ELSEVIER

Thermochimica Acta 279 (1996) 11–25

thermochimica
acta

Formation enthalpies of MBr–$NdBr_3$ liquid mixtures (M = Li, Na, K, Rb, Cs)

Marcelle Gaune-Escard[a,*], Aleksander Bogacz[b],
Leszek Rycerz[b], Wlodzimierz Szczepaniak[b]

[a] *IUSTI, UA 1168 CNRS, Université de Provence, Centre de St. Jérôme,
F-13397 Marseille Cedex 20, France*

[b] *Institute of Inorganic Chemistry & Metallurgy of Rare Elements, Technical University,
50-370 Wroclaw, wyb. Wyspianskiego 27, Poland*

Received 27 June 1995; accepted 12 January 1996

Abstract

Molar enthalpies of mixing $\Delta_{mix}H^0_m$, of the LiBr–$NdBr_3$, NaBr–$NdBr_3$, KBr–$NdBr_3$, RbBr–$NdBr_3$, and CsBr–$NdBr_3$ liquid binary systems have been measured with a Calvet-type high-temperature microcalorimeter under argon at 1063 K over the whole composition range. Mixing of the two liquid components was carried out using a break-off ampoule technique. For all the systems, the enthalpies of mixing were negative and their minima (at $x_{NdBr_3} \approx 0.4$) were -0.7, -5.4, -12.4, -17.8 and -20.1 kJ mol^{-1}, respectively. The results have been compared with data previously published for MCl–$NdCl_3$ systems and discussed in terms of possible complex formation.

Keywords: Alkali bromides; Enthalpy of mixing; High temperature calorimetry; Molten bromides; Molten salt mixture; Neodymium bromide

---

1. Introduction

We have recently published [1] some preliminary results of the calorimetric investigation of mixing enthalpies for the three systems: LiBr–$NdBr_3$, NaBr–$NdBr_3$, and KBr–$NdBr_3$. These are now completed with studies on RbBr–$NdBr_3$ and CsBr–$NdBr_3$ systems; all are presented in this paper including experimental values. The

---

[*] Corresponding author.

PII: S0040-6031(96)02855-9

results of calorimetric investigations of mixing enthalpies of chloride systems MCl–$NdCl_3$, where M = Na, K, Rb, and Cs [2] were also included for discussion, together with some other results concerning the enthalpies of phase transitions [3,4], heat capacities [5], and electrical conductivities [6]. This is part of a more general program of investigation of the thermodynamic and transport properties of lanthanide halides and their melts with alkali metal halides. These investigations are the main purpose of the collaboration between the Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw and the University of Provence (IUSTI).

2. Experimental

The details of synthesis and experimental procedures have been described elsewhere [1,2]. Some of the most important features are given below.

2.1. Chemicals

$NdBr_3$ was prepared from Nd_2O_3 (99.9%) produced by the Chemistry Department of the University of Lublin (Poland). Nd_2O_3 was dissolved in concentrated HBr solution and NH_4Br was added to the solution in the molar ratio $NdBr_3:NH_4Br = 1:4$. The solution was heated to vaporize the water and the wet mixture of $NdBr_3 \cdot xH_2O$ plus NH_4Br was placed in quartz ampoule. The rest of the water was removed by gradual heating to 570 K. The temperature was further increased and ammonium bromide sublimated. At 1100 K the synthesis was complete. The ampoule containing $NdBr_3$ was cooled and opened in a dry-box. The $NdBr_3$ was purified by distillation under vacuum in quartz tubes at 1070 K. Because neodymium bromide is very sensitive to moisture, it was ground under argon in the dry-box and stored in sealed glass ampoules.

MBr alkali metal bromides (M = Li, Na, K, Rb, Cs) were Merck Suprapur reagents (minimum 99.9%). These bromides were dehydrated and dried by heating and melting under an atmosphere of gaseous HBr in quartz ampoules. Excess HBr was removed from the melt with argon, and the dry salts were ground in the dry-box and stored in sealed glass ampoules.

2.2. Procedure

The general measurement procedure, calibration of the Calvet-type calorimeter, and details of experiments have been described previously [2, 7, 8]. The present procedure was very similar to that adopted for the chlorides [2]—mixing experiments were liquid–liquid type and were carried out in a Calvet calorimeter under argon at atmospheric pressure. A break-off ampoule was used to mix the two liquids—alkali metal bromide and neodymium bromide. Formal accuracy for the single measurement depended on the value of $\Delta_{mix}H_m^0$ and was estimated to be 3–6% of the measured value on the basis of calibration experiments.

3. Results

All calorimetric experiments were carried out at 1063 K. The systems: LiBr–$NdBr_3$, NaBr–$NdBr_3$, KBr–$NdBr_3$, RbBr–$NdBr_3$, and CsBr–$NdBr_3$ were investigated over the whole range of compositions. Only single points were disregarded from some sets of experimental data when incomplete mixing (due to too thick walls of the break-off ampoule) was observed. Moreover, some enthalpy values given below were taken as the average of several independent runs.

The results are presented for each binary system in the following way;

(1) Original values of mixing enthalpy calculated from calorimetric experiments (tables);

(2) Plots of $\Delta_{mix}H_m^0$ versus x_{NdBr_3} with experimental values and the curve of polynomial based on the fitting of λ values; and

(3) Plots of λ versus x_{NdBr_3} with experimental values of the parameter and their polynomial fitting.

