Calorimetric Investigation of NdI_3-MI Liquid Systems (M = Li, Na, K, Rb, Cs)

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The molar enthalpies of mixing, $\Delta_{\mathrm{mix}} H_{\mathrm{m}}$, of the liquid alkali metal iodide – neodymium iodide binary systems have been measured over the whole composition range at 1068 K with an accuracy of about 6%. The apparatus used was a Calvet – type high – temperature microcalorimeter. In all the systems under investigation the enthalpies of mixing are negative, with minimum values close to –1.1, –4.8, –10.3, –16.2, and –20.0 kJ mol^{-1} for LiI-NdI_3, NaI-NdI_3, KI-NdI_3, RbI-NdI_3, and CsI-NdI_3, respectively, at the mole fractions $x_{NdI_3} \simeq 0.30 - 0.40$ except the LiI-NdI_3 system, where it is at the NdI_3-rich compositions. The molar enthalpies of formation $\Delta_{\mathrm{form}}H_{\mathrm{m}}$ at 1068 K for M = Li, Na, K, Rb, and Cs, arising from the reaction 3 $MI_{(l)}$ + $NdI_{3(l)}$, are found to be –4.5, –17.5, –39.1, –59.9, and –73.3 kJmol^{-1}, respectively They are compared with the formation enthalpies determined previously for the (3MCl, $NdCl_3$) and (3MBr, $NdBr_3$) liquid mixtures. These enthalpies become less negative with increase of the radius of the halide ion.

Key words: Calorimetry; Mixing Enthalpy; Formation Enthalpy; Neodymium Iodide; Alkali Metal Iodides.

Introduction

Numerous investigations have been carried out to study the composition and thermochemistry of lanthanide chlorides and bromides and their binary systems with the alkali halides [1 - 13]. In contrast, our knowledge of lanthanide iodides is comparatively scanty. Beyond their fundamental interest for chemistry, a special interest arises for lanthanide iodides due to their importance for metal halide lamps [14, 15]. Thermochemical parameters of lanthanide iodides are required for the calculation of the chemical composition in some high-pressure discharge lamps to assist in the understanding, and hence prediction, of tungsten corrosion, silica corrosion and spectral output. The data are also needed for predicting the behaviour of doses by modelling multicomponent metal halide systems. In these rare earth iodides containing lamps the silicon iodides, formed by the reaction of the lanthanide iodides with the fused silica wall, are responsible for both the transport of silicon to the electrodes and the transport of silica along the wall. For a better description of the reaction of rare earth iodides with silica, reliable thermodynamic data of the rare earth silicates and of the mixing and complex formation of the lanthanide iodides with alkali metal iodides are necessary.

The lanthanide iodide – sodium iodide systems have attracted particular attention because of the volatility enhancement of the lanthanide iodide caused by vapour complexation of the following general type [16]:

$$MLnI_{3(s)} + NaI_{(g)} = Na_nLn_mI_{3m+n(g)}.$$

When such a reaction occurs inside the lamp, the sodium and lanthanide ion concentrations increase in the arc. Thereby, the efficiency for generation of radiation from excited Na ions in the high temperature arc column is improved, and in addition better colour production results due to enhancement of the Ln^{3+} ion concentration.

Knowledge of lanthanide iodide vapours has been increased by mass spectrometry [16 - 20] and Raman spectroscopy [21]. Among others, the NaI-DyI_3, NaI-

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ScI_3, NaI-ErI_3, NaI-TbI_3 and CsI-ScI_3 systems were investigated. The present work is a complementary investigation of the condensed phase. Some preliminary results were presented previously [22].

Experimental

Chemicals

NdI_3 was synthesised from Nd_2O_3 (99.9%) produced by the Chemistry Department of Lublin University (Poland) according to the method proposed by Kutscher and Schneider [23]. Neodymium oxide was dissolved in hot concentrated hydroiodic acid, mixed with ammonium iodide in the molar ratio 1:9 and placed into a quartz ampoule connected to the vacuum line. The mixture was gradually heated under vacuum up to 700 K (heating programme: 350 K - 0.25 h, 420 K - 3.25 h, 470 K - 1.25 h, 520 K - 4 h, 570 K - 3 h, and 700 K - 0.75 h). H_2O and NH_3 emanated during the drying process were removed by a vacuum line. At higher temperatures (starting from 520 K) unreacted NH_4I was sublimed. The crude NdI_3 was purified by sublimation in a quartz ampoule coated internally with a tantalum foil. Sublimation of NdI_3 was processed under reduced pressure ($\sim 10^{-2}$ Pa) at 1070 K. NdI_3 purified in this way was stored in sealed glass ampoules. Because of its extreme hygroscopicity, all handling of neodymium iodide and filling of experimental cells were performed in a glove-box filled with purified argon with a water content less than 1 ppm.

