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Densities of Molten Cobalt Chloride and Potassium Chloride Mixtures

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Density measurements of the molten $CoCl_2$–KCl mixtures of high $CoCl_2$ composition with an open vessel are very difficult or almost impossible because of their high volatility. The densities of $CoCl_2$ and KCl mixtures sealed in a quartz cell have been measured by a dilatometric method. The excess molar volume was positive around 30 mol % and around 70 mol % of $CoCl_2$. The results of the present investigation suggested that the title system contains the tetrahedral configuration, $CoCl_4^{2-}$, at the composition $X(CoCl_2) = 0.30$ and the other unknown species at $X(CoCl_2) = 0.70$.

Introduction

In the mixture of cobalt chloride and alkali chloride systems, the volatility of $CoCl_2$ was appreciable even at the melting points (*1*). Many workers studied the emf (*2*), enthalpy of mixing (*3*, *4*), and visible spectra (*5*, *6*) of molten cobalt chloride and the mixtures with alkali chlorides.

Dutt and Østvold (*7*) reported emf of molten alkali chlorides and cobalt chloride mixtures on the lower composition range of cobalt chloride ($X(CoCl_2)$, 0–0.6). They suggested that all systems except LiCl–$CoCl_2$ contain the divalent cobalt ion in the tetrahedral configuration, $CoCl_4^{2-}$, and that the tendency for "complex" formation increased with increasing size of the alkali metal ion. On the basis of visible spectral observation, Trutia and Musa (*8*) reported a change in the coordination symmetry about the Co^{2+} ion from octahedral in the solid state into tetrahedral in the liquid state for pure cobalt chloride.

In this paper we tried to measure on the whole composition range from $X = 0.0$ to $X = 1.0$ and a wide temperature range (from melting point up to 1000 °C). Similar studies on the density and refractive index in the molten $MnCl_2$–KCl system (*9*) and $ZnCl_2$–KCl system (*10*) with the same experimental technique were reported by us.

Experimental Section

Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was dehydrated under vacuum at 200 °C for a day. The dehydrated cobalt chloride and potassium chloride were mixed and melted at a temperature 50 °C higher than the melting point in a quartz refining cell, cleaned by bubbling dry HCl gas, and then sealed off after evacuation into a quartz ampule. The ampule was made up of a tank of volume 1.80–2.80 cm^3 and a neck of uniform bore, 4 mm in diameter. In this tube was made a horizontal mark on the upper part, and the volume below the mark and cross section of the tube were previously calibrated with distilled water.

The sample tube was then mounted on the electrical furnace which has a window (20 mm × 35 mm) of optically flat silica glass. The temperature measured by a Pt–Pt13%Rh thermocouple touching sample cell. Temperature measurement calibration was previously done by using another Pt–Pt13%Rh thermocouple inserted into the empty sample cell. This reference thermocouple was already calibrated with the melting points of ice, Sn, Pb, and Cu as references.

Figure 1 shows the density measurement apparatus. The subheater was necessary to avoid the condensation of sample vapor on the inner wall of the upper part of the sample cell. The lamp was useful at lower temperature to light the meniscus of the sample melt. The distance between the meniscus and the mark of the sample cell was measured with the cathetometer. At high temperature, sometimes the meniscus level disappeared from the window area, and then the jack was used to control the meniscus level back into the observation window.

The experimental error in this density measurement method came from four points mainly. First, the reproducibility of a particular composition and temperature was measured. This maximum error was calculated as 0.0065 g/cm^3. Second, the meniscus shape changes from the reference liquid. This error was obviously significant at high temperature and at high KCl content. For example, at 1000 °C, the meniscus of pure KCl melt was almost completely flat. In this case the error was calculated as 0.0064 g/cm^3. Third, the error in temperature measurement produces the error in calculated density. The maximum temperature irregularity in this furnace was about ±5 °C at the lower temperature (about 500 °C), and this leads to a density error of about ±0.002 g/cm^3. Fourth, the meniscus and the level measurement inevitably cause some error. The cathetometer used in this measurement has an accuracy of ±0.01 cm. Even if the level-measuring error was half of the accuracy (±0.005 cm), the error of the obtained density was ±0.0044 g/cm^3 in this case.

