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Mass-spectrometric Measurements of Thermodynamic Properties of the Molten KCl-MnCl$_2$ System

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Activities and heats of mixing for the molten KCl-MnCl$_2$ system were determined mass-spectrometrically by the ion-current ratio method. Activities of components KCl and MnCl$_2$ show large negative deviations from Raoult's law, indicating a very strong interaction between KCl and MnCl$_2$. Entropies of mixing calculated from measured activities and heats of mixing have minimum values in the vicinity of 33% MnCl$_2$, and have been compared with those calculated on the basis of some molten structure models to infer possible chemical species in the molten salt.

Thermodynamic measurements on molten salts have so far been made mainly by the calorimetric or the emf method. In our previous investigation[1] we measured mass-spectrometrically activities in both solid and liquid solutions of the KCl–NaCl system, and showed that mass spectrometry had a wide range of application in the measurement of thermodynamic properties in multicomponent salt systems.

The aim of the present study is to measure activities, heats of mixing, and entropies of mixing for the KCl–MnCl$_2$ system by mass spectrometry and to discuss the relation between thermodynamic properties and molten salt structures in such binary charge-unsymmetrical molten salt mixtures as an alkali-metal halide–transition metal halide system.

There have been many reports on physical properties of the molten KCl-MnCl$_2$ system: density,[2,3] molar refractivity,[4] electrical conductivity,[2,3] magnetism,[5] liquid structure according to the X-ray diffraction analysis,[6] Raman spectra,[7] and absorption spectra.[8] Papatheodorou and Kleppa[9] and Kleppa and McCarty[10] measured enthalpies of mixing for alkali-metal chloride–MCl$_2$ systems (M=Mn, Co, Ni, and Mg) by using calorimeters. They found that exothermic enthalpies of mixing, ΔH^{M}, increase sharply with increasing ionic radius of alkali-metals and that the interaction parameter, $\lambda^{\mathrm{M}}=\Delta H^{\mathrm{M}}/X_1X_2$ (X_1 and X_2 are mole fractions of MCl$_2$ and ACl, respectively), has a minimum near $X_{\mathrm{MnCl_2}}=1/3$ only, indicating an appreciable formation of tetrahedral complex MCl$_4^{2-}$ in the mixture. On the other hand, the emf method also has been applied to the charge-unsymmetrical alkali-metal chloride–MCl$_2$ molten salts: M=Mn,[11,12] Co,[13] Ni,[14] Zn,[15] Mg,[16] Ca, Sr, and Ba.[17] These reports showed that each heat of mixing agreed roughly with each of those obtained by the variation of mixing entropy with composition was characterized by an S-shaped curve in the vicinity of $X_{\mathrm{MnCl_2}}=0.33$. The S-shaped behavior of entropy has been explained by a few investigators[11,16,18] in terms of the partial dissociation of ionic complex species through the reaction

$$[\mathrm{MCl_4}]^{2-} \rightleftharpoons \mathrm{M}^{2+} + 4\mathrm{Cl}^-, \qquad (1)$$

whereas Kucharski and Flengas[12] adopted configurational terms of MCl$_4^{2-}$, A$^+$, M^{2+}, and Cl$^-$ ions. It has been found by Φstvold and Kleppa[19] that the PbO–SiO$_2$ system also shows an S-shaped behavior which they attributed to formation of orthosilicate anion, [SiO$_4$]$^{4-}$.

Experimental

Instrument. The instrument used was a JEOL JMS-01BK doubly-focused mass spectrometer with a Knudsen cell source. As the details of the instrument were described elsewhere,[1,20] we would mention here only on the Knudsen cell which differed from the one used in our previous experiment.[1] The nickel Knudsen cell (Ni metal over 99.9% in purity) had a conical orifice, 0.005—0.006 cm in diameter, bored by electric discharge processing. In order to prevent the clogging of the cell orifice caused by wetting and crawling-up of molten salt, a fence made of thin Ni-foil was fixed in the upper part of the inside cell wall.

