Densities of Eutectic Mixtures of Molten Alkali Chlorides below 673 K

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Densities of eutectic mixtures of LiCl + KCl, LiCl + CsCl and LiCl + KCl + CsCl melts have been measured by the Archimedean method using an electronic balance. Densities of LiCl + CsCl and LiCl + KCl + CsCl melts have been measured at temperature below 673 K.

Introduction

Molten alkali chlorides and their mixtures have been widely used as solvents for electrochemical studies,[1] because they have relatively low liquidus temperatures. In many cases, they dissolve various chemical species at sufficiently high concentrations, and they have a wide electrochemical window; that is, the accessible potential range is available between alkali metal deposition (cathodic limit) and chlorine gas evolution (anodic limit). Recently, these advantages have led to new electrochemical studies using molten alkali chloride as electrolyte solutions,[2] including alloy-forming reactions,[3] SiH_4 gas-producing reactions,[4] and thermally regenerative fuel cells.[5]

The physical properties of many molten alkali chlorides were measured by several researchers and have been reviewed by Janz et al.[6] Among them, the LiCl + KCl melt is well-known, and its physical properties have been extensively measured. The melting point is 625 K, and the standard operating temperature is 723 K.

In applications for fuel cells, a lower operating temperature is advantageous for the electrolyte because the electromotive force becomes larger. There are several eutectic alkali chloride mixtures with melting points lower than that of the LiCl + KCl eutectic melt;[7] for instance, LiCl + CsCl (mp = 596 K), LiCl + RbCl (mp = 593 K), LiCl + NaCl + CsCl (mp = 593 K), LiCl + NaCl + RbCl (mp = 591 K), and LiCl + KCl + CsCl (mp = 538 K).[8] However, the density data for these melts below 673 K are seldom found in the literature.

In this work, we have measured the densities of LiCl + CsCl and LiCl + KCl + CsCl below 673 K, as well as the LiCl + KCl eutectic melt, using the Archimedean method.

Experimental Section

Chemicals. Analytical-grade (AR) anhydrous reagents (LiCl, KCl, and CsCl; Wako Pure Chemical Co.), with purities higher than 99.0 mass %, were used for the density measurements. Prior to mixing, each reagent was dried in a vacuum oven at 433 K for more than 2 days. Mixtures were prepared by weighing appropriate amounts of reagents at room temperature. The uncertainty in the compositions is estimated to be ±0.1%.

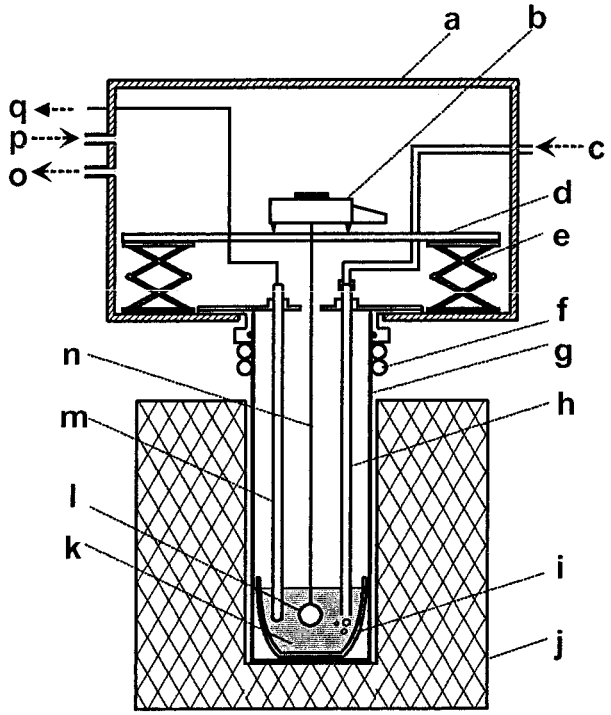

Figure 1. Schematic diagram of apparatus: (a) vacuum tight glovebox, (b) electrical balance, (c) gas inlet for bubbling, (d) acryl sheet, (e) jack, (f) cooling water jacket, (g) Pyrex container, (h) alumina gas bubbler, (i) alumina crucible, (j) electric furnace, (k) molten salt, (l) nickel sinker, (m) thermocouple, (n) nickel wire, (o) argon outlet, (p) argon inlet, (q) temperature signal to a recorder.