The interaction parameter λ (which represents the energetic asymmetry of the melt) is defined as:

$$\lambda = \frac{\Delta_{mix}H_m^0}{x_{NdBr_3} \times (1 - x_{NdBr_3})} \qquad (1)$$

The coefficients of its polynomial dependence on x_{NdBr_3} are given in Table 1.

3.1. LiBr–$NdBr_3$ System

The systems, LiBr–$NdBr_3$ and LiCl–$NdCl_3$ have not been studied but taking into account that the system NaBr–$NdBr_3$ [9] is a simple eutectic it is very probable that the LiBr–$NdBr_3$ system is also of this kind. Unfortunately, the mixing enthalpy of the system LiCl–$NdCl_3$ has also not been determined, so the results presented have no link to a neodymium system analog. Measured mixing enthalpies (Table 2) are very small in comparison with the values for systems with other alkali metal bromides. The change of enthalpy sign to positive at $x_{NdBr_3} \approx 0.8$ seems the most interesting feature of this system

Table 1
Least-square coefficients of the dependence of λ on composition for liquid MBr–$NdBr_3$ mixtures, $\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4$, in kJ mol^{-1}

Alkali metal	*A*	*B*	*C*	*D*	*E*
Li	−2.700	−8.850	27.10	−14.67	–
Na	−40.32	−86.29	−123.0	67.84	–
K	−66.64	2.954	116.5	−95.34	–
Rb	−80.98	−210.9	891.0	−949.7	311.4
Cs	−88.67	−317.8	1504	−2102	948.9

Table 2
Molar enthalpies of mixing, $\Delta_{mix}H^0_m$, and interaction parameter λ of the LiBr–NdBr$_3$ liquid system at 1063 K

x_{NdBr_3}	$-\Delta_{mix}H^0_m$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})	x_{NdBr_3}	$-\Delta_{mix}H^0_m$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})
0.095	0.26	−3.1	0.604	0.33	−1.3
0.205	0.64	−4.0	0.696	0.20	−0.93
0.299	0.69	−3.3	0.801	0.014	−0.088
0.402	0.69	−2.9	0.899	−0.044	0.48
0.499	0.43	−1.7	0.923	−0.064	0.90

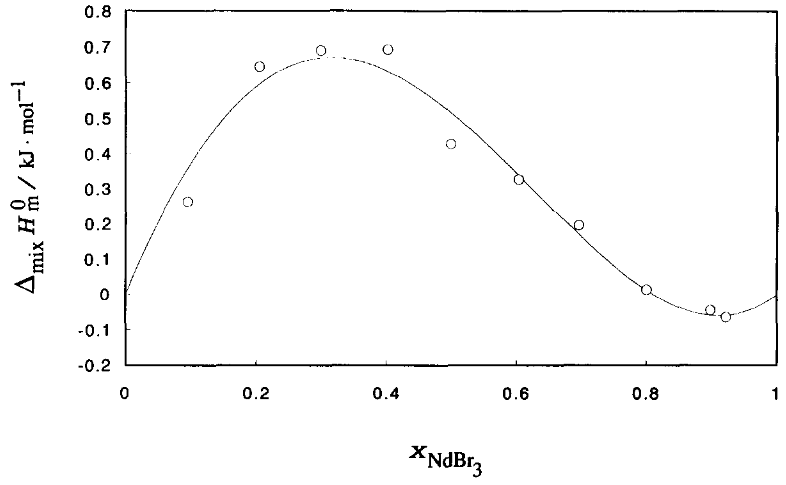

Fig. 1. Dependence of $\Delta_{mix}H^0_m$ (LiBr–NdBr$_3$) on composition.

(Fig. 1). This change does not influence the regularity of the λ curve in the right-hand part of the system (Fig. 2). The minimum of the λ curve appears at $x_{NdBr_3} \approx 0.2$ and suggests that at this composition interactions between both components are more distinct.

3.2. NaBr–NdBr$_3$ System

The system NaBr–NdBr$_3$ is a typical simple eutectic [9]. Measured mixing enthalpies (Table 3) are negative over the whole range of compositions (Fig. 3). The dependence of λ on x_{NdBr_3} did not exhibit a typical minimum at low concentrations of the alkali metal bromide and could be fitted by a straight line in the range $0.1 < x_{NdBr_3} < 1$, see Fig. 4, so that there should be no variation in the interactions between the components in this range of compositions. The only deviation from this regularity appears at $x_{NdBr_3} < 0.1$. The system NaBr–NdBr$_3$ is the only one for which

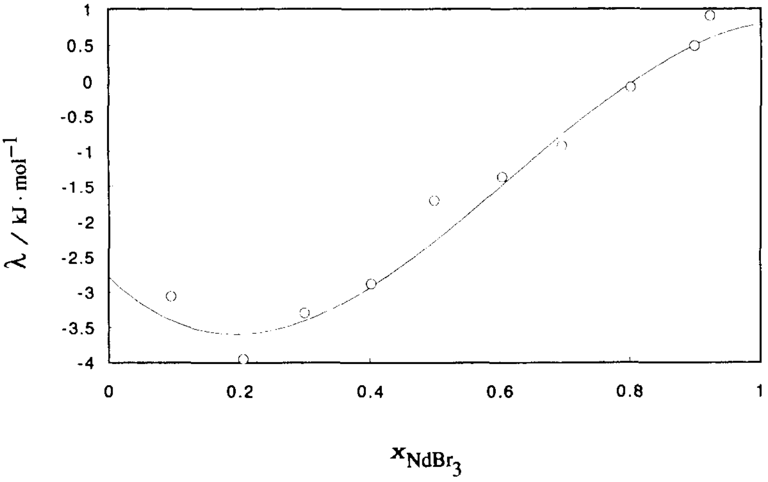

Fig. 2. Dependence of the λ parameter ($LiBr–NdBr_3$) on composition, and its polynomial fitting (Table 1).