Sample. Vacuum-dried MnCl$_2$ and KCl powders were used as starting materials. Anhydrous MnCl$_2$ powder was obtained from MnCl$_2$·2H$_2$O by dehydration at 200 °C. Solid solution samples for the KCl–MnCl$_2$ system were prepared by the following processes: (1) preparing a mixture of KCl and MnCl$_2$ powders by weighing in dry Ar, (2) fusing the mixture in a stream of HCl gas in quartz tube to remove impurities such as alkali-metal oxides and water, and (3) replacing the HCl gas by Ar to remove the HCl dissolved in the molten salt and then cooling down the mass to room temperature. The product was pulverized just before measurement, and a sample of approximately 1 g for each run was charged in the cell in a dry box.

Calibration of Cell Temperature. As the cell temperature was measured with a W-5%Re/W-26%Re thermocouple positioned under the outside bottom of the cell, the temperature difference between the sample in the cell and the outside in contact with the thermocouple was determined by measuring some of the melting points of LiCl (883 K), MnCl$_2$ (923 K), KCl (1044 K), and NaCl (1074 K). The temperature difference was about 25 K, increasing slightly with a rise in cell temperature.

Procedure of Mass-spectrometric Measurement. Ion identification and intensity measurement for derived species were

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made by the usual mass spectrometric technique in the temperature range from melting temperature to several hundreds degrees above the melting point. Prior to starting an ion intensity measurement the constant ion intensity was examined.

The ionic species detected were K^+, KCl^+, K_2Cl^+, Cl^+, Mn^+, $MnCl^+$, and $MnCl_2^+$. Their appearance potentials, relative to H_2O^+, were 11.0, 10.5, 10.8, 15.5, 13.0, 8.5, and 7.5 eV, respectively. No other ions such as $Mn_2Cl_3^+$ (dimer ion), $KMnCl_3^+$ (mixed dimer ion), and $NiCl_n^+$ ($n=1$, 2) were detected. Both by considering appearance potentials and by using an analogy with other chlorides,[1,21-23] the molecular ions formed by simple ionization were estimated to be KCl^+, K_2Cl^+, and $MnCl_2^+$. In view of the apparent potentials for all the ions, an ionization potential of 17.5 eV was used.

Activity coefficient, γ, and heat of mixing, ΔH^M, were calculated from ion-current ratios of related ionic species by the previously outlined procedure.[1] According to Belton and Fruehan,[24] for example, the activity coefficient, γ_{MnCl_2}, and heat of mixing, $\Delta H^M_{MnCl_2}$, for the $MnCl_2$ component are given by

$$\ln \gamma_{MnCl_2} = \int_{X_{MnCl_2}=1}^{X_{MnCl_2}} \frac{X_{KCl}}{1+X_{MnCl_2}} \times \mathrm{d}\left[\ln \frac{I_{K_2Cl^+}}{I_{MnCl_2^+}} - \ln \frac{X_{KCl}^2}{X_{MnCl_2}}\right], \quad (2)$$

$$\Delta H^M_{MnCl_2} = -R \int_{X_{MnCl_2}=1}^{X_{MnCl_2}} \frac{X_{KCl}}{1+X_{MnCl_2}} \times \mathrm{d}\left\{\frac{\mathrm{d}[\ln(I_{K_2Cl^+}/I_{MnCl_2^+}) - \ln(X_{KCl}^2/X_{MnCl_2})]}{\mathrm{d}(1/T)}\right\}, \quad (3)$$

where X is mole fraction, $I_i{}^+$ the ion intensity of ion i^+, and R the gas constant.

Results and Discussion

Activity. Figure 1 shows the ion-current ratio as a function of temperature. The relationship between the ion-current ratio and the reciprocal of absolute temperature was determined by the regression analysis. In Table 1 the regression coefficients and standard deviations of error were summarized. The ion-current ratio values for the 10 mol% KCl–90 mol% $MnCl_2$ system at temperatures above 1083 K are not included in the regression analysis, since they deviated greatly from the regression line. This was probably because $MnCl_2$ gas molecules did not satisfy the Knudsen