LiI, NaI, KI, RbI, and CsI were purchased from Merck (99.9% min.). They were dehydrated by slow continuous heating just above the melting point under an atmosphere of gaseous HI in quartz ampoules. Excess HI was removed by bubbling argon through the melt. The salts were then handled in the glove-box and stored in sealed glass ampoules.

Calorimetric Procedure

The mixing experiments were performed under argon at atmospheric pressure. The Calvet-type high temperature microcalorimeter, mixing devices and experimental method have been described in detail in [3 - 4]. For every system under investigation, one component was weighed in the glove-box within $\pm 10^{-5}$ g and placed in the break-off quartz ampoule. The other component, weighed in the same way, was placed in a quartz crucible. The break-off ampoule was evacuated under controlled argon pressure in order to obtain a pressure of 1 atmosphere at the temperature of the experiment. It was then welded to a quartz tube, which could be moved up and down the calorimetric cell through a special gas - tight ring. The calorimetric cell was filled with argon and introduced into the Calvet calorimeter together with a reference cell. After thermal stabilisation of the system, the ampoule was broken off against the inner break-off tip at the bottom of the quartz crucible, and the thermal effect resulting from mixing was recorded.

However, because of the reported reaction of NdI_3 with quartz, preliminary experiments have been performed in order to confirm that the above method was suitable. In these tests, neodymium iodide was contained in a molybdenum crucible and blank mixing experiments were performed with an empty break-off quartz ampoule. No visible thermal effects were observed on the corresponding thermograms after breaking off the quartz ampoules, nor after several subsequent drops of small quartz pieces. These observations confirmed that, at the experimental temperature, quartz corrosion by NdI_3 has a negligible influence on enthalpy of mixing. The same conclusion was obtained from DSC experiments, where the melting enthalpy and temperature of NdI_3 were determined in quartz ampoules. After several successive runs, no evolution of the thermogram shapes was observed, and an identical temperature and enthalpy of melting were obtained. This confirms again that quartz corrosion is very small and can be neglected in mixing enthalpy measurements. Therefore, in the mixing experiments, NdI_3, which is the most hygroscopic salt, was put into a quartz break-off ampoule while a quartz crucible was used as container for the alkali metal iodides.

Calibration of the calorimeter was performed with NIST α-alumina. After the mixing experiments, pieces of α-alumina (30 - 100 mg) were dropped into the melt and the corresponding enthalpy increments were measured. The experimental uncertainty on calibration was about 3%. The uncertainty of the enthalpy of mixing data is estimated to be 6%, since these data were obtained from independent experiments.

Results

All calorimetric experiments were carried out at 1068 K. According to the phase diagrams reported in

Table 1. Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the NdI_3-LiI liquid system at 1068 K.

x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}	x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}
0.0501	0.215	4.518	0.4461	0.472	1.910
0.1050	0.398	4.235	0.5014	0	0
0.1527	0.812	6.276	0.5044	0.630	2.520
0.1993	1.269	7.952	0.5539	–0.198	–0.801
0.2507	1.244	6.622	0.6564	–0.666	–2.953
0.2959	1.084	5.203	0.6976	–1.062	–5.034
0.3570	0.705	3.071	0.8291	–0.847	–5.978
0.3919	0641	2.690			

Table 2. Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the NdI_3-NaI liquid system at 1068 K.

x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}	x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}
0.0474	1.160	25.690	0.5046	4.820	19.282
0.1015	3.048	33.422	0.5405	4.560	18.360
0.1546	3.220	24.637	0.6457	4.152	18.149
0.2428	4.462	24.270	0.7137	3.706	18.137
0.2585	4.271	22.282	0.7985	2.916	18.123
0.2924	4.510	21.798	0.8734	1.875	16.957
0.4231	4.739	19.415			

