Calorimetric Investigation of the $CeBr_3$−MBr Liquid Mixtures (M = Na, K, Rb, Cs)[†]

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The molar enthalpies of mixing ($\Delta_{mix}H_m$) in the liquid cerium(III)−alkali metal bromide mixtures were measured with a Calvet- type high temperature microcalorimeter over the entire composition range at 1073 K. Mixing the two liquid components was achieved by using the "break-off ampule technique". All the melts are characterized by negative enthalpies of mixing with a minimum value of approximately −5.3 kJ·mol^{-1}, −12.7 kJ·mol^{-1}, −16.1 kJ·mol^{-1}, and −18.4 kJ·mol^{-1}, for M = Na, K, Rb, and Cs, respectively. For all the systems, the minimum of the enthalpy of mixing is shifted toward the alkali bromide-rich compositions and located in the vicinity of $x(CeBr_3) \sim 0.4$. The composition dependence of the interaction parameter λ, with a broad minimum at $x(CeBr_3) \sim 0.2$ for the systems with KBr, RbBr, and CsBr is indicative of $LnBr_6^{3-}$ complexes formation in the melts.

1. Introduction

The specific electronic structure of lanthanides (filling of inner 4f sub shell) reflects in their physical and chemical properties. It causes the "lanthanide contraction": as the lanthanide series is traversed from lanthanum to lutetium, the atomic (and ionic) radii decrease. Both in solutions and in the solid state the lanthanides adopt predominantly the + 3 oxidation state. This oxidation state has been characterized for all the lanthanide halides, which provide an excellent object for studying the effect upon the structure of varying the radii of cation and anion. When combined with alkali metal halides, lanthanide halides form different binary compounds in the solid state and complexes in liquids. Their existence and stability depend on the ionic radii of lanthanide, halide, and alkali metal. Thus correlations were evidenced between thermodynamic and transport properties and ionic radii and structure both for pure lanthanide halides and for their compounds with alkali metal halides.[1−3] All these properties and their correlation are important also from a technological point of view. Rare earth halides and their systems with alkali metal halides play a significant role in everyday life and in many industrial applications. Whatever the targeted technological application, basic knowledge is required for process development and optimization, in particular the thermodynamic and transport properties of lanthanide compounds and their mixtures with alkali metal halides. However, these data are scarce and not easily accessible in literature. As a consequence, intensive efforts are being made at an international level both on research and development aspects and also on data bank development.[4]

The present work is part of our wide and systematic research program performed on the LnX_3−MX systems (where Ln = lanthanide, M = alkali metal and X = halide). It reports mixing enthalpy measurements performed on the whole series of $CeBr_3$−MBr (M = Na, K, Rb, Cs) liquid systems over the entire composition range.

2. Experimental Section

2.1. Chemicals. Cerium(III) bromide was synthesized from the cerium(III) carbonate hydrate (Aldrich 99.9 %). $Ce_2(CO_3)_3 \cdot xH_2O$ was dissolved in hot concentrated HBr acid. Solution was evaporated and $CeBr_3 \cdot xH_2O$ was crystallized. Ammonium bromide was then added, and this wet mixture of hydrated $CeBr_3$ and NH_4Br was first slowly heated to 450 K and then to 570 K to remove the water. The resulting mixture was subsequently heated to 650 K for sublimation of NH_4Br. Finally, the salt was melted at 1100 K. Crude $CeBr_3$ was purified by distillation under reduced pressure (∼ 0.1 Pa) in a quartz ampule at 1150 K. $CeBr_3$ prepared in this way was of a high purity, minimum 99.9 %. Chemical analysis was performed by mercurimetric (bromine) and complexometric (cerium) methods. The results were as follows: Ce, (36.91 ± 0.03) % (36.89 % theoretical); Br, (63.09 ± 0.04) % (63.11 % theoretical).

Sodium, potassium, rubidium, and cesium bromides were Merck Suprapur reagents (minimum 99.9 %). Prior to use, they were progressively heated to fusion under a gaseous HBr atmosphere. HBr in excess was then removed from the melt by argon bubbling.