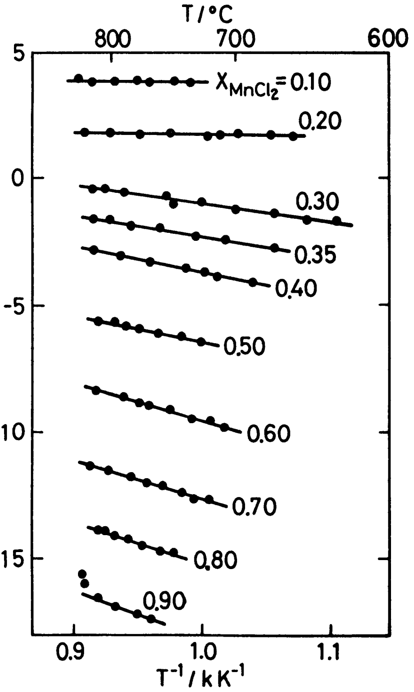

Fig. 1. Observed ion-current ratio in the molten KCl–$MnCl_2$ system.

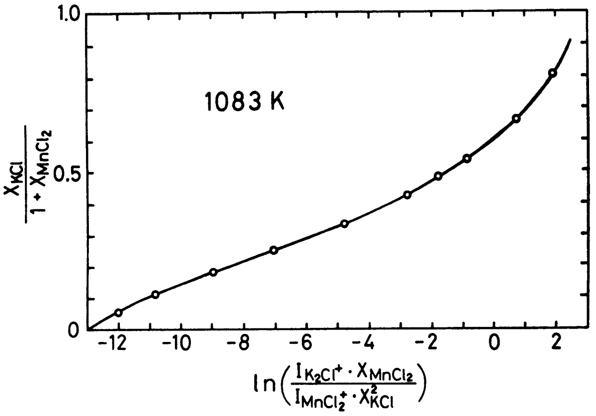

Fig. 2. Preliminary curve for the graphical integration in Eq. 2.

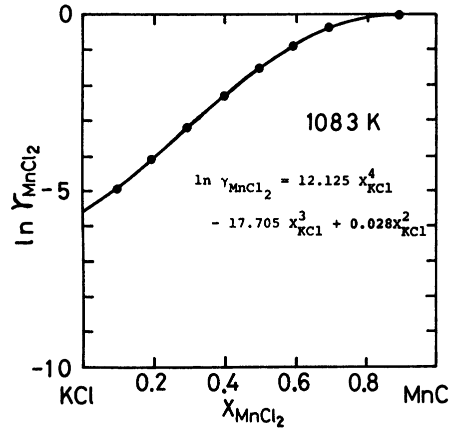

Fig. 3. Plots of $\ln \gamma_{MnCl_2}$ *vs.* X_{MnCl_2} at 1083 K.

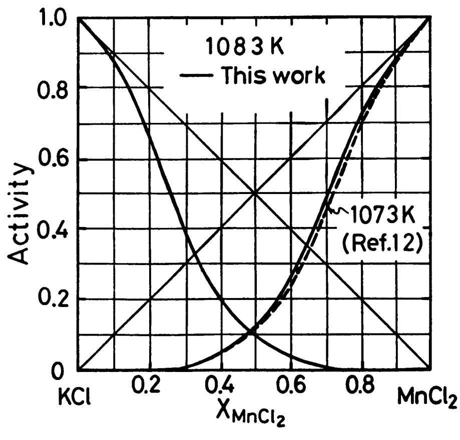

Fig. 4. Activity in the molten KCl–$MnCl_2$ system at 1083 K.

Table 1. Line-fitting parameters for lines drawn in Fig. 1.

X	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\dfrac{\mathrm{d}\ln (I_{\mathrm{K_2Cl^+}}/I_{\mathrm{MnCl_2^+}})}{\mathrm{d}(1/T)}$	−325	−930	−7990	−9800	−11400	−14800	−16100	−17300	−18200
b[a]	4.169	2.651	5.876	5.686	6.176	5.439	4.772	3.543	0.06382

a) b is the constant used in the equation: $\ln(I_{\mathrm{K_2Cl^+}}/I_{\mathrm{MnCl_2^+}})=a(10^4/T)+b$, where a=slope.