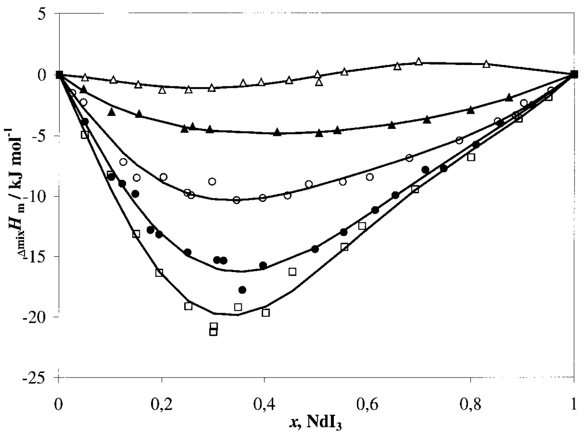

Fig. 1. Experimental mixing enthalpies $\Delta_{mix}H_m$ in the NdI_3-MI liquid systems. Open triangles: NdI_3-LiI, black triangles: NdI_3-NaI, open circles: NdI_3-KI, black circles: NdI_3-RbI, open squares: NdI_3-CsI.

[24], the components and mixtures studied are liquid over the whole composition range at this temperature.

The experimental enthalpies obtained for the systems under investigation are presented in Tables 1 - 5 and plotted vs. composition in Figure 1.

Table 3. Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the NdI_3-KI liquid system at 1068 K.

x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}	x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}
0.0255	1.489	59.920	0.4434	9.984	40.454
0.0472	2.248	49.986	0.4848	9.039	36.189
0.1242	7.188	66.082	0.5512	8.852	35.783
0.1502	8.500	66.593	0.6033	8.452	35.315
0.2023	8.444	52.325	0.6799	6.880	31.612
0.2488	9.743	52.130	0.7765	5.428	31.277
0.2563	9.946	52.180	0.8515	3.851	30.455
0.2973	8.833	42.281	0.8862	3.359	33.307
0.3447	10.370	45.909	0.9023	2.351	26.669
0.3952	10.191	42.637	0.9551	1.328	30.967

Table 4. Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the NdI_3-RbI liquid system at 1068 K.

x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}	x_{NdI_3}	$-\Delta_{mix}H_m$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}
0.050	3.841	83.305	0.3962	15.764	67.175
0.1015	8.426	84.885	0.4973	14.424	57.316
0.1223	8.982	84.946	0.5531	13.027	52.161
0.1476	9.828	84.628	0.6139	11.187	47.061
0.1771	12.823	83.771	0.6530	9.950	44.153
0.1938	13.197	83.079	0.7105	7.850	40.489
0.2495	14.691	79.861	0.7461	7.741	38.615
0.3070	15.322	75.410	0.8092	5.772	36.058
0.3198	15.375	74.305	0.8572	4.021	34.761
0.3565	17.798	70.971	0.9193	2.505	33.854

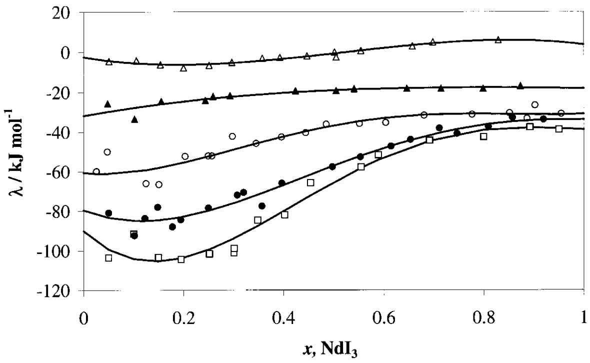

Fig. 2. Variation of the interaction parameter λ with concentration in NdI_3-MI liquid systems. Open triangles: NdI_3-LiI, black triangles: NdI_3-NaI, open circles: NdI_3-KI, black circles: NdI_3-RbI, open squares: NdI_3-CsI.

The interaction parameter,

$$\lambda = \Delta_{mix}H_m / x_{NdI_3}(1 - x_{NdI_3}),$$

Table 5. Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ and interaction parameters λ of the NdI_3-CsI liquid system at 1068 K.

