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Calorimetric investigation of $NdCl_3$–MCl liquid mixtures (where M is Na, K, Rb, Cs)

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Abstract

The molar enthalpies of mixing $\Delta_{mix}H_m$ in the liquid NaCl–$NdCl_3$, KCl–$NdCl_3$, RbCl–$NdCl_3$ and CsCl–$NdCl_3$ binary systems have been measured over the whole composition range at 1124, 1065, 1122 and 1122 K, respectively, with an accuracy of about 6%. The apparatus used was a Calvet-type high-temperature microcalorimeter and mixing of the two liquid components was obtained by the break-off ampoule technique. In the investigated systems, the enthalpies of mixing are negative with minimum values at about −5.7, −16.6, −20.2 and −23.4 kJ mol^{-1}, respectively, at $x_{NdCl_3} = 0.4$. These values are almost identical, within the experimental accuracy, to those in other previously investigated MCl–$LnCl_3$ mixtures. The molar enthalpies of formation $\Delta_f H_m(K_3NdCl_6, l, 1065)/\mathrm{kJ\,mol^{-1}}$, $\Delta_f H_m(Rb_3NdCl_6, l, 1122)/\mathrm{kJ\,mol^{-1}}$ and $\Delta_f H_m(Cs_3NdCl_6, l, 1122)/\mathrm{kJ\,mol^{-1}}$, according to the reaction $3\,MCl(l) + LnCl_3(l) = M_3LnCl_6(l)$, are equal to −55.2, −68.8 and −80.8 kJ mol^{-1}, respectively. The least-squares coefficients A, B, C, D, E of the equation for the interaction parameter $\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4$ (in kJ mol^{-1}) are presented.

INTRODUCTION

The thermodynamics of mixtures of $NdCl_3$ with alkali chlorides play an important role in the production of neodymium by molten salt electrolysis and by metallothermic reduction.

We have initiated a general research program on the thermodynamic properties and electrical conductivities of MCl–$LnCl_3$ liquid mixtures (where M is Li, Na, K, Rb, Cs; and Ln is lanthanide). The definite compounds M_3LnCl_6, which only exists for the heavier alkali metals (where M is K, Rb, Cs), have been investigated by several experimental techniques, both in the solid and in the liquid state. Electrical conductivities [1], the temperatures and enthalpies of phase transition, and heat capacities [2] have been determined.

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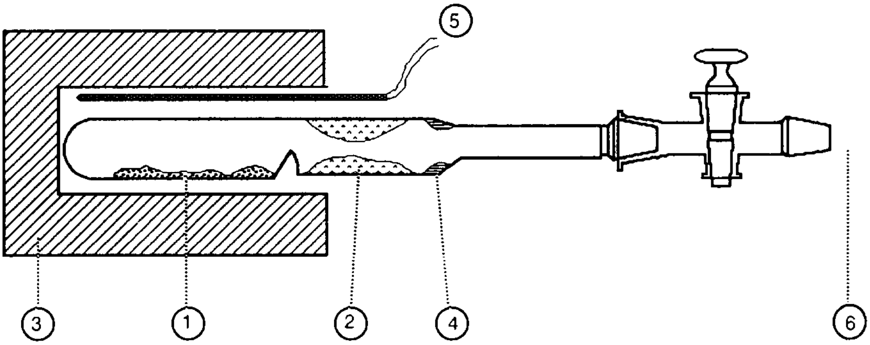

Fig. 1. Scheme of the distillation ampoule for purification of $NdCl_3$: 1, distillation residue (NdOCl); 2, pure $NdCl_3$; 3, furnace; 4, volatile impurities; 5, Pt/Pt–Rh thermocouple; 6, to vacuum.

The present work is part of the thermodynamic research performed on $NdCl_3$–MCl systems and it follows the preliminary calorimetric investigations recently presented [3, 4]. It reports the experimental enthalpies of mixing of the NaCl–$NdCl_3$, KCl–$NdCl_3$, RbCl–$NdCl_3$ and CsCl–$NdCl_3$ mixtures. Also the enthalpies of formation at the composition $x_{NdCl_3} = 0.25$ have been determined for all the liquid $NdCl_3$–MCl melts (where M is Li, Na, K, Rb, Cs).

EXPERIMENTAL

Chemicals

$NdCl_3$ was synthesized from Nd_2O_3 (99.9%) produced by the Chemistry Department at the University of Lublin (Poland). The main steps of this synthesis are: dissolution of Nd_2O_3 in concentrated HCl; crystallization of the hydrate $NdCl_3 \cdot 6H_2O$; partial dehydration of $NdCl_3 \cdot 6H_2O$ to obtain $NdCl_3 \cdot H_2O$; preparation of anhydrous neodymium chloride; and purification by distillation.