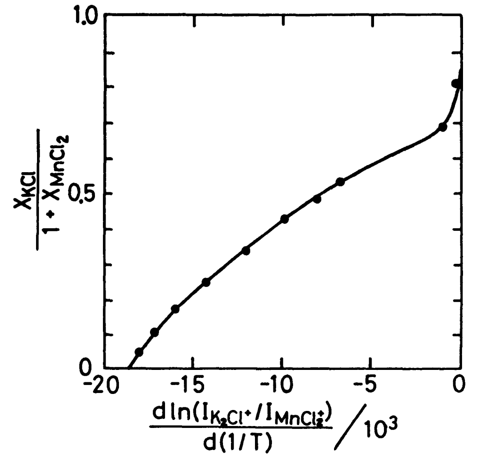

Fig. 5. Integration plots for the KCl–MnCl$_2$ system.

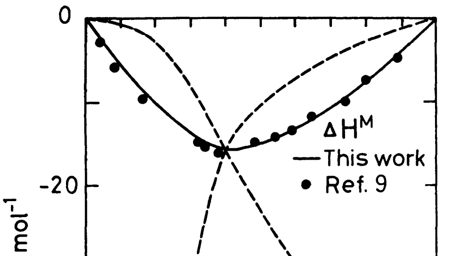

Fig. 6. Enthalpy of mixing in the molten KCl–MnCl$_2$ system.

molecular flow condition when allowed to effuse out from the orifice. In order to integrate Eq. 2 graphically and to obtain the activity coefficient, the term $[\ln(I_{\mathrm{K_2Cl^+}}/I_{\mathrm{MnCl_2^+}})-\ln(X/^2_{\mathrm{KCl}}X_{\mathrm{MnCl_2}})]$ was plotted against the composition, X, as illustrated in Fig. 2. The solid line in Fig. 2 was given by the regression analysis. The relationships of composition *vs.* logarithmic activity coefficient and composition *vs.* activity are shown in Figs. 3 and 4. Braunstein[25)] proposed a method to obtain the equilibrium constant for Reaction 1 by extrapolating the log γ *vs.* X line to $X=0$, as applicable when the excess Gibbs energy, ΔG_{XS}, is attributable to the excess entropy. His method, however, was not adopted in this case since ΔG_{XS} depends mainly on the large heat of mixing, as will be described later. It is seen from Fig. 3 that $\ln\gamma$ has an inflection point at the concentration of 30—40 mol% MnCl$_2$, which suggests a structural change in the molten salt. As shown in Fig. 4, the activity shows a great deviation from Raoult's law, suggesting a presence of strong interaction between KCl and MnCl$_2$.

Heat of Mixing and Entropy of Mixing. Figure 5 shows a preliminary curve for obtaining the heat of mixing, ΔH^{M}, from both Eq. 2 and the data in Table 1. An integration along the curve in Fig. 5 gives the $\Delta \bar{H}$'s in Fig. 6. This result is in good agreement with the values determined by Papatheodorou and Kleppa[9)] and hence the interaction parameter λ^{M} also agrees with them. Although the heats of mixing obtained here are considered to be average values for a wide range of temperature, they are in close agreement with those determined calorimetrically at a constant temperature. This fact suggest that the liquid structure of the KCl–MnCl$_2$ molten salt is independent of temperature, in accord with the fact that the intensity of Raman spectra in this system is independent of temperature.[7)]

The partial molar entropy, $\Delta\bar{S}_{\mathrm{i}}$, and the integral entropy of mixing, ΔS^{M}, for the molten salt were calculated from the well-known thermodynamic relations

$$\Delta\bar{G}_{\mathrm{i}} = \Delta\bar{H}_{\mathrm{i}} - T\Delta\bar{S}_{\mathrm{i}}, \tag{4}$$

$$\Delta S^{\mathrm{M}} = \sum_{\mathrm{i}} X_{\mathrm{i}}\Delta\bar{S}_{\mathrm{i}}, \tag{5}$$

the results obtained being shown in Fig. 7.

