ABSTRACT

Lanthanide and actinide halides and their mixtures with alkali metal halides are important for electrolytic production of rare-earth metals but also in the processing of nuclear wastes and recycling of spent nuclear fuel. However, reference data are still missing both for the pure salts and the mixtures. Several thermodynamic, physicochemical and structural properties investigations have been or are being conducted with a variety of experimental methods. Other more theoretical approaches include molecular dynamics calculations and new modeling aspects.

The present work deals with the EuCl₂ and EuCl₂-NaCl melts. Temperatures and enthalpies of phase transitions, heat capacity and density were determined for EuCl₂ while enthalpy of mixing and phase diagram investigations were conducted for the EuCl₂-NaCl mixtures. These data were tested for thermodynamic consistency by assessing the phase diagram. The agreement obtained between experimental and calculated phase diagrams is discussed in terms of the relevance of the models used in the numerical procedure.
INTRODUCTION

Rare earth halide melts and their mixtures with alkali halides are important for industrial electrolytic processes where they have been used for either the production of the corresponding rare earth metals (1) or as additives to improve the electrolytic production of light metals (2). They also play a major role in the processing of nuclear wastes and recycling of spent nuclear fuel (3, 4). The structural and thermodynamic properties of several rare earth chloride-alkali chloride melts have been studied rather extensively as more recently, bromide (5-6) and iodide (7) melts. These investigations were conducted by Raman spectrometry (8-9), calorimetry (10-11) and neutron diffraction (12-13).

Although lanthanide elements are usually trivalent, divalent stable compounds are formed with Sm, Eu et Yb. The corresponding chlorides were shown to vaporize without decomposition, and EuCl$_2$ to have the greatest stability (e.g. the lowest vapor pressure). Very few investigations were carried out on melts including divalent lanthanides. On the other hand, no reference data exist so far on the divalent dichlorides. For instance, the melting points reported in literature for EuCl$_2$ range from 1004 to 1127 K while most physicochemical properties are still undetermined.

In order to identify the thermodynamic, physicochemical and structural properties, several investigations have been or are being conducted with a variety of experimental methods (high temperature direct calorimetry, DSC, neutron diffraction (14) X-rays and Raman spectroscopy (15)) but also with more theoretical approaches including molecular dynamics calculations and new modeling aspects. The present work will focus on very recent results concerning the macroscopic aspects.

EXPERIMENTAL

Chemicals

EuCl$_2$ was synthesized from Eu$_2$O$_3$. Thionyl chloride was used as a chlorinating agent to obtain EuCl$_3$ at 773-823 K which was then reduced to EuCl$_2$ with Zn. Purification was processed by sublimation. Chemical analysis indicated EuCl$_{1.998}$ for the europium dichloride composition. For molar volume determinations, EuCl$_2$ was provided by Anderson Physics Laboratory Engineering Materials, Inc. (Urbana, USA) : the value of x in EuCl$_x$ was 1.99.
The sodium chloride was a Merck Suprapur reagent (Minimum 99.9%). It was purified and treated by progressive heating up to fusion under a gaseous HCl atmosphere. Excess HCl was removed from the melt by argon.

All handling and preparations of experimental samples were carried out in a controlled purified argon atmosphere glove box.

**Differential Scanning Calorimetry**

A Differential Scanning Calorimeter (DSC) was used for the determination of temperatures and enthalpies of phase transition. The experimental procedure were described elsewhere (16). The samples were contained into sealed quartz ampoules, 5mm diameter and 15 mm high. The side walls and bottom were grounded in order to make these cells fit snugly into the heat flux detector. This consists of two thermopiles, connected in electrical opposition, accommodating the previous experimental cell with the sample and another empty and identical cell which acts as a reference. This experimental DSC set up is caracterized both by a high sensitivity and an excellent integration of the thermal flux since the sensing thermocouples in each thermopile are evenly distributed on all the cell surface.

The same apparatus was also employed for the determination of heat capacity by the “step method” (16).

Because of the inconsistency observed on EuCl₂ melting, the phase diagram investigation was also repeated.

The determination of the fusion temperature and enthalpy of EuCl₂ was performed separately with a high temperature Calvet microcalorimeter because of the temperature limit of the DSC.

