Calorimetric Investigation of MCl-EuCl$_2$ Melts (M = Na, K, Rb)

F. Da Silva$^a$, L. Rycerz$^{a,b}$, and M. Gaune-Escard$^a$

$^a$ IUSTI, U.M.R. - C.N.R.S. 6595, Technopôle de Château Gombert, 5 rue Enrico Fermi, 13453 Marseille Cedex 13, France

$^b$ Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

Reprint requests to M. G.-E.; Fax : +33 (0)4 91 11 74 39; E-mail: mge@iusti.univ-mrs.fr

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The molar enthalpies of mixing ($\Delta_{\text{mix}} H_m$) of MCl-EuCl$_2$ (M = Na, K, Rb) liquid binary systems were measured at 1138 K over the whole composition range by direct calorimetry. A Calvet type calorimeter was used, and mixing of the two liquid components was achieved by the ampoule break-off technique under argon at atmospheric pressure. The enthalpy of mixing of these systems is negative over the whole composition range with a minimum of approximately -0.5, -3.5 and -4.5 kJ mol$^{-1}$ for M = Na, K, Rb, respectively. The least-squares coefficients $A$, $B$, $C$ in the equation $A$ (kJ mol$^{-1}$) = $A + Bx + Cx^2$, where $\lambda$ is an interaction parameter, are reported. From the trend observed in these MCl-EuCl$_2$ systems it was possible to estimate the mixing enthalpy of the CsCl-EuCl$_2$ system.

Key words: Mixing Enthalpy; Europium Dichloride; Alkali Chlorides; Calvet Calorimeter.

Introduction

Lanthanide elements, also called rare earths, can not anymore be considered as such. La, Ce, and Nd are even more abundant in nature than Pb. They are mainly produced from monazite, xenotime and bastnesite ores and are nowadays intensively used in all sorts of industrial applications.

Due to their ferromagnetic properties they are employed in the production of high efficiency magnets with low volume and weight (SmCo$_5$, Nd-Fe-B).

Some of the lanthanides are used in the lighting industry for their fluorescent and luminescent properties (TV, light bulbs, lasers). In high-pressure discharge lamps [1], lanthanide halide - alkali halide systems (lanthanide iodide - sodium iodide for instance) have attracted particular attention because of the enhanced volatility of the lanthanide halide caused by a vapour complex reaction [2]. The high concentration of alkali and lanthanide ions increases the generation of radiation, and in addition better colour rendering is obtained.

The study of lanthanide halides is actually of particular interest in the field of recycling of spent nuclear fuel [3 - 7]. The aim is to remove the actinides and lanthanides from spent fuel. Lanthanides and actinides due to their physical and chemical properties, are the elements the most difficult to separate. Until now, the various elements present in nuclear wastes are separated by hydrometallurgical processes. The Purex process is the most used technique but permits to recover only U and Pu. Thus many investigations actually focus on alternative technologies based on pyrochemical processes to obtain more compact fuel cycles, allowing the reduction of all wastes. In such techniques, molten alkali salt baths are widely used. In order to contribute to the knowledge of these media, we decided to study the thermodynamic properties of lanthanide halide - alkali halide mixtures. The study of these properties is important for the understanding of the fundamental mechanism in these melts and the mastery of the operations applied in such processes.

We present in this article the mixing enthalpies measured on MCl-EuCl$_2$ systems (M = Na, K, Rb).

Experimental

Chemicals

The EuCl$_2$ synthesis was described in [8]. Europium trichloride was synthesised from Eu$_2$O$_3$ (Johnson Matthey, 99.9%). Thionyl chloride (John-

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Table 1. Chemical analysis of EuCl$_2$.

<table>
<thead>
<tr>
<th>Cl$_{exp}$/mass%</th>
<th>Cl$_{theor}$/mass%</th>
<th>Eu$_{exp}$/mass%</th>
<th>Eu$_{theor}$/mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.76</td>
<td>31.81</td>
<td>68.23</td>
<td>68.19</td>
</tr>
</tbody>
</table>

son Matthey, 99%) was used as a chlorinating agent. Reduction of europium trichloride to EuCl$_2$ was performed by Zn. Chemical analysis of the prepared EuCl$_2$ was performed by mercurimetry (chloride) and complexometry (EDTA in presence of xylenol orange - europium). Results of the analysis are presented in Table 1.

