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Experimental investigations and thermodynamic modelling of KCl–LiCl–UCl_3 system

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ABSTRACT

Experimental investigations and Gibbs energy modelling of KCl–LiCl–UCl_3 system employing CALPHAD method are reported. Gibbs energy modelling of the subsystems KCl–UCl_3 and LiCl–UCl_3 was carried out primarily using phase diagram data from the literature. For the Gibbs energy modelling of the KCl–LiCl subsystem, new phase boundary data corresponding to four terminal compositions ($x_{LiCl} = 0.03$, 0.05, 0.95 and 0.97) obtained through differential thermal analysis data along with thermochemical and phase diagram data from the literature were used. Thermal analysis was also carried out for KCl–LiCl eutectic mixture containing small amounts of UCl_3 ($x_{UCl_3} = 9.03 \times 10^{-3}$ and 1.79×10^{-2}). The liquidus temperatures for these compositions were found to be 637 K and 674 K. Electromotive force data for dilute solutions of UCl_3 in the KCl–LiCl eutectic melt, measured in the temperature range 708–833 K in the present work, were found to be in good agreement with the literature data. These data were also used as input for the Gibbs energy modelling of the KCl–LiCl–UCl_3 system. In order to improve the quality of the resulting Gibbs energy functions of the quasibinaries and the quasiternary, enthalpies of mixing of the corresponding melts estimated using an empirical correlation based on surrounded-ion model were also used as input. Finally, the generated Gibbs energy functions were used to compute phase equilibria.

1. Introduction

Pyrochemical reprocessing based on molten salt electrorefining is considered to be a viable method for the recovery of actinides and minor actinides from spent fast reactor metallic fuels. The separation scheme developed as a part of Integral Fast Reactor project at Argonne National Laboratory involves initial equilibration of spent metallic fuels with $CdCl_2$ in molten KCl–LiCl eutectic at 773 K for loading of UCl_3 and $PuCl_3$ [1–3]. Subsequently, uranium is electrodeposited at the steel cathode and uranium, plutonium and minor actinides at the liquid cadmium cathode [4–6]. The KCl–LiCl eutectic during the course of electrorefining becomes a multicomponent molten salt system with the loading of host of fission products and actinides from the spent metallic fuel. Understanding the thermochemistry of system, therefore, becomes essential to fine tune the unit operation of electrorefining.

As a starting point for the development of a Gibbs energy database for salts relevant to pyrochemical reprocessing, the thermodynamic assessment of KCl–LiCl–UCl_3 system has been taken up. The present study relates to a revised thermodynamic description of KCl–LiCl binary system based on new phase diagram data close to terminal compositions. The LiCl–UCl_3 and KCl–UCl_3 systems were assessed based on the existing phase diagram data and enthalpy of mixing data estimated using the surrounded-ion model. Based on the limiting partial enthalpies of the three limiting quasibinary systems, the enthalpies of mixing of KCl–LiCl–UCl_3 were estimated using an extended version of surrounded-ion model. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) measurements were also carried out to measure the liquidus temperature for few ternary compositions of KCl–LiCl–UCl_3. The present study also involves electromotive force (emf) measurements on dilute solutions of UCl_3 in molten KCl–LiCl eutectic in the temperature range 708–833 K. Based on these new data, a thermodynamic evaluation of KCl–LiCl–UCl_3 system was performed.