Table 3
Molar enthalpies of mixing, $\Delta_{mix}H^0_m$, and interaction parameter λ of the $NaBr–NdBr_3$ liquid system at 1063 K

x_{NdBr_3}/	$-\Delta_{mix}H^0_m$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})	x_{NdBr_3}	$-\Delta_{mix}H^0_m$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})
0.022	0.90	−42.3	0.503	4.87	−19.5
0.048	1.76	−38.8	0.556	4.50	−18.2
0.062	2.02	−34.6	0.601	4.61	−19.2
0.102	2.55	−27.9	0.647	3.99	−17.4
0.151	3.23	−25.2	0.706	3.37	−16.2
0.200	4.23	−26.5	0.749	2.66	−14.1
0.251	5.02	−26.7	0.804	2.24	−14.2
0.294	5.07	−24.4	0.850	1.67	−13.1
0.347	5.60	−24.7	0.901	1.23	−13.8
0.400	5.41	−22.5	0.949	0.61	−12.6
0.453	5.39	−21.8			

literature data on the mixing enthalpy are available [10]. These values are also presented in Fig. 3—it seems that the two sets of results are in very good agreement.

3.3. $KBr–NdBr_3$ System

The system $KBr–NdBr_3$ is the first which forms compounds which exist in the solid state [10]. Two, K_3NdBr_6 and KNd_2Br_7, melt congruently and the third, K_2NdBr_5, decomposes peritectically. KBr is the phase with the highest melting temperature in the system. Measured enthalpies of mixing (Table 4 and Fig. 5) increase twice in compari-

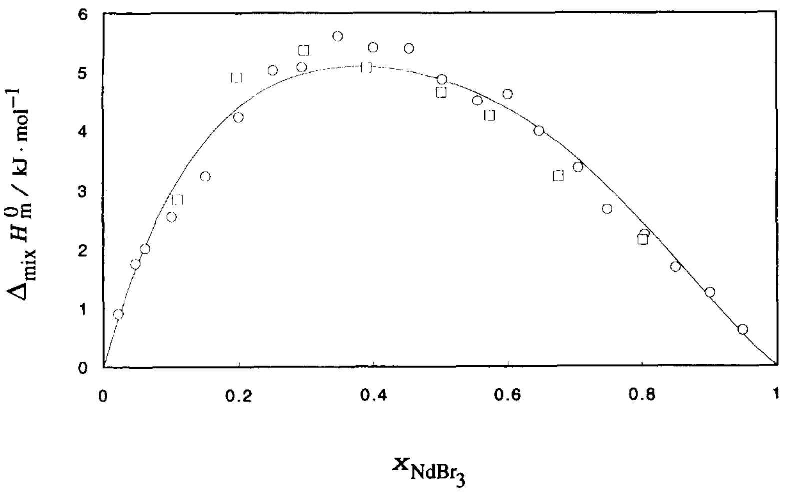

Fig. 3. Dependence of $\Delta_{\mathrm{mix}} H^0_{\mathrm{m}}$ ($NaBr-NdBr_3$) on composition. ○-experimental values, □-experimental values according to Blachnik [10].

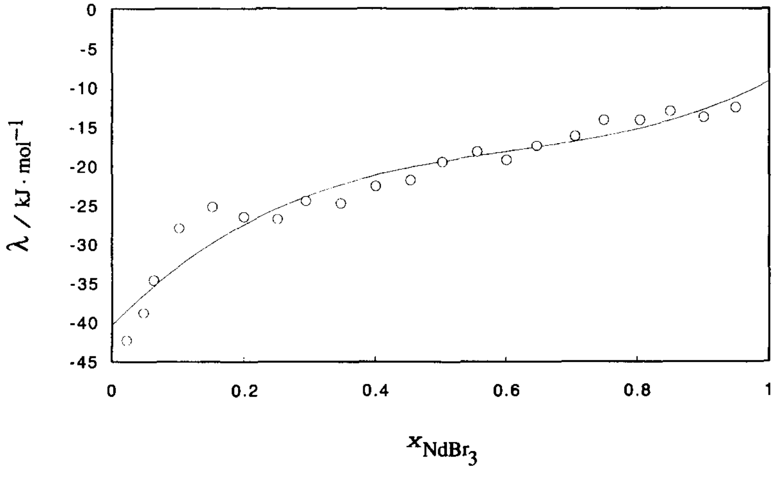

Fig. 4. Dependence of the λ parameter ($NaBr-NdBr_3$) on composition, and its polynomial fitting (Table 1).

son with the system $NaBr-NdBr_3$ and the dependence of λ on $x_{\mathrm{NdBr_3}}$ starts to exhibit a shoulder at compositions with low concentration of $NdBr_3$ (Fig. 6).