**Enthalpy of mixing**

The mixing enthalpy of NaCl-EuCl₂ system was measured at 1132 K with a Calvet microcalorimeter, using a direct liquid-liquid “break-off” method. Experimental runs were performed under argon at atmospheric pressure. The more volatile component (i.e. EuCl₂) was weighted with precision of 10⁻⁵ g and placed in the break-off ampoule. NaCl also weighted with the same precision was placed in a quartz crucible. The quartz ampoule was welded to a quartz tube which could be moved up and down along the calorimetric cell through a gas-tight ring. Argon entered the calorimetric cell by the same quartz tube. The ampoule was broken after thermal equilibrium had been achieved and the thermal effect resulting from mixing was recorded. Calibration of the calorimeter was performed with NIST α-alumina by dropping it to the calorimetric cell with the melt and registering the thermal effect of its heating from ambient temperature to that of the experiment.
Molar volume

The experimental method used to measure the molar volume of EuCl₂ consisted in determining the density with a high temperature picnometer.

RESULTS AND DISCUSSION

The thermograms obtained at the heating rate 5 K/min show in a reproducible way that a thermal effect, assessed to a solid-solid phase transition occurs at 1014 K. Another peak, observed at 1114 K in DTA curves obtained with a Calvet microcalorimeter, correspond to fusion. All temperatures were taken from heating runs since undercooling was observed upon cooling.

The enthalpies related to phase transition and melting were determined as 11.5 kJ/mol and 10.7 kJ/mol, respectively. They are close to the values obtained in (15) also with the same DSC technique (10.6 and 11.1 kJ/mol, respectively). The enthalpies determined by Kulagin and Laptev (17), 20.5 and 23.0 kJ/mol respectively, differ significantly from these values, probably because of the poor precision of the thermographic method used.

For some authors (18-21) the temperature of fusion reported correspond in fact to the transition temperature. Also in a recent work (15) though an enthalpic effect was observed at T = 1124 K in pure EuCl₂, it was not assessed to melting but suggested to be due to a structural change in the liquid. Melting was thus assumed to take place at T = 1017 K, i.e. at the temperature of the actual solid-solid phase transition. This confusion can be understood however since structural observations obtained both by Raman spectroscopy (15) and neutron diffraction (14) suggested a liquid-like behavior of EuCl₂ above this temperature.

Equilibrium phase diagram.

The NaCl-EuCl₂ phase diagram is of the simple eutectic type. Twenty-three mixtures of different compositions were investigated by DSC. Heating and cooling runs, performed at 5 K/min, showed undercooling on crystallisation. Equilibrium temperatures were thus taken from heating thermograms. The related enthalpies were used to determine the eutectic composition. The corresponding Taman construction (figure 1) yielded x (EuCl₂) = 0.49 while the eutectic temperature, observed in all thermograms, is T = 847 K. The thermograms relative to the EuCl₂-richest mixtures are somewhat different from those generally observed in a solid-liquid phase transition and correspond to a low kinetics. Thus both equilibrium temperatures and enthalpies were obtained with a larger experimental error. This unusual behavior upon melting may be related to the noticeable viscosity of those melts, as visually observed from separate experiments. Therefore the thermal method
employed here shows a limitation in this composition range where thermal effects are weak, and thus temperatures at which they appear, are obtained with a limited accuracy. These investigations should be complemented by other techniques and electrical conductivity measurements are planned in this respect.

The phase diagram obtained is given in figure 2. Some differences and contradictions can be noted with previous investigations. Fink and Seifert (22) also found a simple eutectic phase diagram: they only reported the eutectic at the composition \( x(\text{EuCl}_2) = 0.50 \), in good agreement with our result, while the corresponding temperature \( 747 \text{ K} \) is significantly lower than ours. The eutectic composition determined recently (15) differs significantly from these values \( (x(\text{EuCl}_2) = 0.62) \), while the corresponding temperature \( 848 \text{ K} \) agrees quite well with ours. However disagreement can also be noted in the \( \text{EuCl}_2 \) rich region reported in the same work (15): As explained above, fusion was confused with the actual phase transition and, as a consequence, the \( \text{NaCl}-\text{EuCl}_2 \) phase diagram is uncompleted in the temperature range above transition.

**Heat capacity**

Heat capacity \( C_p \) was measured by Differential Scanning Calorimetry from 306 to 1085 K by the "step method". The only \( C_p \) measurements available in literature (23) were performed at low temperature from 6.58 to 310 K by adiabatic calorimetry. Figure 3 reports the temperature dependence of heat capacity. There is a reasonable agreement between these two set of data, especially in view of the different experimental techniques used: in the small common temperature range, a deviation less than 5.5% is observed. The variation of \( C_p \) against temperature is almost linear in the range 306-900 K (figure 3). At higher temperature, two discontinuities appear and correspond to the transition from orthorhombic to cubic, and to the fusion of \( \text{EuCl}_2 \). The heat capacity of the liquid could not be measured on a large temperature range because of the experimental limit of the apparatus.