The first and the fourth points were not related to the temperature or the composition of the samples, but the second was significant at high temperature and at high KCl content, while the third was observable at lower temperature and at lower KCl content. Then, the experimental error in density measurement

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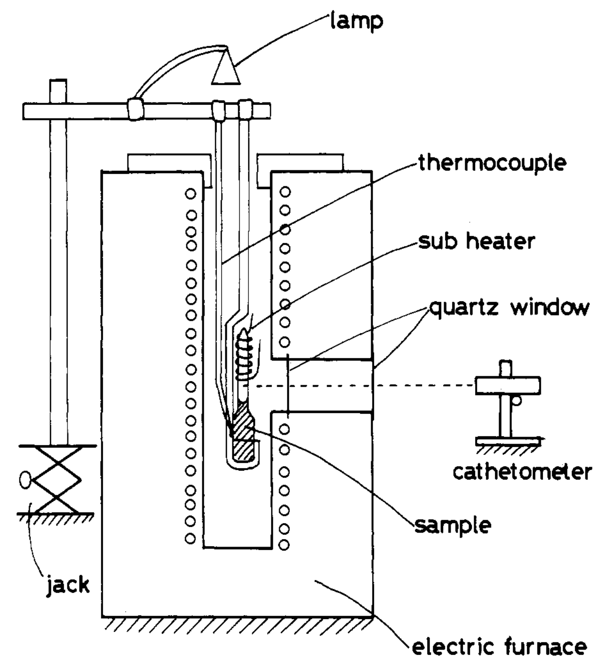

Figure 1. Density measurement apparatus.

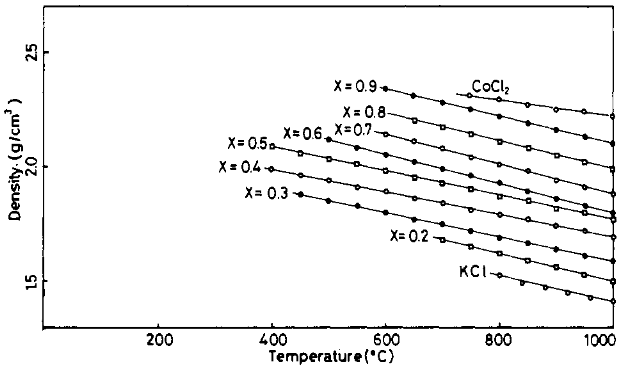

Figure 2. Density vs. temperature for molten $CoCl_2$–KCl system.

Table I. Experimental Results of Densities of Molten $CoCl_2$–KCl System

$X(CoCl_2)$	d/g·cm^{-3}	temp range/°C	sd^a/%
0.00	$1.914 - (5.030 \times 10^{-4})T$	770–1000	0.265
0.20	$2.094 - (5.865 \times 10^{-4})T$	680–1000	0.432
0.30	$2.121 - (5.291 \times 10^{-4})T$	430–1000	0.899
0.40	$2.187 - (4.900 \times 10^{-4})T$	400–1000	1.044
0.50	$2.302 - (5.275 \times 10^{-4})T$	380–1000	0.782
0.60	$2.438 - (6.345 \times 10^{-4})T$	500–1000	0.402
0.70	$2.552 - (6.710 \times 10^{-4})T$	580–1000	0.584
0.80	$2.584 - (5.883 \times 10^{-4})T$	650–1000	0.784
0.90	$2.699 - (5.959 \times 10^{-4})T$	650–1000	0.622
1.00	$2.576 - (3.526 \times 10^{-4})T$	730–1000	0.272

^{a} Standard deviation.

is estimated to be ±0.006 g/cm^3 (about 0.4%).

Results and Discussions

Densities of melts at various temperatures for 10 different compositions (X = 0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0) are shown in Figure 2 and are listed in Table I. Density for each specimen decreases linearly with rising temperature. The molar volume V_M (cm^3/mol) in molten mixture is given by the expression

$$V_M = [XM_1 + (1 - X)M_2]/d \qquad (1)$$

Densities vs. composition and molar volume vs. composition of the molten mixtures for various temperatures, 400, 500, 600, 700, 800, 900, and 1000 °C, are shown in Figures 3 and 4, respectively.