Apparatus and Measurements. The densities of the eutectic mixtures were measured by the Archimedean method,[9,10] that is, by the measurement of the buoyancy of a sinker in a sample melt. A schematic diagram of the experimental apparatus is shown in Figure 1. A pure alumina crucible (99.5%, Al_2O_3; Nikkato Co.) was placed in a closed-end Pyrex tube that was hermetically connected

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to a vacuum-tight glovebox and heated by an electric tubular furnace. The temperature of the melt was measured by a thermocouple (type K) sheathed in an alumina tube together with an alumina gas bubbler tube. The uncertainty in temperature was less than 1 K.

The sample mixture was put into the alumina crucible and evacuated in the Pyrex container for 2 days at 453 K. Then, the mixture was melted under an argon atmosphere. Argon gas was bubbled through the melt for more than 10 h to remove impurities such as heavy metals and carbon. The argon gas used in the glovebox had a purity higher than 99.999%.

An electronic balance (Mettler-Toledo, AG104, readability = 0.1 mg) was placed on an acryl plate whose level could be adjusted by a pair of precision screw jacks. After bubbling of the argon, a nickel sinker welded to a nickel wire (0.1 mm diameter) was hung from the balance. The diameter of the wire was small enough to neglect the effect of surface tension. The mass of the sinker was measured under an inert atmosphere in the glovebox at a constant pressure of 1 atm. When the temperature of the melt was being changed, the sinker was raised out of the melt. The condition of the melt and the sinker inside the Pyrex container could be observed temporarily during experiments by lowering the furnace.

Mass measurements were taken at each temperature when the melt was in thermal equilibrium. Nickel was chosen as the sinker material because of its many advantages in heat resistance, corrosion resistance, and machinability. After the experiments, the sinker was cleaned by water, and the difference in its mass before and after the experiments was found to be within ±0.003%.

An accurate volume of the sinker was obtained by measuring the buoyancy in pure water at 293.15 K. The accuracy of the temperature measurement was within ±0.3 K in this temperature range. Corrections for the thermal expansion of nickel were applied at each measuring temperature. The temperature distribution in the melt was uniform when the system reached thermal equilibrium.

Results and Discussion

Before the density measurements of the molten salts, the volume of the sinker was verified using methanol and ethanol[11] at 293.15 K. The volumes of the sinker measured using pure water and these alcohols agreed with each other, to within ±0.04%. The density data of molten salts obtained in this work are listed in Table 1 and plotted in Figure 2.

The LiCl + KCl eutectic melt is known as a standard molten alkali chloride salt, and its thermophysical properties can be found in the literature.[12−15] The most extensive measurements of the density of LiCl + KCl was carried out by Artsdalen and Yaffe,[12] and they measured the eutectic mixture of LiCl + KCl (58.8 + 41.2 mol %) in the temperature range from 668 to 866 K.

Density measurements were made at the same composition of the melt to confirm the accuracy of our measurement system at higher temperature. The experimental data for the density (ρ in g cm^{-3}) were correlated as a function of temperature using the expression

$$\rho/(\text{g cm}^{-3}) = 1.9998 - 4.6677 \times 10^{-4}(T/\text{K}) \qquad (1)$$

with a standard deviation of ±0.03%. For the LiCl + KCl eutectic melt purified by the same procedure as electrolyte solutions for electrochemical measurements using the same apparatus,[16] the residual current was less than 0.5 mA cm^{-2} at the cathodic potential sweep (0.1 V s^{-1}) using nickel electrodes in an argon atmosphere. The unexpected wave was not detected in the voltammogram, which suggests that our purification procedure was satisfactory. These results are higher than those of Artsdalen and Yaffe[12] by about 1.0% (Figure 2), and the difference between them is beyond the combined uncertainties. Artsdalen and Yaffe [12] paid attention to the purification and handling of the melt; they did not carry out the argon gas bubbling through the melt before making measurements. In addition, the cell assembly was probably open to the air during weighing. In consideration of these experimental procedures, our data are considered to be more accurate than previous data.

59.3 mol % LiCl + 40.7 mol % CsCl. The densities of the LiCl + CsCl melt have been obtained by Smirnov et al.[17] and Zuca and Borcan[13] in the relatively higher temperature range between 873 and 1073 K. However, there are no data for the eutectic mixture below 673 K. We measured the density of the LiCl + CsCl eutectic melt between 613 and 753 K. The experimental data can be represented by the equation

$$\rho/(\text{g cm}^{-3}) = 2.9532 - 7.2205 \times 10^{-4}(T/\text{K}) \qquad (2)$$

with a standard deviation of ±0.09%.