$NdCl_3 \cdot 6H_2O$ was mixed with NH_4Cl (10% of the $NdCl_3 \cdot 6H_2O$ mass) and heated progressively up 450 K over 12 h, under reduced pressure ($\approx$270 Pa). At this stage, the initial mixture was converted into $NdCl_3 \cdot H_2O$ and NH_4Cl. It was then placed in an alumina crucible inside a quartz tube and heated under gaseous HCl atmosphere up to the melting point of $NdCl_3$ and then to 1100 K. Gaseous HCl was passed through the melt for 10 min and then argon was passed through for 10 min. The $NdCl_3$ obtained in this way was transferred into a glove-box and stored in gas-tight bottles. This product still contained traces of NdOCl, the oxychloride. NdOCl, less volatile than $NdCl_3$, can be removed by distillation. Raw $NdCl_3$ was placed in a quartz ampoule (Fig. 1) and distillation was performed under reduced pressure (≈ 0.1 Pa) with progressive heating up to 1170 K. During distillation, the temperature did not exceed 1200 K because of the slow reaction of $NdCl_3$ with the SiO_2 container at 1270 K, resulting in NdOCl formation [5]. After distillation, the tube was cooled down and sealed. Impurities were removed in the glove-box and the remaining product put in another quartz ampoule for a further distillation. After this second distillation, it was remelted in a quartz crucible under dry gaseous HCl atmosphere and, finally, excess HCl was removed from the melt by argon. In order to facilitate further handling, these chemicals, which are very sensitive to moisture, were ground in the glove-box and stored in ampoules sealed under dry argon atmosphere. The $NdCl_3$ obtained in this way, after two successive distillations, was of high grade (min. 99.9%).

The MCl alkali chlorides (where M is Li, Na, K, Rb, Cs) were Merck Suprapur reagents (min. 99.9%). Before their use in the calorimeter, the alkali chlorides were purified and treated by progressive heating up to fusion under gaseous HCl atmosphere. Excess HCl was removed from the melt by argon. They were stored in the glove-box.

Procedure

The mixing experiments were all of the simple liquid–liquid type, performed under atmospheric pressure. The calorimetric apparatus, a Calvet-type high-temperature microcalorimeter, the mixing devices used and the experimental methods adopted have all been described in some detail elsewhere [6]; only the experimental cell is shown in Fig. 2. For any system under investigation, the most volatile component was weighed in the glove-box within 10^{-5} g and placed in the break-off quartz ampoule. The other component, weighed in the same conditions, was placed in a quartz crucible. The break-off ampoule was evacuated under controlled argon pressure in order to obtain the proper pressure at the temperature of the enthalpy-of-mixing experiment. It was then welded to a quartz tube as indicated in Fig. 2. This quartz tube and its attached ampoule could be moved up and down through a special gas-tight ring. Argon entered the calorimetric cell trhough the orifice drilled at the end of the quartz tube during welding. After thermal equilibrium the ampoule was broken off and the thermal effect resulting from mixing was recorded. Calibration of the calorimeter was performed with NIST α-alumina [7]; known amounts of alumina were dropped directly into the melt. Integration of the surface of the thermograms was done automatically by a computer.

RESULTS

Calorimetric experiments were carried out at 1124 K ($NaCl–NdCl_3$), 1065 K ($KCl–NdCl_3$) and 1122 K ($RbCl–NdCl_3$ and $CsCl–NdCl_3$). The

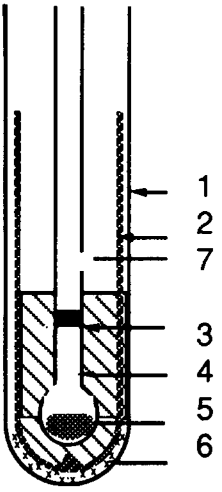

Fig. 2. Calorimetric cell: 1, quartz tube; 2, quartz crucible; 3, less volatile component; 4, break-off ampoule; 5, more volatile component; 6, kaowool plug; 7, orifice for argon flow.

experimental enthalpies of mixing are given in Tables 1 to 4 and are plotted against composition in Figs. 3 to 6. In evaluating the results of our measurements, all uncertain experimental data were disregarded as when evaporation or poor homogeneity of the melt during mixing were noticed.

The calibration of the calorimeter, performed with α-Al_2O_3, was obtained with an accuracy of about 3%. Therefore, molar enthalpies of mixing were obtained with an accuracy of about 6%, because they are measured during separate experimental runs.

Figures 7 to 10 indicate the composition dependence of the interaction parameter λ for all the systems under investigation

$$\lambda = \Delta_{\text{mix}}H_{\text{m}}/x_{\text{MCl}}x_{\text{NdCl}_3} \quad (1)$$

which is representative of the energetic asymmetry in these melts.