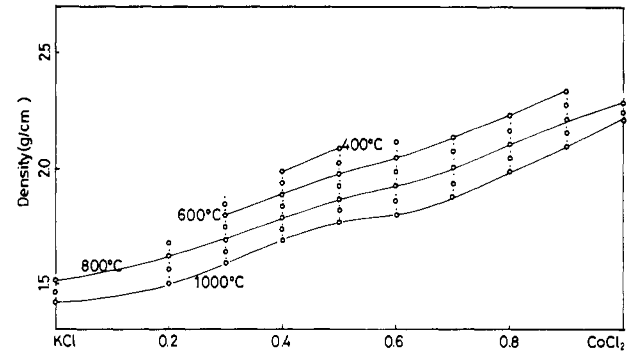

Figure 3. Density vs. composition for molten $CoCl_2$–KCl system.

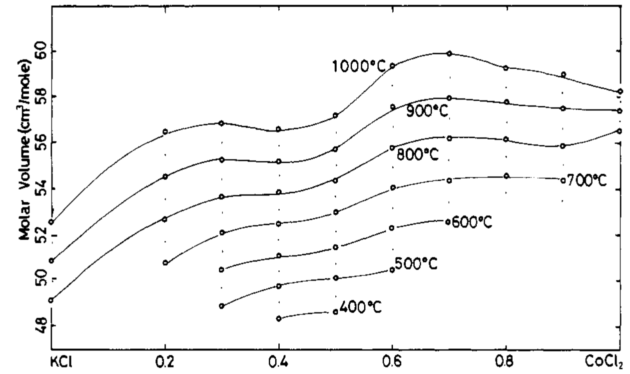

Figure 4. Molar volume vs. composition for molten $CoCl_2$–KCl system.

Crystalline cobalt dichloride is known to have a $CdCl_2$-type structure (*11*), which consists of a close-packed layer of Cl atoms in fcc arrangement with Co atoms in the octahedral sites of every other layer. It is reasonable that the octahedral symmetry about Co^{2+} in the solid state changes to tetrahedral symmetry in the molten state, as reported by visible spectra (*8*), on the analogy of the case of $MnCl_2$, which is known to have $CdCl_2$-type structure in the crystalline state and is believed to form an edge-shared tetrahedral structure in the molten state as reported by us (*12*, *13*).

Because of a valence number of two and a smaller ionic size compared to K^+, Co^{2+} cation has a stronger tendency to make a tetrahedral complex anion $CoCl_4{}^{2-}$ in the molten $CoCl_2$–KCl system. The positive deviation at X = 0.30 in molar volume in Figure 4 is related to isolated $[CoCl_4]^{2-}$ complex anions formation. On the basis of the temperature dependence of the Raman spectra of the molten $2ZnCl_2$·KCl composition reported by Itoh et al. (*14*), the positive deviation at X = 0.70 in molar volume in Figure 4 suggests a structural change at the composition $2CoCl_2$·KCl from the $CoCl_2$-based molten salt (presumably $[CoCl_4]$tetrahedra with all corner Cl atoms shared) into the $CoCl_2$·KCl-based molten salt (presumably $[CoCl_4]$ tetrahedra with half of the corner Cl atoms shared).

Glossary

d	density, g/cm^3
M_1	formula weight of $CoCl_2$
M_2	formula weight of KCl
V_M	molar volume, cm^3/mol
X	mole fraction of $CoCl_2$
T	temperature, °C

Registry No. $CoCl_2$, 7646-79-9; KCl, 7447-40-7.

