DENSITY AND ELECTRICAL CONDUCTIVITY OF MOLTEN MgCl\textsubscript{2}-CaCl\textsubscript{2} BINARY MELT

Yuzuru Sato, Yukio Kuroda, Takeshi Nagatsu, Masayoshi Hoshi, *Jong-Il Kim, and Tsutomu Yamamura

Department of Metallurgy, Tohoku University, Sendai 980-8579, Japan.
*Department of Metallurgical Engineering, Inha Technical Junior College, Inchon, 402-752 Korea.

ABSTRACT

Density and electrical conductivity of MgCl\textsubscript{2}-CaCl\textsubscript{2} binary melt have been measured in whole composition range by using a manometric method and an AC bridge method, respectively. Molten MgCl\textsubscript{2} itself showed considerably low expansion coefficient, larger molar volume and relatively lower molar conductivity etc. compared with CaCl\textsubscript{2}. The unique properties of MgCl\textsubscript{2} are considered to be due to the neutral species in the melt because of incomplete ionic dissociation. For the mixture melt, the molar volume negatively deviated from the additivity and the maximum deviation was found at almost equimolar composition, the molar conductivity showed positive deviation and the maximum deviation was also found at equimolar composition. From the phenomena obtained, the complex MgCl\textsubscript{4}\textsuperscript{2-} is considered to be formed even in the mixture with divalent CaCl\textsubscript{2} and the effects of complex formation on the properties were discussed.

INTRODUCTION

Since molten MgCl\textsubscript{2} has the unique properties such as the extremely low surface entropy(1), and is well known as the complex, MgCl\textsubscript{4}\textsuperscript{2-} forming compound(2) by mixing with anion donor such as the alkali chlorides. A remarkable maximum in isothermal molar volume was found in MgCl\textsubscript{2}-CsCl binary melt(3) at the composition near 67mol\%CsCl which was corresponding to Cs\textsubscript{2}MgCl\textsubscript{4} complex. Furthermore, large negative deviation in isothermal molar conductivity was also found in MgCl\textsubscript{2}-Alkali chloride melts except MgCl\textsubscript{2}-LiCl, and the amount of the deviation increases in the order of atomic number of alkaline cation(4). However, the physicochemical properties of the mixture with divalent compounds, which is considered to be weaker anion donor than monovalent compounds, are not necessarily known.

In this work, it was planned to measure the density and electrical conductivity of MgCl\textsubscript{2}-CaCl\textsubscript{2} binary melt to make clear the behavior of the mixture. Calcium belongs to same group of magnesium and is next order in a periodic table as an alkaline earth metal, and the mixture of the chlorides is, in general, expected to behave almost ideally. However, the unique and different properties of MgCl\textsubscript{2} from other alkaline earth chlorides mentioned...
above give us the expectation that the mixture may behave non-ideally. Namely, complex \( \text{MgCl}_4^{2-} \) may be formed and affects the physicochemical properties of the mixture if \( \text{CaCl}_2 \) is expected to be a Cl* donor due to its relatively larger cationic radius. Therefore it is interesting to compare the effects on the properties of mono- and di-valent chlorides as the additive into molten \( \text{MgCl}_2 \).

**EXPERIMENTAL**

**Density**

Density has been measured by using a manometric method(3,5). The apparatus is shown in Fig. 1. The method is based on the hydrostatic pressure caused by the density of the melt and the gravitational acceleration. Two U-type tubes made of quartz containing molten sample and a reference liquid with known density are connected and isolated from the air. Therefore, density of the melt is obtained by comparing the hydrostatic heads of the melt and the density of reference liquid. The pressure difference is given by the mercury reservoir. The reference liquid used was a fluoro-compound oil which had low vapor pressure, high density of about 1.8g·cm\(^{-3}\), good fluidity and excellent chemical stability. The U-type tube for the oil was immersed into thermostated bath kept to 303K. Another U-type tube for the sample melt was put into the transparent electric furnace with very long temperature uniformity up to about 1200K. The height of the menisci were measured by using a cathetometer with telescope in the resolution of 0.01mm from outside of the furnace. In this apparatus, wettability between quartz and the melt is important. If the contact angle is not zero, the reproducibility of height measurement becomes poor. Therefore, the measurement was carried out several times for identical temperature of the melt by moving the menisci through moving the mercury reservoir although the wettability was good in this work. The atmosphere inside the tubes was dry argon.

**Electrical Conductivity**

Electrical conductivity was measured by using AC bridge method(4). Whole apparatus is shown in Fig. 2. The conductivity cell was dipped into the melt and the immersion depth was kept constant by moving the cell vertically. Figure 3 shows the detail of the conductivity cell. It is made of all quartz and has a U-type capillary. Total length of the capillary was about 50mm and the cell constant was about 2x10\(^4\)m\(^{-1}\). Melt comes from a hole at the bottom of the capillary. Each electrode made of Pt was welded with two Pt-13%Rh lead wires to compensate the resistance of the wires. The principle of the compensation is shown in Fig. 4. The measurements of resistance are carried out by changing the frequency to minimize the impedance at the surface of electrode. The frequencies used were 1.1, 1.6, 2.5, 4.5 and 10kHz and the resistance measured was extrapolated to infinite value of square root of the frequencies. The atmosphere was also dry argon.