2. Literature review

2.1. Thermochemical data

Thermochemical measurements employing emf method and transient electrochemical techniques on KCl–LiCl–UCl_3 system were undertaken by many researchers to obtain thermochemical properties of UCl_3 in molten KCl–LiCl eutectic. Inman et al. [7]

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studied the electrode reaction of $U^{3+}|U$ at 736 K at various current densities to study the thermodynamics for various amounts of UCl_3 in KCl–LiCl eutectic. Subsequently, they also commented on the mechanism of formation of dendritic and powdery deposits during cathodic deposition of uranium. A similar study was reported for the system by Inman et al. [8,9] by emf method using an Ag|AgCl reference electrode with $x_{AgCl} = 2.2 \times 10^{-3}$. For dilute solutions of UCl_3 in the range of $x_{UCl_3} = 1.7 \times 10^{-3}$–$5.6 \times 10^{-3}$, they reported the activity coefficient to be $\sim 10^{-2}$. Gruen and Osteryoung [10] carried out emf measurements in the temperature range 725–807 K by varying the composition of UCl_3 by anodic polarization of uranium wire and also varying x_{AgCl} from 1.16×10^{-2} to 2.07×10^{-2} in the reference electrode. Caligara et al. [11] measured the potential of $U|U^{3+}$ couple against Ag|AgCl with $x_{AgCl} = 2.058 \times 10^{-3}$ at various compositions of UCl_3 in the temperature range 673–823 K. Knacke et al. [12] carried out emf measurements against Ag|AgCl reference with $x_{AgCl} = 0.0378$ for the temperature range 723–925 K.

Roy et al. [13] and Fusselman et al. [14], as a part of TRUMP-S pyropartitioning separation process, carried out emf measurements on UCl_3, $PuCl_3$, $NpCl_3$ and $AmCl_2$ in molten KCl–LiCl eutectic using an Ag|AgCl reference electrode with $x_{AgCl} = 4.87 \times 10^{-3}$ in order to evaluate the standard electrode potentials (E°) and Gibbs energy of formation ($\Delta_f G^\circ$) of these chlorides at various temperatures. They reported γ_{UCl_3} to be $(2.77 \pm 0.67) \times 10^{-3}$ in the temperature range of 673–723 K. Partridge [15] compared the results of Inman et al. [9], Gruen et al. [10] and Yang et al. [16] and concluded that UCl_3 exhibited positive deviation from Raoult's law in the KCl–LiCl eutectic. Yang et al. [16] reported γ_{UCl_3} to be 0.84 for $x_{UCl_3} = 5 \times 10^{-3}$ at 770 K, which is in disagreement with other measurements.

The measurement of E° using cyclic voltammetry for UCl_3 in KCl–LiCl eutectic has also been reported by several workers. Shirai et al. [17] carried out cyclic voltammetry of UCl_3 in KCl–LiCl eutectic at various inert and active electrodes like Cd and Bi, to obtain $\Delta_f G^\circ$ of UCl_3, UCd_{11} and UBi_2. The apparent E° for $U^{3+}|U$ couple was deduced from transient electrochemical methods by Masset et al. [18,19] to obtain $\Delta_f G^\circ$ of UCl_3 at infinite dilution in KCl–LiCl eutectic. They also reported γ_{UCl_3} to be in the range of 0.29×10^{-3} to 4.47×10^{-3} in the temperature range between 673 and 823 K. Similar transient measurements were carried out as a part of PYROREP project [20], where the electrochemistry of uranium and several rare-earths in KCl–LiCl eutectic was studied by transient techniques. The activity coefficient of the ions, partial molar enthalpies and apparent standard electrode potentials were also reported. Kuznetsov et al. [21] also reported E° for $U|U^{3+}$ couple in KCl–LiCl eutectic using various electrochemical methods like cyclic voltammetry. The partial Gibbs energies of mixing for UCl_3 and UCl_4 in KCl–LiCl eutectic were also reported by them.

As seen from the above literature survey, the emf measurements on UCl_3 in KCl–LiCl eutectic have been carried out under a variety of experimental conditions. We therefore investigated the inherent consistency of the emf measurements carried out by several workers by having our own set of emf data and subsequently used them as input for the optimization of Gibbs energy functions of the KCl–LiCl–UCl_3 system.