Estimation of Chemical Species in Molten Mixture. The integrated and partial molar entropies of mixing, as shown in Fig. 7, from an S-shaped curve in the vicinity of $X_{\mathrm{MnCl_2}}=0.33$, which suggests that some marked structural change occurs in this composition range. If anions and cations in the system behave as those in an ideal solution, the entropy of mixing should be in agreement with the values calculated from the equation $\Delta S^{\mathrm{M}}_{\mathrm{ideal}}=-R\sum_{\mathrm{i}} X_{\mathrm{i}}\ln X_{\mathrm{i}}$. Obviously, this is not the case, as seen from Fig. 7. Kucharski and Flengas[12)] explained the deviation from ideal entropy on the basis of possible ionic species: (1) Mn^{2+} and Cl$^-$ ions in the pure molten MnCl$_2$; (2) A$^+$ (alkali-metal ion), Cl$^-$, and [MnCl$_4$]$^{2-}$ ions in the composition region of $0<X_{\mathrm{MnCl_2}}<0.33$; (3) only [MnCl$_4$]$^{2-}$ and A$^+$ ions at $X_{\mathrm{MnCl_2}}=0.33$; (4) A$^+$, Mn^{2+}, Cl$^-$, and [MnCl$_4$]$^{2-}$ ions in the region $X_{\mathrm{MnCl_2}}>0.33$. On the basis of this model the theoretical entropy of mixing was calculated from the equations

$$\begin{aligned}\Delta S^{\mathrm{M}} &= -R[\textstyle\sum n(\mathrm{i}^+)\ln N(\mathrm{i}^+) + \sum n(\mathrm{j}^-)\ln N(\mathrm{j}^-)] \\ &= -R[n(\mathrm{K}^+)\ln N(\mathrm{K}^+) + n(\mathrm{Mn}^{2+})\ln N(\mathrm{Mn}^{2+}) \\ &\quad + n(\mathrm{Cl}^-)\ln N(\mathrm{Cl}^-) + n(\mathrm{MnCl_4^{2-}})\ln N(\mathrm{MnCl_4^{2-}})],\end{aligned} \tag{6}$$

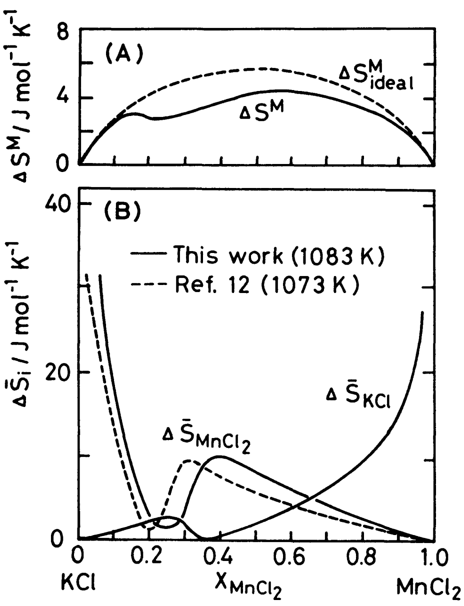

Fig. 7. Partial moral entropy of mixing and integral entropy in the molten KCl-$MnCl_2$ system.

where $n(i^+$ or $j^-)$ and $N(i^+$ or $j^-)$ denote the mole number and ionic fraction of i^+ or j^- ion, respectively, and

$$\Delta\bar{S}_{KCl} = -\frac{R}{2}\ln\frac{X_{KCl}^3(4X_{MnCl_2}-X_{KCl})}{(1+X_{KCl})(2X_{MnCl_2}-X_{KCl})^3} \quad (7)$$

in the composition region of $X_{MnCl_2}>1/3$. Equation 6 was derived simply on statistical thermodynamics by assuming that the cations and anions will distribute randomly and that the contribution of a vibration of molecule to the entropy can be neglected. Figure 8 shows the entropies calculated from Eqs. 6 and 7. As for a comparison of Figs. 7 and 8, the model described above can explain the decrease in entropy in the vicinity of $X_{MnCl_2}=0.33$, but can not explain the value of ΔS^M at $X_{MnCl_2}=0.33$ since the ΔS^M should be 0 at $X_{MnCl_2}=0.33$ if the model is correct. Furthermore, the observed values of ΔS^M and $\Delta\bar{S}_{KCl}$ are smaller than the calculated. Therefore, we must further modify Kucharski and Flengas' model.