NaCl, KCl, and RbCl were purchased from Merck (99.9% min.). They were dehydrated by heating just above the melting point under gaseous HCl. Excess HCl was removed from the melt by argon. The salts were handled in a glove box and stored in sealed glass ampoules.

**Experimental Procedure**

The mixing enthalpy of the MCI-EuCl$_2$ systems (M = Na, K, Rb) was measured at 1138 K with the "break-off ampoule" method. Experimental runs were performed under argon at atmospheric pressure. The components were weighed with a precision of 10$^{-5}$ g. The alkali halides were introduced into quartz crucibles. EuCl$_2$, which is the most hygroscopic compound, was placed in a quartz break-off ampoule welded to a quartz tube, which could be moved up and down along the calorimetric cell through a gas-tight ring. The calorimetric cell was filled with argon and introduced in a Calvet calorimeter together with a reference cell. After thermal stabilisation of the system, the ampoule was broken in the quartz crucible by moving the quartz tube. The heat resulting from the mixing of the compounds was recorded simultaneously by an amplifying recorder and a computer. The surface of the thermograms was automatically obtained by a computer. Calibration of the high temperature calorimeter was performed by the drop calorimetry method using NIST $\alpha$ - Al$_2$O$_3$: the heat content between room temperature and the experimental temperature was measured with a reproducibility better than 3%.

**Results and Discussion**

No former enthalpy data on the MCI-EuCl$_2$ systems (M = Na, K, Rb) were available. Our experimental results are reported in the following: for all the systems the mixing enthalpies are negative over the whole composition range (Fig. 1).

The exothermicity is weak, and therefore the results are scattered. For all systems the interaction parameter $\lambda = \Delta_{mix}H_m/x_{EuCl_2}(1-x_{EuCl_2})$ was obtained from the experimental enthalpies.

This parameter is representative for the energetic asymmetry in molten salt systems, and its composition dependence may be indicative of complex formation in the melt. The variation of $\lambda$ against the composition was fitted to a polynomial

$$\lambda = A + Bx + Cx^2,$$

where $x$ is the mole fraction of one component (EuCl$_2$ for instance). Table 2 reports the values of the coefficients $A$, $B$, and $C$, obtained by the least-squares method.

These coefficients were used to calculate the interaction parameters (Fig. 2), and then to obtain the calculated enthalpy curves (Fig. 1).
The mixing enthalpies become more negative with increasing radius of the alkali ion. The composition dependence of the interaction parameter (Fig. 2) shows the same trend: for each system the values at $x = 0$ and $x = 1$, which correspond to the partial enthalpies at infinite dilution, become more negative when the size of the alkali cation increases.

On the other hand, the composition at the minimum of the enthalpy is nearly the same for all systems. This composition ($x(\text{EuCl}_2) \approx 0.4$) evidences the difference between the behaviour of alkali systems with EuCl$_2$ investigated here and those with trivalent lanthanide chlorides which have been examined earlier. Indeed in the MCI-LaCl$_3$, MCI-PrCl$_3$, MCI-NdCl$_3$ and MCI-TbCl$_3$ systems (where M stands for alkali metals) [9 - 13] a minimum enthalpy was observed, but it was far more exothermic and occurred at compositions more depleted towards the alkali-rich side ($x(\text{LnCl}_3) \approx 0.25$). Also, in those MCI-LnCl$_3$ melts, a minimum in the $\lambda$ dependence on composition was observed in the vicinity of that composition, thus indicating that formation of LnCl$_6^{3-}$ complexes in the melt was likely. Further evidence of complex formation was indicated by Raman spectroscopy in liquid LaCl$_3$ [14], YCl$_3$ [15] and NdCl$_3$ [16].

In the NaCl-DyCl$_3$ system, the minimum of the enthalpy of mixing [17 - 18] also occurred at the composition $x(\text{DyCl}_3) \approx 0.25$, but no minimum was clearly visible in the composition dependence of the interaction parameter $\lambda$. However, X-ray [19] and neutron diffraction experiments [20 - 21] showed the existence of DyCl$_6^{3-}$ in the liquid.

The experimental partial distribution functions are well reproduced by molecular dynamics simulations [22] based on the Polarizable Ion Model (PIM) [23]. The computations were consistent with the existence of mostly DyCl$_6^{3-}$ complexes, and to a less extend of also of Dy$_2$Cl$_{11}^{5-}$ and Dy$_3$Cl$_{16}^{7-}$.