3.4 $RbBr-NdBr_3$ System

There are also three compounds in the system $RbBr-NdBr_3$, i.e. Rb_3NdBr_6 and $RbNd_2Br_7$ melting congruently and Rb_2NdBr_5 which decomposes peritectically. In

Table 4
Molar enthalpies of mixing, $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$, and interaction parameter λ of the KBr–NdBr$_3$ liquid system at 1063 K

$x_{\mathrm{NdBr_3}}$	$-\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})	$x_{\mathrm{NdBr_3}}$	$-\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})
0.025	0.99	−40.1	0.451	11.97	−48.4
0.049	3.71	−79.0	0.501	11.49	−46.0
0.071	5.06	−76.7	0.550	11.31	−45.7
0.100	6.20	−69.1	0.601	10.59	−44.1
0.125	7.43	−67.8	0.653	9.40	−41.5
0.149	9.46	−74.7	0.707	9.06	−43.7
0.198	9.06	−57.0	0.752	7.66	−41.1
0.247	10.73	−57.7	0.801	6.46	−40.6
0.302	11.42	−54.2	0.854	4.98	−40.0
0.352	11.69	−51.3	0.900	3.31	−36.8
0.401	12.44	−51.8	0.953	1.71	−38.5

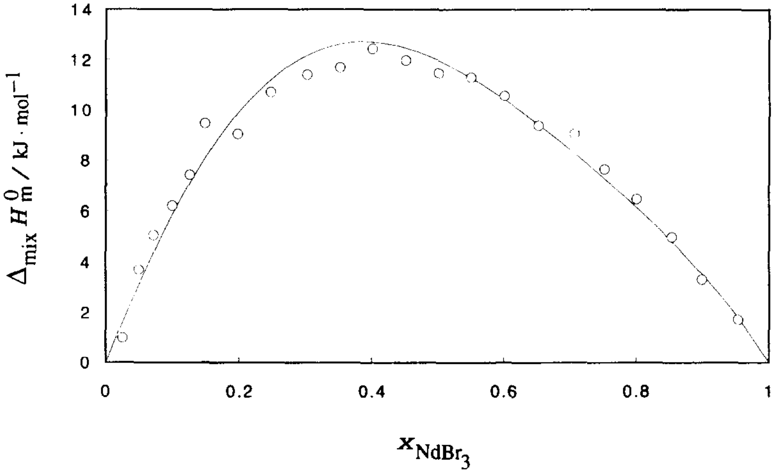

Fig. 5. Dependence of $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$ (KBr–NdBr$_3$) on composition.

this system Rb$_3$NdBr$_6$ is the phase with the highest melting temperature, but the precise value of this temperature is not given in the literature—it was estimated from the results in Ref. [10] as 1008 K. Enthalpies of mixing of this system (Table 5) again decrease (in comparison with the system KBr–NdBr$_3$) but this decrease is not as distinct as previously—a little more than 40% at the maximum (Fig. 7). The shape of the λ curve is well fitted by a 4th order polynomial (Fig. 8) with a minimum at $0.1 < x_{\mathrm{NdBr_3}} < 0.2$.

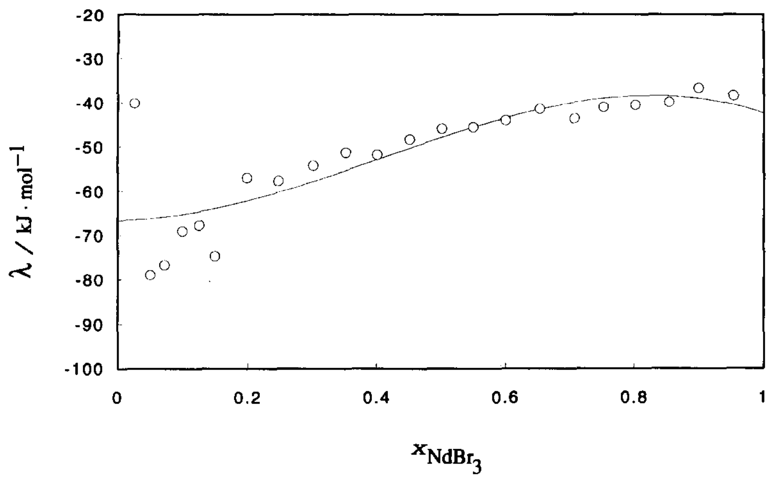

Fig. 6. Dependence of the λ parameter (KBr–NdBr$_3$) on composition, and its polynomial fitting (Table 1).

Table 5
Molar enthalpies of mixing, $\Delta_{mix}H^0_m$, and interaction parameter λ of the RbBr–NdBr$_3$ liquid system at 1063 K

x_{NdBr_3}	$-\Delta_{mix}H^0_m$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})	x_{NdBr_3}	$-\Delta_{mix}H^0_m$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})
0.024	2.01	−86.1	0.474	16.55	−66.4
0.050	4.22	−89.4	0.501	15.34	−61.4
0.075	6.11	−88.5	0.552	14.81	−59.9
0.101	8.05	−89.0	0.601	13.26	−55.3
0.123	10.63	−98.8	0.627	12.00	−51.3
0.150	12.58	−98.7	0.650	10.58	−46.5
0.175	14.40	−99.9	0.709	9.32	−45.1
0.201	16.08	−100.2	0.754	7.21	−38.9
0.252	16.84	−89.4	0.799	4.97	−31.0
0.303	17.47	−82.8	0.851	5.40	−42.5
0.351	17.41	−76.4	0.900	2.75	−30.6
0.399	17.83	−74.3	0.953	1.89	−41.9
0.453	16.87	−68.1			

3.5. CsBr–NdBr$_3$ System

There are only two compounds in the system CsBr–NdBr$_3$, i.e. Cs$_3$NdBr$_6$ and CsNd$_2$Br$_7$, both melting congruently. Cs$_3$NdBr$_6$ is the phase with the highest melting temperature (1040 K) [9]. The decrease in the mixing enthalpy (Table 6 and Fig. 9) was not very high—only two units in comparison with the RbBr–NdBr$_3$ system. The