$x_{\mathrm{NdI_3}}$	$-\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}	$x_{\mathrm{NdI_3}}$	$-\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}
0.051	4.922	103.621	0.4020	19.686	81.900
0.1002	8.252	91.526	0.4533	16.292	65.741
0.1492	13.134	103.467	0.5546	14.244	57.664
0.1945	16.384	104.577	0.5887	12.503	51.637
0.2515	19.150	101.728	0.6908	9.468	44.327
0.3005	21.263	101.156	0.7996	6.812	42.511
0.3011	20.804	98.860	0.8920	3.621	37.587
0.3479	19.215	84.698	0.950	1.845	38.842

Table 6. Least-squares coefficients for the equation of λ for the liquid alkali iodide – neodymium iodide mixtures: $\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4$, in kJ mol^{-1} ($x$ = mole fraction of NdI_3).

System	A kJ mol^{-1}	B kJ mol^{-1}	C kJ mol^{-1}	D kJ mol^{-1}	E kJ mol^{-1}
LiI-NdI_3	–2.43	–43.09	137.07	–87.86	–
NaI-NdI_3	–31.76	43.14	–41.18	11.67	–
KI-NdI_3	–60.57	–24.28	342.29	–505.56	217.16
RbI-NdI_3	–79.50	–101.21	530.23	–568.91	185.62
CsI-NdI_3	–90.07	–236.47	1071.31	–1216.10	432.49

which represents the energetic asymmetry in a melt, was calculated. The limiting interaction parameter $\lambda_{(0)}$, i. e. λ at infinite dilution of NdI_3 in alkali metal iodides, was determined in separate experiments. For each system, with the exception of NdI_3-LiI, an average value was taken from at least 5 measurements. The corresponding $\lambda_{(0)}$ values are –31.76, –60.57, –79.50, and –90.07 kJmol^{-1} for NaI, KI, RbI, and CsI, respectively. This limiting parameter for the NdI_3-LiI system was calculated from the general dependence of λ on concentration. In Fig. 2, the interaction parameters are plotted versus the composition of the mixture. For all systems, these λ values are also included in Tables 1 - 5. For each system, the values of λ were fitted by the least squares method to a polynomial of the form

$$\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4,$$

where x is the mole fraction of NdI_3. Experimentally determined values $\lambda_{(0)}$ were used as constraints in this fitting. The polynomial coefficients are presented in Table 6.

Discussion

The enthalpy of mixing becomes more negative with increasing size of the alkali metal cation. For the NdI_3-LiI binary system, at concentrations rich in NdI_3, positive enthalpies of mixing were observed.

In all systems, the minimum enthalpy occurs at compositions $x_{\mathrm{NdI_3}} \approx 0.3$ - 0.4, similar to those found in the neodymium chloride [5] and bromide [25] systems. However, these values in the iodide mixtures (–1.1, –4.8, –10.3, –16.2 and –19.7 kJ mol^{-1}, in the sequence LiI to CsI, respectively) are smaller, in absolute magnitude, than those in the previous systems.

Figure 2 presents the dependence of the interaction parameter λ on the concentration of neodymium iodide for all systems under investigation. This dependence, not very far from linear for the systems with LiI and NaI, becomes more complicated for systems with heavier alkali metal iodides. Firstly, the relative changes of λ are significantly larger in the alkali iodide-rich region. Secondly, a broad minimum, still not clearly marked in the system with KI, appears at $x_{\mathrm{NdI_3}}$ close to 0.2 in the systems with RbI and CsI. These trends have been observed previously in the $NdCl_3$-MCl and $NdBr_3$-MBr liquid systems [5, 25]. Taking into account literature data concerning the possibility of complex formation in molten salts and their structure [1, 2, 26 - 29] we postulated the formation of octahedral complexes $NdCl_6^{3-}$ and $NdBr_6^{3-}$ in the corresponding melts. Unfortunately, no structural information is available in literature on lanthanide iodide – alkali metal iodide melts. However, looking at the dependence of λ on neodymium iodide concentration, which is very similar to that for the chloride and bromide systems, it is likely that similar octahedral complexes NdI_6^{3-} may exist in NdI_3-MI melts.

As postulated in YCl_3-MCl systems [30], the shift of the minimum of λ towards NdI_3 compositions smaller than 0.25 ($x_{\mathrm{NdI_3}} \approx 0.2$) in the KI, RbI and CsI systems can be attributed to the increasing polarising strength of the solvent cation and/or interactions between NdI_6^{3-} species in these melts. The larger volume of the NdI_6^{3-} ion and the large number of I^- anions associated with the Nd^{3+} cation increases the probability of having two of these species as nearest neighbours at concentration below $x_{\mathrm{NdI_3}} = 0.25$. Consequently, the NdI_6^{3-} ions will share iodides, the octahedra will be distorted, and the Nd-I interactions will be weakened. These effects are expected to shift the minimum of λ to mol fractions of NdI_3 below 0.25.