2.2. Phase diagram data

The LiCl–UCl_3 phase diagram is a simple eutectic system as reported by Thoma [22] and Desyatnik et al. [23]. There are no intermediate compounds reported for this system. The KCl–UCl_3 phase diagram is characterized by two eutectic points and an intermediate congruently melting stoichiometric phase, K_2UCl_5 (orthorhombic, Space Group: *Pnma*), reported by Thoma [24] and Posypaiko et al. [25]. Suglobova et al. [26] reported the existence of K_3UCl_6 but this was not substantiated by Thoma et al. The stoichiometric phase K_2UCl_5 was also well established by X-ray diffraction and neutron diffraction studies [27,28]. Since we have not come across any other information concerning K_3UCl_6 phase, it was not considered in the Gibbs energy modelling of KCl–UCl_3 system. Recently, Barnes et al. [29] and Sutherland et al. [30] have investigated KCl–UCl_3 phase diagram. However, their limited experimental data has not been considered in the present work because of uncertainties involved.

Thamer [31] carried out DTA of various ternary mixtures of UCl_3 with KCl–LiCl, $MgCl_2$–KCl and NaCl–KCl for their applicability as a molten blanket based on molten salt reactor fuel. Thermal analysis of KCl–LiCl–UCl_3 was carried out at higher mole fractions of UCl_3 up to 44 mol% and a eutectic with LiCl, UCl_3 and K_2UCl_5 as solidifying phases at 691 ± 2 K and a few isothermal contours were also reported. Recently, Nakayoshi et al. [32] have carried out X-ray diffraction and differential thermal analysis for various compositions of KCl–LiCl–UCl_3 and established the partial phase diagram along $(KCl–LiCl)_{eut.}$–UCl_3 section up to 25 mol% UCl_3.

3. Experimental details

3.1. Chemicals

All the chemicals used in the emf studies were of analytical grade. Anhydrous lithium chloride and potassium chloride were obtained from Sigma-Aldrich and Alfa-Aesar, respectively. Reactor grade uranium metal rod was obtained from Bhabha Atomic Research Centre (BARC), Mumbai, India. LiCl and KCl which are hygroscopic in nature were handled in an inert atmosphere glove box with oxygen and moisture levels below 20 ppm.

3.2. Emf measurements

A two electrode assembly was used for the emf measurements in molten KCl–LiCl eutectic. Schematic of the electrochemical assembly is shown in Fig. 1. The uranium electrode of 5 mm diameter and 20–30 mm length was prepared by initially cleaning it with dilute nitric acid and subsequently rinsing with distilled water followed by methanol or acetone until its surface had a shining lustre. The uranium electrode was tied to a 6 mm × 40 mm tantalum sheet using a 0.5 mm diameter tantalum wire for the integrity of the electrode during the measurements. The tantalum sheet was in turn connected to a 1.5 mm diameter tantalum wire for electrical contact. The 1.5 mm tantalum wire was insulated from the electrochemical cell flange by inserting it through a 4-bore 3/8 inch alumina tube which was attached to the cell through a veeco coupling. The tantalum components used in the experiments were of 99.9% purity.

The reference electrode was prepared by dissolving anhydrous AgCl in KCl–LiCl eutectic by passing chlorine gas at 773 K for 6 h. The salt was subsequently cooled and powdered inside an inert atmosphere glove box. The powder was loaded inside a one end closed 6.0 mm diameter quartz tube with a bulb at the bottom. A high purity Ag wire (1.5 mm diameter) was dipped into the powder for electrical connections. The open end of the reference electrode was sealed by a teflon plug. The composition of Ag in the salt was estimated by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). All potentials in this paper reported here are given with respect to this reference electrode.

The eutectic mixture of KCl–LiCl was vacuum dried at 420 K for 120–150 h. It was further purified by bubbling chlorine gas through it at 773 K for 30 min. The salt was cooled and stored in the glove box for future use. The ternary salt mixture of KCl–LiCl–UCl_3 was prepared by adding excess uranium in the KCl–LiCl