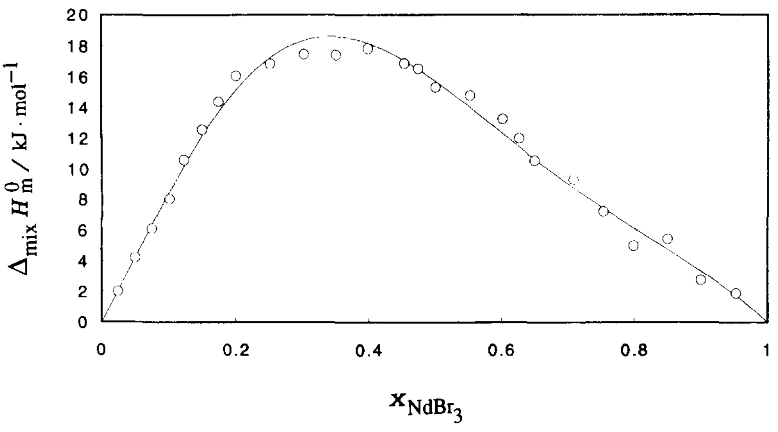

Fig. 7. Dependence of $\Delta_{mix}H_m^0$ (RbBr–NdBr$_3$) on composition.

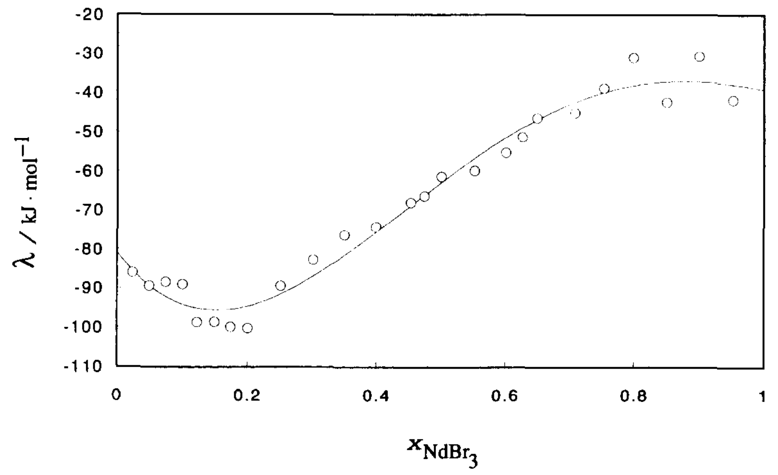

Fig. 8. Dependence of the λ parameter (RbBr–NdBr$_3$) on composition, and its polynomial fitting (Table 1).

minimum in the λ curve appears again at $0.1 < x_{NdBr_3} < 0.2$. The unexpected increase in λ close to $x_{NdBr_3} \approx < 1$ (Fig. 10) is the result of polynomial fitting only and has no justification in the measured values of λ.

4. Discussion

Bromide systems behave similarly to their chloride homologs and are characterized by negative enthalpies of mixing over the whole range of compositions. These enthal-

Table 6
Molar enthalpies of mixing, $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$, and interaction parameter λ of the CsBr–NdBr$_3$ liquid system at 1063 K

$x_{\mathrm{NdBr_3}}$	$-\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})	$x_{\mathrm{NdBr_3}}$	$-\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$/ (kJ mol^{-1})	λ/ (kJ mol^{-1})
0.039	2.93	−77.4	0.500	18.81	−75.2
0.051	5.08	−105.6	0.552	20.07	−81.1
0.097	11.95	−136.3	0.601	17.15	−71.5
0.153	14.30	−110.6	0.650	15.78	−69.3
0.199	16.83	−105.6	0.701	14.70	−70.1
0.257	17.98	−94.1	0.759	12.43	−67.8
0.297	19.16	−91.8	0.804	10.59	−67.1
0.354	20.08	−87.8	0.847	7.31	−56.4
0.400	19.66	−81.9	0.903	5.63	−64.5
0.450	19.79	−80.0	0.951	3.22	−69.1

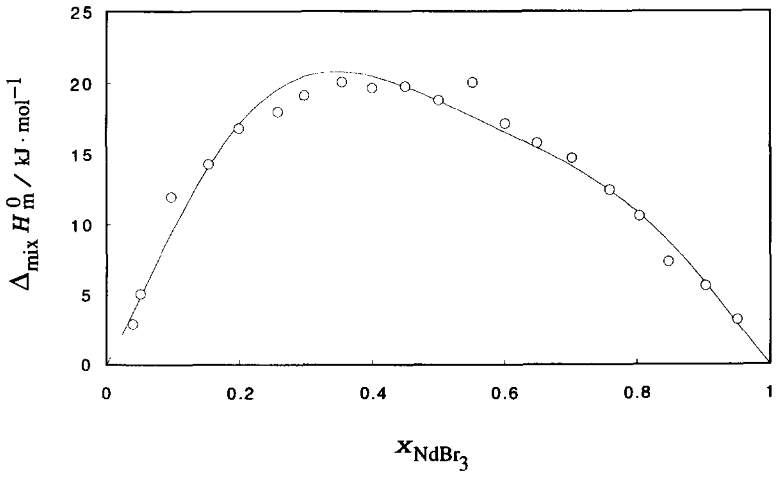

Fig. 9. Dependence of $\Delta_{\mathrm{mix}}H^0_{\mathrm{m}}$ (CsBr–NdBr$_3$) on composition.

pies decrease with a decrease in the ionic radius of the alkali metal. The LiBr–NdBr$_3$ system is an interesting exception (unfortunately, the system LiCl–NdCl$_3$ has not been investigated)—the enthalpy of mixing of this system is positive over a small range of compositions. Generally, for all the systems investigated a minimum of mixing enthalpy is shifted to compositions with $x_{\mathrm{NdBr_3}}$ varying from 0.3 to 0.4. This trend was observed also in neodymium chloride systems [2] and may be found in results published by Papatheodorou and Kleppa [9] as well as by Papatheodorou and Østvold [12] for cerium chloride and lanthanum chloride with alkali metal chlorides.