All chemicals were handled in an argon glovebox with a measured volume fraction of water of about 2 ppm and continuous gas purification by forced recirculation through external molecular sieves.

2.2. Measurements. The mixing experiments were all of the simple liquid−liquid type, performed under pure argon at atmospheric pressure. The Calvet-type high-temperature microcalorimeter, the mixing device and the "break-off bubble" experimental method have all been described in details elsewhere.[1,2,5] For any system under investigation, one component was weighed in the glovebox within 10^{-5} g and placed in the break-off quartz ampule. The other component, weighed

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under similar conditions, was placed in a quartz crucible. The break-off ampule was evacuated under controlled argon pressure to obtain a pressure of 1 atm at the temperature of experiment. It was then welded to a quartz tube, which could be moved up and down the calorimetric cell through a special gastight ring. The calorimetric cell was filled with argon and introduced in a Calvet calorimeter together with a reference cell. After thermal stabilization of the system, the ampule was broken off against the inner break-off tip at the bottom of the quartz crucible and thermal effect resulting from mixing was recorded. Calibration of the calorimeter is described below.

2.3. Calorimeter Constant Determination. The surface of thermogram (S) obtained from a calorimetric experiment is proportional to the amount of heat (Q_p) evolved in the experimental cell: $Q_p = K \cdot S$. The coefficient K is the calorimeter constant. It is determined by a usual calibration procedure with a reference material. Calibration of the calorimeter was performed with α-alumina obtained from NIST. After the mixing experiments, pieces of α-alumina [(30 to 100) mg] were dropped into the melt and the corresponding enthalpy increment was measured.

The calorimeter constant K was determined from eq 1:

$$\frac{Q_p}{S} = \frac{n\int_{T_0}^{T} C_{p,m}(T)\,dT}{S} = \frac{\Delta H_{(T_0 \to T)}}{S} = K \qquad (1)$$

where n and $C_{P,m}$ are the mole number and molar heat capacity, $\Delta H_{(T_0 \to T)}$ is the enthalpy increment from temperature T_0 up to T, and S is the corresponding thermogram surface in a calibration experiment run by drop calorimetry with the reference standard material.

The calorimeter constant was obtained from four calibration tests, each one run in the same experimental device where mixing experiments have been performed before.

2.4. Thermocouple Calibration. A Pt−Pt/Rh(10) thermocouple was used to measure the experimental temperature in the calorimetric block. It was calibrated with high purity metals (99.999 %): In, Sn, Zn, Sb, and Ag (melting temperatures: 430 K, 505 K, 693 K, 804 K, and 1233 K, respectively).[6] The experimental temperature was measured within 1 K.

2.5. Error on Mixing Enthalpy Measurements. A detailed discussion of experimental errors in mixing enthalpy measurements by Calvet microcalorimetry was given by Hatem.[7]

The relative error in the calorimetric constant determination ΔK/K and its influence on the mixing enthalpy $\Delta_{\mathrm{mix}}H_m$ are described by eqs 2 and 3, respectively:

$$\frac{\Delta K}{K} = \pm\left\{\left(\frac{\Delta(S/n)}{(S/n)}\right)^2 + \left(\frac{\Delta(\Delta H_{(T_0 \to T)})}{\Delta H_{(T_0 \to T)}}\right)^2\right\}^{1/2} \qquad (2)$$

$$\frac{\Delta(\Delta_{\mathrm{mix}}H_m)}{\Delta_{\mathrm{mix}}H_m} = \pm\left\{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta K}{K}\right)^2 + \left(\frac{\Delta(S/n)}{(S/n)}\right)^2\right\}^{1/2} \qquad (3)$$

where $\Delta x/x$ is the relative error of composition related to error in weighing of components and n is the mole number of mixed components.

