|Cl^-,AlCl_4^-)\), the thermodynamic properties were discussed. The activities of components were calculated for the quasi-binary systems containing common cations. From the difference between the slopes around LiCl and NaCl, the standard free energy change of the following reaction is considered to be positive.

\[
\text{LiCl}(\ell) + \text{NaAlCl_4}(\ell) = \text{LiAlCl_4}(\ell) + \text{NaCl}(\ell)
\]

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U.I. Shvartsman: Zh. Fiz. Khim., 14(1940), 253.
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Fig. 1  Schematic diagram of the apparatus for the direct visual observation method.

Fig. 2  Schematic diagram of DTA cell arrangement.

A: Cell holder made of boron nitride  
B: DTA cell made of Pt  
C: Sample  
D: $\alpha$-Alumina  
E: Thermocouple for temperature measurement  
F: Thermocouple for $\Delta T$ measurement
Fig. 3  Schematic diagram of the apparatus for the first stage distillation of AlCl\textsubscript{3}.

Fig. 4  Schematic diagram of the apparatus for the second stage distillation of AlCl\textsubscript{3}.
Fig. 5 Phase diagram of LiCl-AlCl₃ binary system.

Fig. 6 Phase diagram of NaCl-AlCl₃ binary system.
Fig. 7  Phase diagram of LiCl-NaCl binary system.

Fig. 8  Phase diagram of LiAlCl₄-NaAlCl₄ quasi-binary system.
Fig. 9  Phase diagram of LiCl-NaCl-AlCl₃ ternary system.

Fig. 10  Phase diagram of (Li⁺, Na⁺, Cl⁻, AlCl₄⁻) reciprocal system.
Fig. 11  Activities of components in LiCl-LiAlCl₄ quasi-binary melt at 883K.

Fig. 12  Activities of components in NaCl-NaAlCl₄ quasi-binary melt at 1074K.