Several semi-empirical approaches have been made to correlate interactions in molten salt mixtures to physicochemical parameters of the mixed

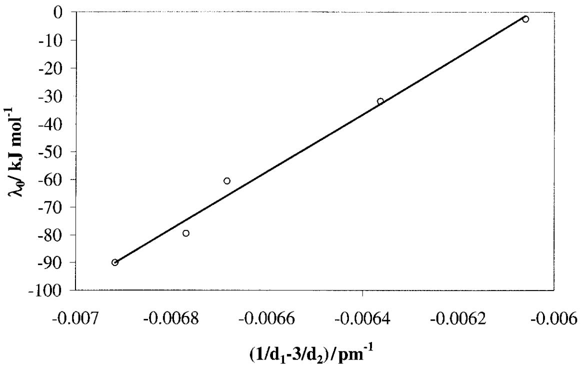

Fig. 3. Dependence of the limiting interaction parameter $\lambda_{(0)}$ on the "modified size parameter" δ'_{12} in the NdI_3-MI liquid systems.

salts [31]. Except the most simple, charge-symmetrical common anion systems, the enthalpy interaction parameter λ varies strongly with composition and eventually shows a minimum located around 0.33 and 0.25 for AX-BX_2 and AX-BX_3 charge-asymmetrical mixtures. A correlation of this interaction parameter λ with energetic factors related to characteristic ionic distances was made. However, there is no universal procedure. It depends not only on the nature of systems, but also on the authors. The interaction parameter, evaluated at an *ad hoc* composition (λ_0, $\lambda_{0.33}$ or $\lambda_{0.25}$) is correlated to size parameters as diverse as

- ionic radii (cationic r_{A+} and anionic r_{X-}),
- ionic distances ($d_1 = r_{A+} + r_X$, $d_2 = r_{Bn+} + r_{X-}$),
- size parameter ($\delta_{12} = (d_1 - d_2)/d_1d_2$),

that appear as variables in linear or quadratic equations.

For instance, in a number of divalent-monovalent mixtures [32 - 37], the limiting interaction parameter for $x_2 \rightarrow 0$ (i. e. λ_0) varies linearly with the size parameter ($d_1 - d_2$) or δ_{12}:

$$\lambda_0 = \alpha + \beta(d_1 - d_2)$$

Measurements on a series of lanthanide halide – alkali halide binary melts [1 - 2, 38] and of certain binary fluoride melts [39 - 41] have indicated that a quadratic term [2] should be added to the above equation for suitable representation of calorimetric data:

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

Here a, b and c are functions of temperature, pressure, and composition.

Table 7. Molar enthalpy of formation $\Delta_{\mathrm{form}}H_{\mathrm{m}}$ (3MX, NdX_3, l, T) kJ mol^{-1} of the liquid mixtures according to the reaction 3 MX(l) + NdX_3(l) = (3MX, NdX_3)(l), where M = Li, Na, K, Rb, Cs; X = Cl, B, I.

MX	$\Delta_{\mathrm{form}}H_{\mathrm{m}}$ (3MCl, $NdCl_3$) kJ mol^{-1}	$\Delta_{\mathrm{form}}H_{\mathrm{m}}$ (3MBr, $NdBr_3$) kJ mol^{-1}	$\Delta_{\mathrm{form}}H_{\mathrm{m}}$ (3MI, NdI_3) kJ mol^{-1}	r_{M+} pm [42][a]
LiX	–6.9 (1065 K)	–2.6 (1122 K)	–4.5 (1068 K)	74
NaX	–24.8 (1122 K)	–19.4 (1122 K)	–17.5 (1068 K)	102
KX	–55.2 (1065 K)	–43.9 (1122 K)	–39.2 (1068 K)	138
RbX	–68.8 (1122 K)	–65.7 (1122 K)	–59.9 (1068 K)	149
CsX	–80.8 (1122 K)	–73.2 (1122 K)	–74.6 (1068 K)	170

[a] r_{Cl-} = 181 pm , r_{Br-} = 196 pm , r_{I-} = 216 pm, $r_{Nd^{3+}}$ = 99.5 pm [42].