The data on mixing enthalpy are given in the literature for the NaBr–NdBr$_3$ system only [13]. They are very close to the results presented in this paper (Fig. 3).

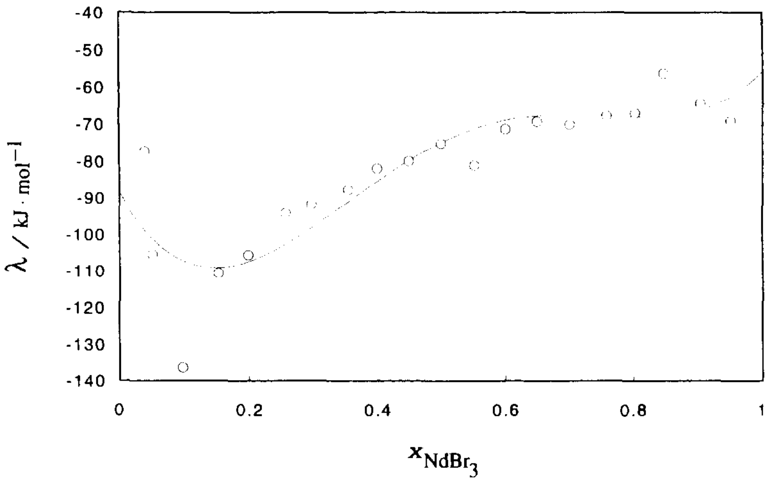

Fig. 10. Dependence of the λ parameter ($CsBr-NdBr_3$) on composition, and its polynomial fitting (Table 1).

Changes in the λ parameter with composition seems very regular in the series from the sodium bromide system to that with cesium (Figs 2, 4, 6, 8, 10). Irregularities in this dependence in the range x_{NdBr_3} from 0 to 0.2 for systems with sodium and potassium bromides transform to a broad minimum for rubidium and cesium bromide systems. For the $LiBr-NdBr_3$ system, values of the λ parameter are very close to 0 (in the range x_{NdBr_3} from 0.8 to 1, they were very small but positive) and the general shape of this dependence seems different, even if a minimum at $x_{NdBr_3} = 0.2$ is also observed.

There are many papers analyzing the possibilities of complexation in systems of alkali metal halides with lanthanide halides (or, more generally, trivalent metal halides) on the basis of spectroscopic, X-ray, or electrical conductivity data [12–22]; some have been discussed in previous papers [1,2]. The general conclusion coming from these papers is that octahedral complexes of the type AX_6^{3-} should exist in the halide melt of a trivalent A^{3+} cation with an alkali metal halide . Two other forms, $A_2Cl_{11}^{5-}$ and $A_3Cl_{10}^{-}$, are also possible in chloride melts.

Davis [25] introduced the dependence of the parameter λ on the size parameter δ_{12}:

$$\lambda = a(T,p,x) + b(T,p,x)\delta_{12} + c(T,p,x)\delta_{12}^2 \quad (2)$$

In the case $\delta_{12} = (d_1 - d_2)/d_1 d_2$, where $d_1 = r_{M^+} + r_{Cl^-}$ and $d_2 = r_{Ln^{3+}} + r_{Cl^-}$. So we defined $\Delta_f H_m^0$ as the enthalpy of mixing of the melt with the composition of the compound M_3NdBr_6 and presented its dependence of δ_{12} parameter in Fig. 11 together with similar dependence for chloride analogs. Generally, both dependencies are almost the same—the only small difference observed is at low values of the δ_{12} parameter (i.e. for lithium and sodium compounds). The dependence of $\Delta_f H_m^0$ on ionic radii may be fitted by an almost straight line for both types of compound (Fig. 12) and only very small curvature may be noticed. Generally, this dependence is the same as presented above for the δ_{12} parameter. Additionally, the values of $\Delta_f H_m^0$ for chloride and bromide compounds are summarized in Table 7.

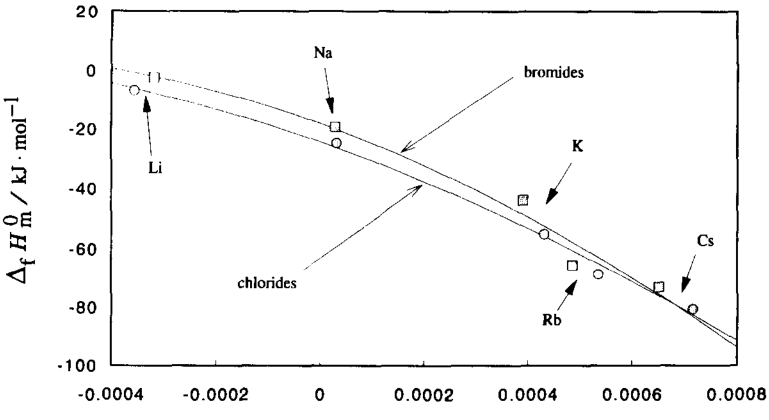

Fig. 11. Dependence of $\Delta_f H^0_m$ (M_3NdCl_6) and $\Delta_f H^0_m$ (M_3NdBr_6) on the δ_{12} parameter.