**Enthalpy of mixing**

The mixing enthalpy is slightly exothermic in the whole composition range with a minimum at about 0.7 kJ/mol. The composition dependence does not show any particular feature (figure 4) and the shape of the curve is almost symmetrical. The small thermicity upon mixing made experiments rather difficult to carry out since they had to be repeated several times at the same composition in order to balance noticeable scattering. This small thermicity is also indicative of weak interactions in the melt as suggested by the rather simple eutectic phase diagram. Very often complex formation in molten salt melts can be related to strong energetic interactions and also to the occurrence of stable stoichiometric compounds in the solid phase. These enthalpic results cannot thus suggest the possibility of existence of any complex in the liquid.
Molar volume

Molar volume determination were needed not only to complement a characterization of EuCl$_2$ but also for practical reasons. As structural investigations by neutron diffraction isotopic substitution (NDIS) were planned, it was crucial to know EuCl$_2$ molar volume in order to optimize the amount, thus the cost, of the expensive isotopic sample.

An estimation procedure was first carried out, in Marseille, while experimental determinations were started in Japan. The results, which will be published separately (24), were in close agreement: just above the melting temperature for instance, the estimated and measured molar volumes were 60 and 59.4 cm$^3$/mol, respectively.

Phase diagram assessment

Phase diagram assessment was carried out in order to check for consistency the new thermodynamic data obtained in the present work with those already existing. The optimization was made using Thermo-Calc (25-26), a thermodynamic software including a database of assessed parameters. While reference data existed for pure NaCl, none was available in the database for EuCl$_2$. Our experimental data relative both to pure EuCl$_2$ and to NaCl-EuCl$_2$ mixture were implemented in the database and used in the present assessment. The standard Gibbs free energy of formation of EuCl$_2$, was estimated from those of Eu and EuCl$_3$ from experimental results of chlorine pressure measurements (27).

In a first step, optimization was carried out with a simple substitution model for the liquid phase. Although it could be predicted that such a simple description would not account for the features of the melt under investigation, we wanted to show that estimation procedures should include not only reliable experimental data but also proper modeling hypotheses.

The phase diagram calculated under these simplified assumptions is shown in figure 2, altogether with experimental data. The calculation accounts satisfactorily for the eutectic composition ($X_{\text{EuCl}_2}=0.499$) and temperature (843 K). A good agreement is also observed between calculated and experimental equilibrium temperatures in the NaCl-rich side of the diagram.

In the EuCl$_2$-rich side of the diagram, the calculated liquidus deviates from the experimental one. In particular, the limiting liquidus slope at $X_{\text{EuCl}_2}=1$ is not consistent with the experimental data, even if computation took into account the experimental uncertainty observed on temperatures. Calculations were repeated under the assumption of solid solubility in this composition range (such a solid solubility would have been hardly detected in view of the particular melting behavior in the range).
improvement was obtained and there was still a disagreement between the calculated and experimental liquidus temperatures at the highest EuCl₂ content.

This disagreement may be thus connected to the ideal entropy of mixing used in the model. Clearly this classical ideal entropy, equivalent to assume that one "molecule" of NaCl added to EuCl₂ produces one independent particle, is not relevant.

More realistic descriptions of melts involving ions with different valency (28) were already proposed and gave different formulations of the ideal entropy. While they were found successful to describe the properties of purely ionic liquids, they cannot be employed here as EuCl₁ and EuCl₃-rich mixtures probably have a different structure. It is generally accepted that interactions in lanthanide halides are not purely ionic but show a marked covalent nature. This was confirmed by recent structural observations obtained very recently and reported also at the same Symposium (29). On the other hand, new theoretical advances, dealing with the inclusion of many-body polarization interactions into computer simulations of ionic melts, have been shown to recapture many of the structural effects previously attributed to "covalency" (30-31). Molten salts, and in particular, those obtained from elements with multiple valencies still include several unexplained features. It is hoped that new advances being made from coupled and interactive experimental and theoretical approaches will constitute a step forwards in their internal complexity.

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Figure 1. Tamman diagram

Figure 2. Experimental and calculated phase diagram
Figure 3 Heat capacity $C_p$ of EuCl$_2$: • (this work); • (23).

Figure 4. Enthalpy of mixing of the NaCl-EuCl$_2$ system.