**Chemicals**

\( \text{MgCl}_2 \) anhydride used was prepared by following procedure(3) because it is very hygroscopic and easily hydrolyzes. Reagent grade \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) was dissolved into distilled water with equimolar \( \text{NH}_4\text{Cl} \) and the solution was evaporated to dryness in air to obtain almost trihydrated complex, \( \text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 3\text{H}_2\text{O} \). The trihydrated complex was de-
hydrated and decomposed by gradual heating up to 700K under dry N2 stream. The anhydrinous MgCl2 obtained by heating was melted in purifier tube of quartz under HCl and bubbled by HCl and Ar. Finally it was filtrated and solidified under vacuum. The MgCl2 obtained in this work was transparent layered crystal like mica. The anhydride CaCl2 was also prepared by HCl and Ar bubbling after dehydration under dry N2 stream at about 500K. The anhydride MgCl2 and CaCl2 were mixed and melted under dry Ar atmosphere prior the experiment.

RESULTS

Density and Molar Volume

Densities of MgCl2-CaCl2 binary melts have been measured in the temperature range from liquidus to about 1200K for ten compositions other than pure MgCl2 whose density was taken from author’s previous work(3). The densities obtained are shown in Fig.5. They represent good linear relationship against the temperature for all the compositions. The isothermal densities shown in Fig.6 increase monotonously with increasing the content of CaCl2. An isothermal molar volume calculated at 1100K is shown in Fig.7. The molar volume shows apparently negative deviation from the additive line and a minimum value is found. The results obtained is similar to the tendency in previous reports(6,7). Therefore, the excess molar volume which is the deviation from the additivity is also shown in the top of same figure. The excess molar volume shows considerably large minimum at about equimolar composition and the maximum deviation reaches about 2.7%. This tendency is interestingly opposite to that of MgCl2-CsCl melt(3) in which the excess molar volume was largely positive as described above. Figure 8 shows the expansion coefficient of the binary melt and the partial molar volumes of the components, MgCl2 and CaCl2 calculated from the equation of the molar volume as a function of composition. The expansion coefficient of MgCl2 is considerably low. It increases steeply up to equimolar composition and then decreases moderately with increasing the content of CaCl2. The partial molar volume of MgCl2 decreases almost linearly by adding CaCl2. On the other hand, the partial molar volume of CaCl2 also decreases by adding MgCl2 with increasing the rate of decrease.

Electrical Conductivity

Electrical conductivities have also been measured for ten compositions of MgCl2-CaCl2 binary melts in the temperature range from liquidus to about 1200K. The result of previous result(4) was employed for MgCl2. The results are shown in Figs.9 and 10. All the electrical conductivities were approximated as the quadratic functions of the temperature. Figure 11 represents the isothermal electrical conductivities. They increase almost linearly by adding CaCl2 into MgCl2 in initial stage and then decrease toward CaCl2. The maximum is found at about 80mol%CaCl2. Figure 12 shows an isothermal molar conductivity at 1100K calculated through the density obtained in this work. It also shows maximum. Therefore, the excess molar conductivity, which is deviation from an additivity, is shown in same figure. The maximum value of the excess molar conductivity is found at also nearly equimolar composition. The tendency is similar to previous work(7,8). The
positive deviation is also opposite to that of MgCl₂-Alkali chloride binary melts(4). The activation energy of conduction taken from Arrhenian plot of molar conductivity is shown in Fig. 13. It shows no remarkable change although the small maximum is found at about 80mol%CaCl₂ and the shape of composition dependence is like to that of MgCl₂-Alkali chloride melts(4).

DISCUSSION

The results obtained in this work indicate some interesting phenomena on molten MgCl₂. At first, its molar volume is abnormally larger than that of CaCl₂ although the radius of Mg²⁺ is smaller than that of Ca²⁺ as shown in Fig. 7. At second, it shows very low expansion coefficient as shown in Fig. 8. At third, its molar conductivity is considerably lower than that of CaCl₂. These suggest that the structure of molten MgCl₂ is different from that of molten CaCl₂. Although molten MgCl₂ should dissociate to unit ions, Mg²⁺ and Cl⁻, it is considered that the dissociation is incomplete because Mg²⁺ has small cationic radius and is a strong anion acceptor having the tendency to form stable complex MgCl₄²⁻. Therefore MgCl₂⁻ and undissociated neutral species are assumed in molten MgCl₂ other than unit ions. This phenomena, especially the remained neutral species, may cause the decrease of total electric charge and also decrease of the cohesive force in the melt. Therefore, the molar volume of molten MgCl₂ increases than the hypothetical one with the structure same to more ionic molten CaCl₂. Low expansion coefficient of MgCl₂ can be explained if the degree of dissociation of neutral species into ionic species is promoted with rising temperature. Furthermore, the remained neutral species means low effective electric charge and results the lower molar conductivity of molten MgCl₂.