Taking into account that for α-Al_2O_3 $\Delta(S/n)/(S/n)$ is less than 2 %, and $\Delta(\Delta_{\mathrm{mix}}H_m)/(\Delta_{\mathrm{mix}}H_m)$ less than 0.2 %,[8] the relative error on the calorimetric constant K is

$$\Delta K/K = \pm\sqrt{\left(\frac{2}{100}\right)^2 + \left(\frac{0.2}{100}\right)^2} \approx \pm 2\ \% \qquad (4)$$

Table 1. Molar Enthalpy of Mixing $\Delta_{\mathrm{mix}}H_m$ and Interaction Parameter λ of the $CeBr_3$−NaBr Liquid System at T = 1073 K

$x(CeBr_3)$	$\Delta_{\mathrm{mix}}H_m$ kJ·mol^{-1}	λ kJ·mol^{-1}	$x(CeBr_3)$	$\Delta_{\mathrm{mix}}H_m$ kJ·mol^{-1}	λ kJ·mol^{-1}
0.050	−1.4	−29.8	0.499	−5.0	−20.0
0.098	−2.6	−28.8	0.578	−4.5	−18.2
0.153	−3.6	−27.7	0.650	−4.2	−18.3
0.198	−4.2	−26.5	0.702	−3.5	−16.6
0.247	−4.8	−25.8	0.752	−3.1	−16.4
0.274	−5.0	−25.0	0.781	−2.7	−15.9
0.300	−5.3	−25.0	0.796	−2.6	−16.2
0.351	−5.5	−24.0	0.868	−1.9	−16.1
0.407	−5.5	−22.9	0.897	−1.4	−15.5
0.451	−5.2	−21.2			

Table 2. Molar Enthalpy of Mixing $\Delta_{\mathrm{mix}}H_m$ and Interaction Parameter λ of the $CeBr_3$−KBr Liquid System at T = 1073 K

$x(CeBr_3)$	$\Delta_{\mathrm{mix}}H_m$ kJ·mol^{-1}	λ kJ·mol^{-1}	$x(CeBr_3)$	$\Delta_{\mathrm{mix}}H_m$ kJ·mol^{-1}	λ kJ·mol^{-1}
0.010	−0.5	−53.2	0.457	−13.1	−52.6
0.048	−2.7	−58.7	0.507	−12.1	−48.3
0.075	−4.1	−59.5	0.560	−10.8	−43.9
0.097	−5.2	−59.8	0.609	−9.1	−38.4
0.137	−7.5	−63.2	0.635	−10.2	−44.0
0.202	−10.0	−62.2	0.656	−8.4	−37.0
0.242	−11.6	−63.0	0.749	−6.3	−33.2
0.281	−12.0	−59.3	0.798	−5.5	−34.3
0.323	−12.4	−56.6	0.837	−5.0	−36.8
0.338	−12.2	−54.4	0.903	−2.8	−32.1
0.385	−13.2	−55.5	0.946	−1.0	−20.1
0.419	−13.1	−53.7			

Table 3. Molar Enthalpy of Mixing $\Delta_{\mathrm{mix}}H_m$ and Interaction Parameter λ of the $CeBr_3$−RbBr Liquid System at T = 1073 K

$x(CeBr_3)$	$\Delta_{\mathrm{mix}}H_m$ kJ·mol^{-1}	λ kJ·mol^{-1}	$x(CeBr_3)$	$\Delta_{\mathrm{mix}}H_m$ kJ·mol^{-1}	λ kJ·mol^{-1}
0.040	−2.8	−71.7	0.608	−12.7	−53.1
0.058	−4.2	−75.9	0.660	−11.5	−51.3
0.102	−6.5	−71.0	0.705	−9.8	−47.2
0.154	−10.2	−78.4	0.737	−9.5	−49.0
0.200	−12.7	−79.1	0.800	−6.5	−40.4
0.250	−14.7	−78.6	0.806	−6.2	−39.7
0.297	−16.2	−77.3	0.827	−6.0	−42.2
0.354	−16.8	−73.6	0.875	−4.6	−41.9
0.409	−16.1	−66.7	0.898	−4.1	−44.9
0.481	−15.2	−60.9	0.931	−2.6	−40.0
0.555	−14.7	−59.6	0.959	−1.6	−41.7

The error in weighting each component is 0.2 %; thus the relative error on composition $\Delta x/x$ is ≈ ± 0.4 %. The maximal relative error in the thermal mixing, S/n, is about 4 %. Hence the relative error on mixing enthalpy determination is

$$\frac{\Delta(\Delta_{\mathrm{mix}}H_m)}{\Delta_{\mathrm{mix}}H_m} = \pm\sqrt{0.4^2 + 2^2 + 4^2} \approx \pm\ 4.5\ \% \qquad (5)$$

It should be pointed out that also nonsystematic errors resulting mainly from incomplete crushing of a break-off quartz ampule can influence the mixing enthalpy results. Accordingly, the total relative error on mixing enthalpy determinations was estimated as ± (6 to 8) %.