All these facts suggest that, as for NaCl-DyCl$_3$, even if no minimum is clearly observed in the $\lambda$ curves, some complex species may be formed in the liquid KCl-EuCl$_2$ and RbCl-EuCl$_2$ systems. Neutron diffraction experiments performed recently [24] on the NaCl-EuCl$_2$ system hint at the existence of complexes also in this system and should give information on their structure. In the systems of alkali chlorides with divalent metal chlorides, as for example MCI-MeCl$_2$ (where Me stands for metals such as Mn, Fe, Co, Ni, Cd, Pb), complexes exist and are usually of the tetrahedral MeCl$_4^{2-}$ type [25 - 28]. For these systems, when appreciable tetrahedral “complexing” is present, the interaction parameter curve shows a pronounced minimum around $x(\text{MeCl}_2) \approx 1/3$. The formation of the EuCl$_4^{2-}$ complex may also occur in MCI-EuCl$_2$ systems. However, as no pronounced minimum is observed in the interaction parameter curves, the concentration of such species in the melts, if they exist, is probably small.

Usually, the mixing enthalpy of mixtures containing differently charged cations and common anions is mainly dependent on the size and the charge of the cations. The nature of the common anion has less

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Table 2. Least-squares coefficients of (1) for the liquid alkali chloride - europium dichloride mixtures.

<table>
<thead>
<tr>
<th>System</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
</tr>
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<tbody>
<tr>
<td>NaCl-EuCl$_2$</td>
<td>-1.6549</td>
<td>-5.5195</td>
<td>6.3451</td>
</tr>
<tr>
<td>KCl-EuCl$_2$</td>
<td>-21.388</td>
<td>13.619</td>
<td>-</td>
</tr>
<tr>
<td>RbCl-EuCl$_2$</td>
<td>-25.289</td>
<td>15.797</td>
<td>-</td>
</tr>
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Fig. 2. Variation of the interaction parameter $\lambda$ with the composition of the MCI-EuCl$_2$ liquid binary systems.
Fig. 3. Dependence of the limiting interaction parameter \( \lambda_0(x_{\text{EuCl}_2} \rightarrow 0) \) on the relative ionic potential \( \Delta IP \) in the NaCl-, KCl- and RbCl-EuCl\(_2\) melts.

According to Kleppa [30], \( \alpha \) is positive and is in part due to the London - van der Waals dispersion interaction between second nearest neighbour cations, and in part due to the steric effect associated with the mixing of two cations of different size and charge. The negative term \( \beta \cdot \Delta IP \) arises mainly from the contribution of the coulombic and polarization energy terms to the mixing enthalpy. Figure 3 shows the limiting enthalpy interaction parameter \( \lambda_0(x_{\text{EuCl}_2} \rightarrow 0) \) against the relative ionic potential \( \Delta IP \). A least squares treatment of the experimental data yields

\[
\lambda_0(x_{\text{EuCl}_2} \rightarrow 0) = 63.826 - 7665.5 \left( \frac{2}{r_{\text{Eu}^2+}} - \frac{1}{r_{M^+}} \right) \\
\pm 0.5 \text{ kJ mol}^{-1},
\]

where \( r_{\text{Eu}^2+} \) is the ionic radius of europium and \( r_{M^+} \) the ionic radius of alkali metals. The ionic radii were taken as 139, 102, 138, and 149 pm for \( \text{Eu}^{2+}, \text{Na}^{+}, \text{K}^{+}, \) and \( \text{Rb}^{+} \) [31], respectively.

The dependence of \( \lambda \) on the composition of the CsCl-EuCl\(_2\) system obtained from this estimation is plotted in Figure 2. The obtained highly asymmetric mixing enthalpy is plotted in Figure 1.

**Conclusion**

From this calorimetric investigation it is not evident whether complexes such as EuCl\(_4^-\) exist in these melts. Data refinement of neutron experiments should allow this point to be clarified.

All these experimental mixing enthalpy data were successfully used in a numerical optimisation procedure for the calculation of the corresponding phase diagrams [32]. The same procedure could be applied to the CsCl-EuCl\(_2\) system in order to check the estimated mixing enthalpy for consistency with other data available in the literature.