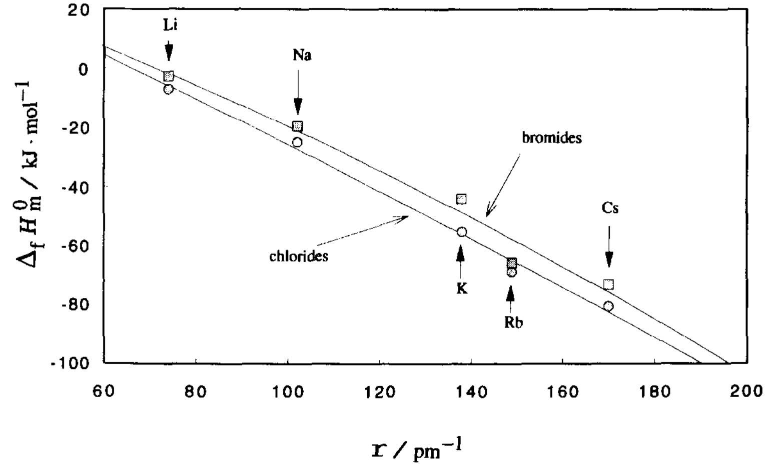

Fig. 12. Dependence of $\Delta_f H^0_m$ (M_3NdCl_6) and $\Delta_f H^0_m$ (M_3NdBr_6) on the ionic radius of the alkali metal cation.

The different coulombic interactions due to the different size of the halide anions seem the most important difference between the two sets of compounds M_3NdCl_6 and M_3NdBr_6. Evaluation of these can be expressed as a dependence of the formation enthalpy on the polarization force defined by the simple equation [26, 27]:

$$F_p = \frac{z_2}{d_2^2} - \frac{z_1}{d_1^2} \qquad (3)$$

where F_p is the polarization force (coulombic force divided by elementary charge of the electron); $z_2 = 3$ (valency of neodymium cation); $z_1 = 1$ (valency of alkali metal cation); $d_2 = r_{Nd^{3+}} + r_{Br^-}$ (or r_{Cl^-}); and $d_1 = r_{M^+} + r_{Br^-}$ (or r_{Cl^-}).

Table 7
Molar formation enthalpy of liquid M_3NdX_6 compounds (where M = alkali metal, X = Cl, Br), $\Delta_f H^0_m$ (M_3NdX_6(l) T/(kJ mol^{-1}), according to reaction: $3MX(l) + NdX_3(l) = $ "M_3NdX_6"(l). Ionic radii necessary for discussion have been included

MCl	$\Delta_f H^0_m$[2] (M_3NdCl_6(l) 1122 K)/ (kJ mol^{-1})	MBr	$\Delta_f H^0_m$ (M_3NdBr_6(l) 1122 K)/ (kJ mol^{-1})	r_{M^+}/pm[28] [a]
LiCl	−6.9 (1065 K)	LiBr	−2.6	74
NaCl	−24.8	NaBr	−19.4	102
KCl	−55.2 (1065 K)	KBr	−43.9	138
RbCl	−68.8	RbBr	−65.7	149
CsCl	−80.8	CsBr	−73.2	170

[a] $r_{Cl^-} = 181$ pm [28], $r_{Br^-} = 196$ pm [28], $r_{Nd^{3+}} = 99.5$ pm [28].

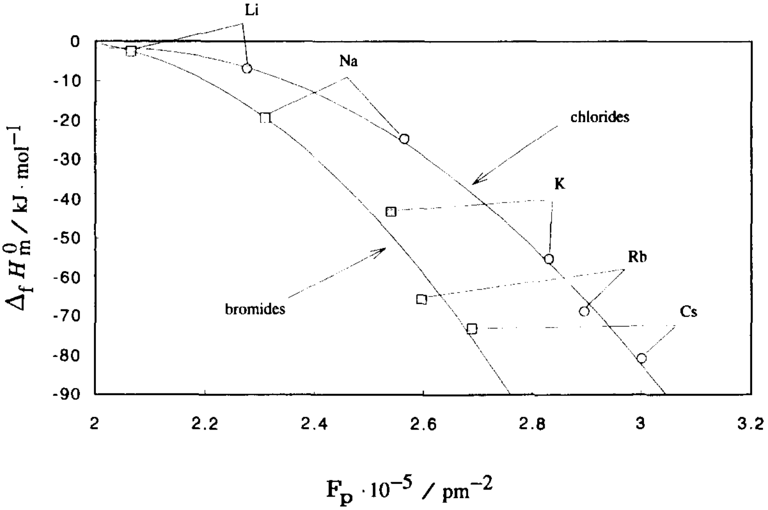

Fig. 13. Dependence of $\Delta_f H^0_m$ (M_3NdCl_6) and $\Delta_f H^0_m$ (M_3NdBr_6) on polarizing force.

Ionic radii are given in Table 7. The dependencies of the formation enthalpies of molten M_3NdCl_6 and M_3NdBr_6 compounds on the polarization force are presented in Fig. 13. This model seems the only one which clearly divides the chloride and bromide compounds into two branches. The lower polarization force of the bromide systems is associated with lower molar enthalpy of formation of M_3NdBr_6 compounds in comparison with the enthalpy of formation of their chloride analogs.