3. Results and Discussion

Calorimetric experiments were performed at 1073 K. The mixing enthalpy values for the four cerium bromide-based systems (NaBr, KBr, RbBr, and CsBr) measured over the entire composition range are presented in Tables 1 to 4 and are plotted against composition in Figure 1.

All melts were characterized by negative enthalpies of mixing with a minimum value of approximately −5.3 kJ·mol^{-1}, −12.7 kJ·mol^{-1}, −16.1 kJ·mol^{-1}, and −18.4 kJ·mol^{-1}, for M = Na, K, Rb, and Cs, respectively. For all systems, the minimum enthalpy of mixing was shifted toward the alkali bromide-rich compositions and located in the vicinity of $x(CeBr_3) \sim 0.4$. It

Table 4. Molar Enthalpy of Mixing $\Delta_{mix}H_m$ and Interaction Parameter λ of the $CeBr_3$−CsBr Liquid System at T = 1073 K

	$\Delta_{mix}H_m$	λ		$\Delta_{mix}H_m$	λ
$x(CeBr_3)$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$x(CeBr_3)$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
0.026	−2.1	−85.2	0.419	−18.3	−75.0
0.052	−4.3	−87.4	0.443	−17.9	−72.7
0.074	−6.3	−91.7	0.500	−17.0	−67.9
0.095	−8.1	−94.1	0.550	−16.0	−64.7
0.125	−10.4	−94.7	0.650	−13.4	−59.0
0.149	−11.9	−93.9	0.692	−12.3	−57.5
0.200	−15.0	−93.6	0.757	−10.1	−54.9
0.226	−16.5	−94.5	0.808	−8.5	−55.0
0.304	−17.9	−84.7	0.851	−6.5	−51.6
0.352	−18.5	−81.2	0.886	−5.2	−51.7
0.368	−18.3	−78.7	0.946	−2.7	−52.8
0.399	−18.0	−75.1			

is evident that the ionic radius of the alkali metal influences the magnitude of mixing enthalpy (Figure 1).

Figure 2 shows the composition dependence of the interaction parameter λ, which is representative of the energetic asymmetry in these melts

$$\lambda = \Delta_{mix}H_m / x \cdot (1 - x) \tag{6}$$

where x is the mole fraction of $CeBr_3$. The λ values for each system are also included in Tables 1 to 4. These λ values were fitted by the least-squares method to the polynomial

$$\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4 \tag{7}$$

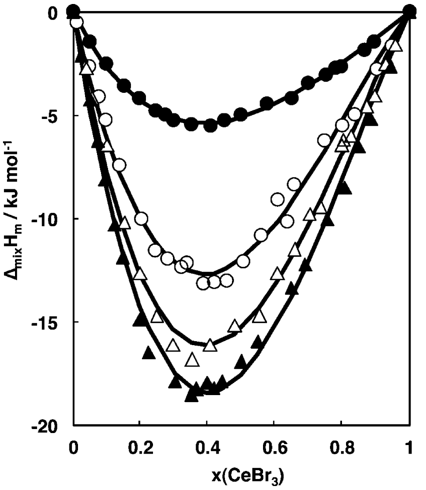

Figure 1. Molar enthalpy of mixing $\Delta_{mix}H_m$ of the $CeBr_3$−MBr liquid systems: black circles, NaBr; open circles, KBr; open triangles, RbBr; black triangles, CsBr; solid line, least-squares fitting from eqs 6 and 7.