The property of MgCl₂ as a strong anion acceptor easily causes the formation of complex anion, MgCl₄²⁻ when Cl⁻ donor is added into MgCl₂. On the other hand, CaCl₂ is known to be also the anion acceptor to form the complex anion by mixing with the alkali chlorides(9,10). However, the property of CaCl₂ as the anion acceptor is considered to be weaker than MgCl₂ because of its larger cationic radius. Therefore, CaCl₂ probably acts as the anion donor by mixing with MgCl₂. These facts may allow the assumption for the formation of the equimolar complex Ca²⁺·MgCl₄²⁻ in molten state although it does not appear as a solid compound in the phase diagram(11) which shows simple eutectic. Neutral species which may be contained in pure MgCl₂ should be converted into ionic MgCl₄⁻ by adding CaCl₂. The conversion increases the ionicity and the cohesive force of the melt and decreases the molar volume. The negative deviation of molar volume from the additivity can be explained by this mechanism. The mechanism is considered to be also effective for the behavior of the molar conductivity. The molar conductivity of molten CaCl₂ is about 50% larger than that of molten MgCl₂ at 1100K as shown in Fig. 12. The difference may be due to the low conductivity of molten MgCl₂ caused by the incomplete ionic dissociation described above. In the range of MgCl₂ rich composition, the ionicity of molten MgCl₂ is enhanced by adding CaCl₂ and the molar conductivity of the mixture increases with increasing CaCl₂. On the other hand, in the range of CaCl₂ rich composition, Cl⁻ is consumed to form MgCl₄⁻ when MgCl₂ is added into CaCl₂. This reaction do not change total electric charge. If the migration velocity of MgCl₄⁻ is less than that of Cl⁻, the molar...
conductivity must decrease by adding MgCl₂ into CaCl₂. However, slight increase in the molar conductivity was found as shown in Fig. 12. This fact suggests two possibilities. One is higher mobility of MgCl₄²⁻ than Cl⁻. Other is the acceleration of Ca²⁺ by changing the constituent species although the transport number of Ca²⁺ in molten CaCl₂ is not so high, to be 0.42(12). It is difficult to say which is correct because the mechanisms above are not yet confirmed in the case of present system. Therefore it is considered that another studies such as the equilibrium of complex formation or the measurement of transport number are necessary to understand the behavior.

CONCLUSION

Density and electrical conductivity of MgCl₂-CaCl₂ binary melt have been measured in entire composition range to study the behavior of MgCl₂ as an anion acceptor by mixing CaCl₂ which was considered to be typical ionic melt. Results obtained showed that molten MgCl₂ had unique properties such as considerably low expansion coefficient, larger molar volume and relatively lower molar conductivity than that of CaCl₂ etc. Following features were obtained for the mixture. The molar volume negatively deviates from additivity and the maximum deviation at 1100K was about 2.7% at equimolar composition. The expansion coefficient showed maximum at about 80mol%CaCl₂. The molar conductivity showed positive deviation and the maximum at 1100K was also at equimolar composition. These phenomena was considered to be due to the presence of neutral species in molten MgCl₂ and the complex formation of MgCl₄²⁻ by mixing with CaCl₂ although the sign of the deviations are opposite to MgCl₂-Alkali chloride mixtures.

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Fig. 1 Schematic diagram of the manometric densitometer.

Fig. 2 Apparatus for the electrical conductivity measurement.
Fig. 3 Conductivity cell made of quartz.

A: Pt-lead wire  
B: Hole  
C: Pt-electrode  
D: U-type capillary  
E: Melt inlet

Fig. 4 Principle for compensating the resistance of wires.

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R_x = \frac{2R_1'(2R_1'-R_1)}{4R_1'-R_1} \\
R_1' = R_1 - \gamma \quad R_x = R_x - \gamma
\]

Fig. 5 Densities measured of MgCl₂-CaCl₂ binary melts.
Fig. 6 Isothermal densities of MgCl₂-CaCl₂ binary melts.

Fig. 7 Molar volume and excess molar volume of MgCl₂-CaCl₂ binary melt at 1100K.
Fig. 8 Partial molar volumes of components at 1100K and expansion coefficient of MgCl₂-CaCl₂ binary melt.

Fig. 9 Conductivities measured for MgCl₂ rich compositions of MgCl₂-CaCl₂ binary melts.
Fig. 10 Conductivities measured for CaCl₂ rich compositions of MgCl₂-CaCl₂ binary melts.

Fig. 11 Isothermal conductivities of MgCl₂-CaCl₂ binary melt.
Fig. 12 Molar conductivity and excess molar conductivity of MgCl₂-CaCl₂ binary melt at 1100K.

Fig. 13 Activation energy of conduction for MgCl₂-CaCl₂ binary melts.