Takagi *et al.*[2] have concluded from electrical conductivity measurements for the KCl-$MnCl_2$ system that free Mn^{2+} ions exist in the molten salt at $X_{MnCl_2}=0.33$. Considering this fact and the proposals of Φstvold,[11] Ikeuchi and Krohn,[16] and Pelton and Thompson,[18] we take into account the following chemical equilibrium in calculating the entropy

$$[MnCl_4]^{2-} \rightleftharpoons Mn^{2+} + 4Cl^-. \quad (8)$$

Figure 9 shows the result computed for $\alpha=0.15$ and 0.50, where α is the degree of dissociation of $[MnCl_4]^{2-}$ into Mn^{2+} and Cl^- on the assumption that the dissociation constant for Eq. 8 is independent of the composition. As can be seen from Fig. 9, the disagreement near $X_{MnCl_2}=0.33$ may be solved by considering Dissociation Reaction 8. The disagreement in the high $MnCl_2$ composition side, however, remains still unsettled.

Takagi *et al.*[6] proposed the following model from an X-ray structure analysis: clusters or polymer ions (made up of $[MnCl_4]^{2-}$ exist even in the pure molten $MnCl_2$, and addition of component KCl will cause the polymeric ions to decompose to $[MnCl_4]^{2-}$ monomer ion through the intermediate cluster ions Mn_5Cl_{10}, $[Mn_4Cl_{10}]^{2-}$, $[Mn_3Cl_9]^{3-}$, and $[Mn_2Cl_7]^{3-}$ at compositions $X_{MnCl_2}=1.0$, 0.666, 0.5, and 0.4, respectively. Based on the model by Takagi *et al.*[6] we attempted again to calculate the entropy of mixing by using Eq. 6. However, we have failed in obtaining consistent results. This is probably attributable to the assumption that (1) such large cluster ions as $[Mn_3Cl_9]^{3-}$ and $[Mn_4Cl_{10}]^{2-}$ are almost negligible and the mixing of each ion is ideal,

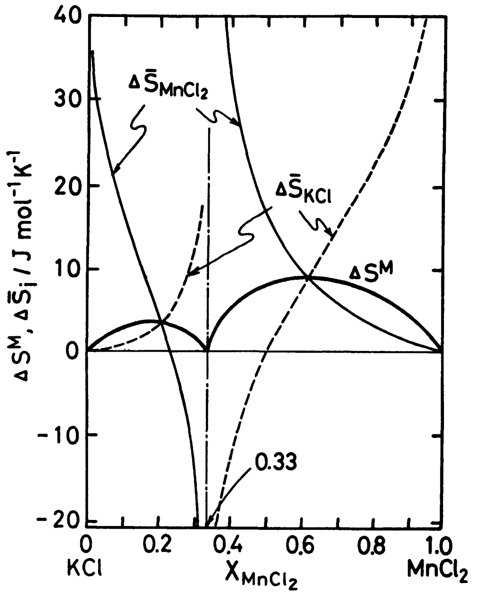

Fig. 8. Entropy of mixing in the KCl-$MnCl_2$ system calculated on the basis of Kucharski and Flengas' model.[12]

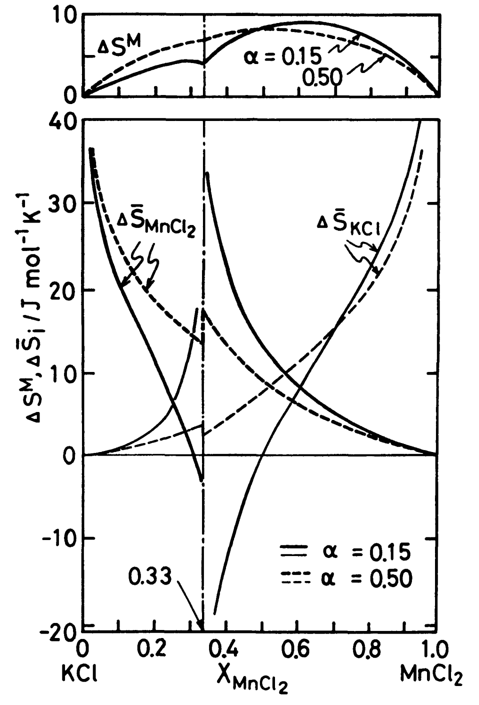

Fig. 9. Entropy of mixing in the KCl-$MnCl_2$ system calculated on the basis of the dissociation model.