It has been stated above that many papers suggest that there is a predominance of the AX_6^{3-} anion in melts similar to those investigated here. This suggestion should be compared with the definite compounds which form in these systems—especially those which melt congruently. Table 8 gives this comparison. There are no data for the

Table 8
Compounds which exist in MBr–$NdBr_3$ systems, according to literature data

Compound	Melting or decomposition	T/K	Ref.
	There are no literature data on the system LiBr–$NdBr_3$		
	(The system NaBr–$NdBr_3$ is a simple eutectic $T_{eutectic} = 651$ K)		[9]
K_3NdBr_6	Congruently melting	933	[10]
KNd_2Br_7	Congruently melting	833	[10]
K_2NdBr_5	Peritectic decomposition	823	[10]
Rb_3NdBr_6	Congruently melting	1008	[10]
$RbNd_2Br_7$	Congruently melting	868	[10]
Rb_2NdBr_5	Peritectic decomposition	773	[10]
Cs_3NdBr_6	Congruently melting	1043	[9]
$CsNd_2Br_7$	Congruently melting	890	[9]

LiBr–$NdBr_3$ system but this system ought to be a simple eutectic similar to that of NaBr–$NdBr_3$ [9]. M_3NdBr_6 and MNd_2Br_7 are congruently melting compounds in the systems KBr–$NdBr_3$ [10], RbBr–$NdBr_3$ [10], and CsBr–$NdBr_3$ [9]. K_2NdBr_5 [9] and Rb_2NdBr_5 [10] are the only compounds which decompose peritectically. M_3NdBr_6 compounds melt at relatively high temperatures in comparison with MNd_2Br_7. Therefore, it may be assumed that complex anions $NdBr_6^{3-}$ dominate in melts of neodymium(III) bromide with alkali metal bromides (especially for systems with heavier alkali metal cations), although the possibility of the existence of other forms of complex should not be excluded.

References

[1] M. Gaune-Escard, A. Bogacz, L. Rycerz, and W. Szczepaniak, J. Therm. Anal., in press.
[2] M. Gaune-Escard, A. Bogacz, L. Rycerz, and W. Szczepaniak, Thermochim. Acta, 236 (1994) 67.
[3] M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, J. Alloys Compounds, 204 (1994) 189.
[4] M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, J. Alloys Compounds, 204 (1994) 193.
[5] M. Gaune-Escard, L. Rycerz, W. Szczepaniak and A. Bogacz, in preparation.
[6] M. Gaune-Escard, L. Rycerz and A. Bogacz, in preparation.
[7] M. Gaune-Escard, in: R. Gale and D.G. Lovering (Eds.), Molten Salt Techniques, Plenum Press, New York, London, 1991.
[8] K.K. Kelley, US Dept. of the Interior, Bureau of Mines, Washington D.C., Bull. 476, 1949.
[9] G. Vogel, Z. Anorg. Allg. Chem., 388(1) (1972) 43.
[10] R. Blachnik and A. Jaeger-Kasper, Z. Anorg. Allg. Chem., 461 (1980) 74.
[11] G.N. Papatheodorou and O.J. Kleppa, J. Phys. Chem., 78 (1974) 178.
[12] G.N. Papatheodorou and T. Ostvold, J. Phys. Chem., 78 (1974) 181.
[13] F. Dienstbach and R. Blachnik, Z. Anorg. Allog. Chem., 412 (1975) 97.
[14] G.N. Papatheodorou, Inorg. Nucl. Chem. Lett., 11 (1975) 438.
[15] G.N. Papatheodorou, J. Phys. Chem., 78 (1974) 1135.
[16] G.N. Papatheodorou, J. Phys. Chem., 66 (1977) 2893.
[17] M. Blander, M.L. Saboungi and A. Rahman, J. Phys. Chem., 85 (1986) 3995.
[18] J. Mochinaga, Y. Iwadate and K. Igarashi, J. Electrochem. Soc., 138 (1991) 3588.

[19] K. Igarashi, M. Kosaka, M. Ikeda and J. Mochinaga, Z. Naturforsch. Teil A: 45 (1990) 623.
[20] J. Mochinaga, Y. Iwadate and K. Fukushima, Mater. Sci. Forum, 73–75 (1991) 3588.
[21] M.P. Tosi, G. Pastore, M.L. Saboungi and D.L. Price, Phys. Scr., 39 (1991) 367.
[22] K. Fukushima, J. Mochinaga and Y. Iwadate, Proc. 25th Symp. Molten Salt Chemistry, November 18–19, 1993, Kobe, Japan.
[23] A. Matsuoka, K. Fukushima, J. Mochinaga, Y. Iwadate, M. Tomita and R. Takagi, Proc. 25th Symp. Molten Salt Chemistry, November 18–19, 1993, Kobe, Japan.
[24] K. Tanaka, K. Fukushima, J. Mochinaga and Y. Iwadate, Proc. 25th Symp. Molten Salt Chemistry, November 18–19, 1993, Kobe, Japan.
[25] H.T. Davis, J. Phys. Chem., 76 (1972) 1629.
[26] T. Forland, Norg. Tekn. Vidensk. Akad., 2 no. 4 (1957).
[27] J. Lumsden, Disc. Faraday Soc., 32 (1961) 138.
[28] A.G. Sharpe, Inorganic Chemistry, Longman , New York, 1986, pp. 146 and 659.