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Osmotic and Activity Coefficients of Aqueous K_2SO_4–$MgSO_4$ and KCl–$MgCl_2$ at 25 °C

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The osmotic coefficients of the two aqueous mixtures K_2SO_4–$MgSO_4$ and KCl–$MgCl_2$ were determined by isopiestic measurements at 25 °C. The measurements have been carried out over an ionic strength range of 1.1–12.4 mol·kg^{-1} (K_2SO_4–$MgSO_4$) and 1.1–12.8 mol·kg^{-1} (KCl–$MgCl_2$). The experimental data were treated by three different methods (Pitzer, Scatchard, Schönert). With both Pitzer's equations and Scatchard's neutral electrolyte equations the agreement between calculated and experimental osmotic coefficients is very good over the entire ionic strength range up to saturation. To examine the mean molal activity coefficients calculated by the different model equations, the solubility curves have been calculated and compared.

Introduction

The osmotic and activity coefficients of aqueous KCl–$MgSO_4$ mixtures within the ionic strength range of 0.8–11.7 mol·kg^{-1} have recently been reported (*1*). Although it was necessary to extrapolate the data of the binary KCl solutions to concentrations far away from the saturation limit, both Pitzer's treatment and Scatchard's neutral electrolyte equations well represented the experimental data over the entire concentration range. Because of the necessity to apply reliable activity coefficients for modeling the thermodynamic properties of more complex multicomponent systems, especially natural saline brines, we extended our measurements and calculations to two further ternary systems of practical interest.

In this report isopiestic data are presented for H_2O–K_2SO_4–$MgSO_4$ and H_2O–KCl–$MgCl_2$ from moderately low concentrations to nearly saturated solutions at 25 °C. Besides the well-known Scatchard and Pitzer formalisms, we tested also a method described by Schönert (*2*) to calculate the mean activity coefficients without consideration of the corresponding binary data. Furthermore, using Scatchard's parameters we calculated the excess Gibbs energies of mixing $\Delta_M G^E$ (referred to 1 kg solvent) characterizing the interactions of the two electrolytes in the ternary solutions at several constant total ionic strengths.

A detailed study of the activity coefficients in K_2SO_4–$MgSO_4$ mixtures was made by Ninkovic and Radovanovic (*3*) using the isopiestic technique, but only up to an ionic strength of 5.5 mol·kg^{-1}.

Examination of the available osmotic coefficients and activity data for aqueous KCl–$MgCl_2$ (*4–7*) measured with solutions of total ionic strengths less than 6 mol·kg^{-1} indicated remarkable discrepancies. Three of these data sets are in reasonably good agreement (*4*, *6*, *7*), while the fourth study (*5*) gives deviating osmotic coefficients. From this arose our intention for reinvestigation to get accurate data within an extended ionic strength range.

Experimental Section

The isopiestic apparatus is the same as previously described (*1*) with KCl, $MgCl_2$, and $MgSO_4$ as the reference electrolytes. For KCl reference solutions, the osmotic coefficients at isopiestic equilibrium were taken from Hamer and Wu (*8*) and corrected by the procedure of Rard et al. (*9*). The osmotic coefficients for $MgCl_2$ and $MgSO_4$ reference solutions have been calculated by means of equations given by Rard and Miller (*10*, *11*) considering newest experimental data.

The preparation and analyses of the KCl and $MgSO_4$ solutions have been described elsewhere (*1*). Doubly recrystallized analytical grade $MgCl_2·6H_2O$ was used for the preparation of a $MgCl_2$ stock solution. Concentration of this $MgCl_2$ stock was determined by mass titration with $AgNO_3$ yielding 5.4860 ± 0.0015 mol·kg^{-1}. The cited uncertainty is the average deviation of 10 independent titrations. Recrystallized analytical grade K_2SO_4 was dried in an oven at 200 °C before preparation of solutions by weight. All weights were converted to mass.

Samples of K_2SO_4 and $MgCl_2$ solutions were analyzed for impurities by using atomic absorption spectrometry (Mg, Ca) and flame photometry (Na, K, Ba). The impurities found in $MgCl_2$ were less than 5 ppm by weight for all four elements. K_2SO_4 had ca. 56 ppm Mg, 10 ppm Na, 6 ppm Ca, and less than 5 ppm Ba.

Duplicate samples of constant ionic strength fraction have been prepared by dilution or evaporation of weighted amounts of stock solutions. All water used in this study was first deionized and then distilled. A few measurements were made on pure aqueous $MgCl_2$ and $MgSO_4$ using KCl reference solutions to confirm our technique.

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