The ionic charge has also been used, and either ionic potentials z_i/r_i [41] (in this case the interaction parameter is a function of their difference, also called relative ionic potential) or a "modified size parameter" [30] $\delta'_{12} = (z_1/d_1) - (z_2/d_2)$ has been employed.

In Fig. 3 we give a plot of the limiting enthalpy interaction parameter vs. a "modified size parameter" δ'_{12} for the family of NdI_3-MI liquid mixtures. A least-squares treatment of the experimental data yields

$$\lambda_{(x\rightarrow 0)} = \left[625.9 + 103489\left(\frac{1}{r_{M^+} + r_{I^-}} - \frac{3}{r_{N^{3+}} + r_{I^-}}\right) \pm 3.6\right] \mathrm{kJmol}^{-1}, r \text{ in pm.}$$

As the existence of NdI_6^{3-} is very likely in the systems under investigation, we have calculated the formation enthalpies of liquid mixtures at $x_{NdI_3} = 0.25$, according to the reaction

$$3\ MI_{(l)} + NdI_{3(l)} = (3\ MI, NdI_3)_{(l)}.$$

The results are presented in Table 7, together with the corresponding values for the chloride and bromide systems.

They illustrate clearly the effect of alkali cations. The formation enthalpy of (3 MX, NdX_3) liquid mixtures increases as the size of the alkali cation increases. This corresponds to an increase in the proportion of the complex ions formation. The role of the alkali halides is to provide additional halide ions to enable Nd^{3+} to expand its coordination shell. But there is a competition between M^+ and Nd^{3+} for X^- in the ionic environment, which is well accounted for by the "modified size parameter" $\delta'_{12} = (z_1/d_1) - (z_2/d_2)$. The result of this competition depends on the

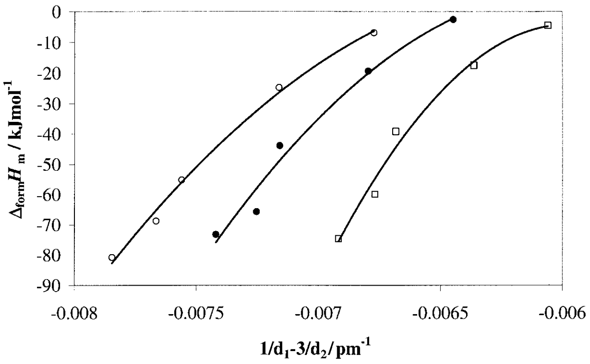

Fig. 4. Dependence of the formation enthalpy of (3MX, NdX$_3$) liquid mixtures on the "modified size parameter" δ'_{12}. Open circles: chloride systems, black circles: bromide systems, open squares: iodide systems.

relative attracting power of the alkali ion. Li$^+$ is the most halide attracting and Cs$^+$ the least. The complex ion formation in MX-NdX$_3$ binary systems will therefore be governed by the radius of the alkali metal ion. Thus the addition of CsX to NdX$_3$ favours complex ion formation more than addition of RbX, and results in a larger enthalpy of formation, etc... Indeed, in the NdX$_3$-MX systems the complex formation enthalpy increases from lithium to caesium. This formation enthalpy is quite small in the presence of the small highly polarising Li$^+$ ion, which is sufficiently polarising to distort the complexes that would be formed and to render them unstable.

The results presented in Table 7 also indicate that the formation enthalpy of (3 MX, NdX$_3$) liquid mixtures decreases from the chloride to the iodide systems for the same alkali metal cation. This phenomenon is due to the different ionic radii of the halide ions, which change the coulombic interaction in the melt (competition between Nd^{3+} and M$^+$ for halide ion).

To take the influence of the halide ion into account, it has been suggested [30] that the interaction parameter λ could be fitted to a second order polynomial in δ'_{12}. Accordingly, a similar equation was used by us to represent $\Delta_{form}H_m$ of (3 MX, NdX$_3$) of the liquid mixtures. Figure 4 shows that a smooth variation is obtained for each of the chloride, bromide and iodide systems.

The larger the halide ion, the smaller the absolute value of the "modified size parameter" δ'_{12} and the coulombic interactions in the melt from chloride to iodide. Indeed, the mixing enthalpy of the NdX$_3$-MX liquid mixtures decreases from chlorides to iodides, as does the formation enthalpy of the (3 MX, NdX$_3$) liquid mixtures.

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