Smirnov et al.[17] measured densities for the melt containing 1.73, 17.33, 30, 45, 53, 60, 75, and 90 mol % CsCl and

Table 1. Densities, ρ, for Eutectic Mixtures of LiCl + KCl, LiCl + CsCl, and LiCl + KCl + CsCl

T (K)	ρ (g cm^{-3})	T (K)	ρ (g cm^{-3})	T (K)	ρ (g cm^{-3})
xLiCl + (1 − x)KCl; x = 0.588					
653.85	1.6943	702.35	1.6716	754.25	1.6475
663.15	1.6905	713.25	1.6671	764.05	1.6428
674.65	1.6851	723.15	1.6621	772.75	1.6387
682.35	1.6810	734.35	1.6575	783.45	1.6342
694.25	1.6756	743.15	1.6532		
xLiCl + (1 − x)CsCl; x = 0.593					
613.55	2.5097	663.65	2.4758	712.95	2.4388
623.25	2.5029	673.45	2.4665	724.45	2.4298
633.45	2.4948	684.25	2.4605	734.15	2.4226
643.35	2.4881	693.05	2.4518	743.95	2.4159
653.55	2.4819	704.95	2.4450	753.65	2.4083
xLiCl + yKCl + (1 − x − y)CsCl; x = 0.575 y = 0.133					
573.35	2.3373	633.85	2.2985	683.85	2.2653
584.05	2.3299	644.25	2.2919	693.45	2.2583
593.45	2.3243	653.75	2.2849	703.65	2.2519
603.65	2.3176	664.15	2.2786	713.15	2.2449
613.95	2.3106	674.45	2.2710	723.65	2.2381
624.05	2.3050				

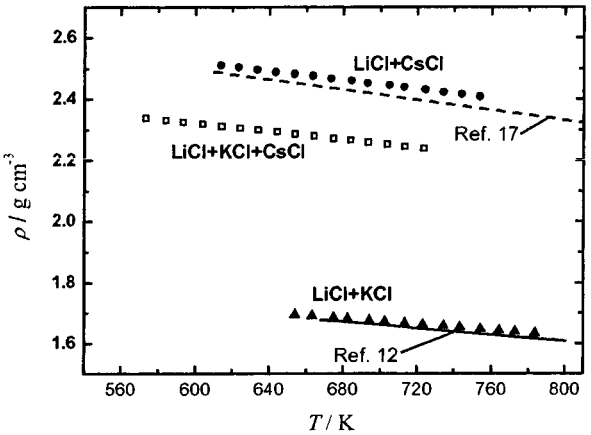

Figure 2. Plot of density of eutectic mixtures vs temperature. ●, LiCl + CsCl; □, LiCl + KCl + CsCl; ▲, LiCl + KCl; (−), Artsdalen and Yaffe[12] for LiCl + KCl; (- - -), extrapolated line from Smirnov et al.[17] for LiCl + CsCl.

obtained the temperature-dependence equations at each composition between 923 and 1023 K. The extrapolated results were obtained at the eutectic composition (40.7 mol % CsCl) between 613 and 753K. The extrapolated line was compared with the present result (Figure 2); the present data exceed the line by 1.4%.

57.5 mol % LiCl + 13.3 mol % KCl + 29.2 mol % CsCl. The melting point for this mixture has been reported as 538.15 K.[8] This mixture has the lowest melting point of the alkali chloride salt electrolytes as far as we know, and the densities of this mixture have not ever been measured. A linear temperature dependence of density was observed over the whole temperature range between 573 and 723 K with a standard deviation of ±0.06%.

$$\rho/(\mathrm{g\ cm^{-3}}) = 2.7154 - 6.5890 \times 10^{-4}(T/\mathrm{K}) \qquad (3)$$

Summary

We have determined the densities of eutectic mixtures of LiCl + CsCl and LiCl + KCl + CsCl below 673 K. It was confirmed that both melts behave similarly to conventional molten chlorides and that the densities change linearly with temperature at least above 613 K for LiCl + CsCl and above 573 K for LiCl + KCl + CsCl.

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