that (2) the degree of dissociation of the complex species is independent of composition, and that (3) vibrational entropy can be neglected. A new model for the structure of a molten mixture containing polymer complex species is needed to provide an explanation for the entropy in the $MnCl_2$-rich side.

Conclusion

(1) Activities of components KCl and $MnCl_2$ in their molten mixtures show large negative deviations from Raoult's law. This suggests a very strong interaction between KCl and $MnCl_2$.

(2) The entropy of mixing has a minimum in the vicinity of $X_{MnCl_2}=1/3$ only, and the minimum has been explained in terms of the formation of complex species $[MnCl_4]^{2-}$.

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References

1) M. Itoh, T. Sasamoto, and T. Sata, *Bull. Chem. Soc. Jpn.*, **54**, 3319 (1981).

2) Y. Takagi, K. Tanemoto, and T. Nakamura, *Rep. Res. Lab. Eng. Matls.* (*Tokyo Inst. Tech.*), **1**, 103 (1976).

3) A. S. Kucharski and S. N. Flengas, *J. Electrochem. Soc.*, **121**, 1298 (1974).

4) K. Tanemoto, Y. Takagi, and T. Nakamura, *Jpn. J. Appl. Phys.*, **15**, 1637 (1976).

5) K. Tanemoto, T. Nakamura, and T. Sata, *Chem. Lett.*, **1973**, 911.

6) Y. Takagi, T. Nakamura, T. Sata, H. Ohno, and K. Furukawa, *J. Chem. Soc., Faraday Trans. 1*, **75**, 1161 (1979).

7) K. Tanemoto and T. Nakamura, *Chem. Lett.*, **1975**, 351.

8) B. R. Sundheim and M. Kukk, *Discuss. Faraday Soc.*, **32**, 49 (1961).

9) G. N. Papatheodorou and O. J. Kleppa, *J. Inorg. Nucl. Chem.*, **32**, 889 (1961).

10) O. J. Kleppa and F. G. McCarty, *J. Phys. Chem.*, **70**, 1249 (1966).

11) T. Φstvold, *Acta Chem. Scand.*, **26**, 2778 (1972).

12) A. S. Kucharski and S. N. Flengas, *J. Electrochem. Soc.*, **119**, 1170 (1972).

13) D. C. Hamby and A. B. Scott, *J. Electrochem. Soc.*, **117**, 319 (1970).

14) D. C. Hamby and A. B. Scott, *J. Electrochem. Soc.*, **115**, 704 (1968).

15) M. Itoh and T. Nakamura, to be published.

16) H. Ikeuchi and C. Krohn, *Acta Chem. Scand.*, **23**, 2230 (1969).

17) G. D. Robbins, T. Førland, and T. T. Φstvold, *Acta Chem. Scand.*, **22**, 3002 (1968).

18) A. D. Pelton and W. T. Thompson, *Can. J. Chem.*, **48**, 1585 (1970).

19) T. Φstvold and O. J. Kleppa, *Inorg. Chem.*, **8**, 78 (1969).

20) T. Sasamoto, H. Hara, and T. Sata, *Bull. Chem. Soc. Jpn.*, **54**, 3327 (1981).

21) J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, **29**, 653 (1958).

22) T. A. Milne and H. M. Klein, *J. Phys. Chem.*, **64**, 1628 (1960).

23) J. R. McCreary, S. A. Rassoul, R. J. Thorn, *High Temp. Sci.*, **1**, 412 (1969).

24) G. R. Belton and R. J. Fruehan, *Metall. Trans.*, **2**, 292 (1971).

25) J. Braunstein, *J. Chem. Phys.*, **49**, 3508 (1968).