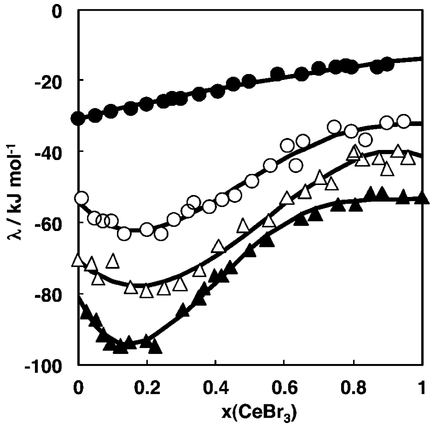

Figure 2. Dependence of the interaction parameter λ on composition for the $CeBr_3$−MBr liquid systems: black circles, NaBr; open circles, KBr; open triangles, RbBr; black triangles, CsBr; solid line, least-squares fitting from eq 7.

Table 5. Least-Squares Coefficients of the λ Interaction Parameter Equation in Liquid Cerium−alkali Bromide Mixtures: λ ($kJ \cdot mol^{-1}$) = $A + Bx + Cx^2 + Dx^3 + Ex^4$ and Standard Deviation S.E. (in $kJ \cdot mol^{-1}$)

system	A	B	C	D	E	S.E.
$CeBr_3$−NaBr	−30.656	23.116	−6.133			0.597
$CeBr_3$−KBr	−54.122	−108.149	423.190	−433.332	140.388	1.893
$CeBr_3$−RbBr	−70.736	−85.957	292.164	−172.124	−4.722	2.434
$CeBr_3$−CsBr	−81.262	−194.285	872.732	−1068.970	418.829	1.348

The A, B, C, D, and E coefficients as well as their standard deviation (S.E.) are reported in Table 5. Figure 2 shows the composition dependence of the enthalpy interaction parameter λ, which follows a pattern similar to that found in a number of previously studied lanthanide halide−alkali halide mixtures.[9−18] All the systems have negative interaction parameters λ, the absolute value of each increases sharply with the alkali metal ionic radius. All systems show more negative λ values in the alkali halide-rich range.

The composition dependence of the interaction parameter λ for the $CeBr_3$−NaBr system is quite close to linear. For the systems with KBr, RbBr, and CsBr, the composition dependence of λ is somewhat more complicated: a broad minimum exists around $x(CeBr_3) \sim 0.2$. Similar λ variations, observed for other lanthanide−alkali halide systems,[9−18] were attributed to the formation of LnX_6^{3-} complexes in the melts. Their existence was confirmed by Raman structural studies.[9,10,19] Unfortunately, no literature information was available on the structure of cerium(III) bromide-based liquid mixtures. However, taking into account the great similarities between lanthanides, the formation of $CeBr_6^{3-}$ octahedral complexes may be assumed, resulting in a specific composition dependence of λ. As already mentioned, this parameter increases with the ionic radius of alkali metal. The role of alkali bromides is to provide additional bromide ions to enable Ce^{3+} to expand its coordination shell. But there is competition between M^+ and Ce^{3+} for Br^- in the ionic environment. The result of this competition depends on the relative attracting power of the alkali ion. Li^+ is the most halide attracting and the Cs^+ the least. The radius of the alkali metal will therefore govern the complex ion formation in the $CeBr_3$−MBr binary systems. Thus the presence of CsBr in $CeBr_3$ mixtures favors more complex ion formation than addition of a lighter alkali metal in the sequence (RbBr > KBr > NaBr) and results in a larger enthalpy of formation, larger activation energy for conductivity, and also the formation of several stoichiometric compounds in the solid state.[20,21]

4. Summary

The molar mixing enthalpies were measured over the whole composition range for the whole series of liquid cerium(III)−alkali metal bromide systems. All melts are characterized by negative enthalpies of mixing. The minimum of the enthalpy of mixing is shifted toward the alkali bromide-rich compositions and located in the vicinity of $x(CeBr_3) \sim 0.2$. The ionic radius of the alkali metal influences the magnitude of mixing enthalpy: the larger the radius, the more negative the mixing enthalpy. The composition dependence of the interaction parameter λ for the $CeBr_3$−NaBr system is indicative of $CeBr_6^{3-}$ octahedral complex formation. The stability of these complexes increases with the alkali metal radius from sodium to cesium.

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