TABLE 1

Molar enthalpies of mixing $\Delta_{\text{mix}}H_{\text{m}}$ and interaction parameters λ of the NaCl–$NdCl_3$ liquid system at $T = 1124$ K

x_{NdCl_3}	$-\Delta_{\text{mix}}H_{\text{m}}$/kJ mol^{-1}	λ/kJ mol^{-1}	x_{NdCl_3}	$-\Delta_{\text{mix}}H_{\text{m}}$/kJ mol^{-1}	λ/kJ mol^{-1}
0.0511	1.65	−34.01	0.576	6.15	−25.19
0.0985	2.92	−32.89	0.651	5.56	−24.45
0.148	3.79	−30.01	0.702	5.40	−25.84
0.200	5.79	−36.20	0.751	4.24	−22.71
0.275	6.06	−30.38	0.800	3.52	−21.99
0.350	6.32	−27.77	0.849	2.99	−23.39
0.424	6.46	−26.43	0.899	1.65	−18.29
0.499	6.74	−26.94	0.950	0.94	−19.89

TABLE 2

Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the KCl–$NdCl_3$ liquid system at $T = 1065$ K

x_{NdCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}	x_{NdCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}
0.0899	5.87	−71.75	0.427	16.70	−68.26
0.129	8.20	−73.08	0.478	16.13	−64.64
0.161	9.03	−66.98	0.501	16.80	−67.20
0.191	10.74	−69.62	0.510	16.69	−66.79
0.204	10.76	−66.29	0.560	15.37	−62.38
0.226	13.28	−76.01	0.650	13.24	−58.21
0.251	13.80	−73.39	0.654	13.08	−57.76
0.278	15.30	−76.14	0.688	13.44	−62.59
0.307	16.30	−76.67	0.694	10.71	−50.47
0.350	16.00	−70.30	0.749	9.69	−51.56
0.356	16.39	−71.49	0.829	6.57	−46.24
0.397	17.46	−72.91	0.838	6.29	−46.36
0.401	15.66	−65.21	0.922	3.66	−50.71
0.424	14.90	−61.03	0.943	2.72	−50.85

For each system listed in Table 5, the values of λ were fitted by the method of least squares to polynomials of x_{NdCl_3}.

Several experiments were also conducted in order to determine accurately the enthalpy of formation at $x_{NdCl_3} = 0.25$ for all the MCl–$NdCl_3$ systems (M is Li, Na, K, Rb, Cs), i.e. the enthalpy variation related to the reactions

TABLE 3

Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the RbCl–$NdCl_3$ liquid system at $T = 1122$ K

x_{NdCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}	x_{NdCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}
0.025	2.340	−96.38	0.400	20.87	−86.96
0.049	4.190	−90.09	0.429	20.43	−83.42
0.075	6.230	−89.58	0.448	19.90	−80.47
0.101	8.800	−97.17	0.490	18.72	−74.91
0.123	9.770	−90.63	0.526	17.78	−71.31
0.150	11.46	−89.83	0.553	17.05	−68.97
0.200	14.88	−93.17	0.599	16.51	−68.75
0.250	17.20	−91.73	0.656	15.25	−67.60
0.251	17.54	−93.42	0.702	12.88	−61.56
0.274	18.19	−91.53	0.752	11.77	−63.13
0.299	19.63	−93.67	0.799	9.140	−56.87
0.326	20.69	−94.18	0.852	8.100	−64.06
0.352	20.66	−90.56	0.901	5.280	−59.19
0.374	20.59	−87.91	0.950	2.680	−56.74

TABLE 4

Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the CsCl-NdCl$_3$ liquid system at $T = 1122$ K

x_{NdCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}	x_{NdCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}
0.025	2.870	−116.83	0.400	23.78	−99.06
0.050	5.750	−121.28	0.403	24.58	−102.17
0.100	10.35	−114.59	0.438	23.23	−94.35
0.148	14.79	−117.03	0.442	22.36	−90.66
0.201	16.92	−105.32	0.446	21.50	−87.01
0.250	19.45	−103.71	0.498	21.89	−87.57
0.250	20.88	−111.27	0.598	19.12	−79.54
0.250	19.76	−105.30	0.705	16.39	−78.84
0.251	20.06	−106.80	0.737	14.81	−76.40
0.252	20.17	−106.92	0.769	12.94	−72.86
0.299	22.09	−105.48	0.820	9.86	−66.83
0.300	22.40	−106.73	0.864	8.68	−73.65
0.349	23.52	−103.46	0.910	6.80	−83.14
0.360	23.94	−103.96	0.941	3.92	−70.87
0.398	22.98	−95.93			

$$3\,MCl(l) + NdCl_3(l) \rightarrow \text{“}M_3NdCl_6\text{”}(l)$$

The notation “M_3NdCl_6” was adopted because there is no compound of the type M_3NdCl_6 formed with LiCl and NaCl.

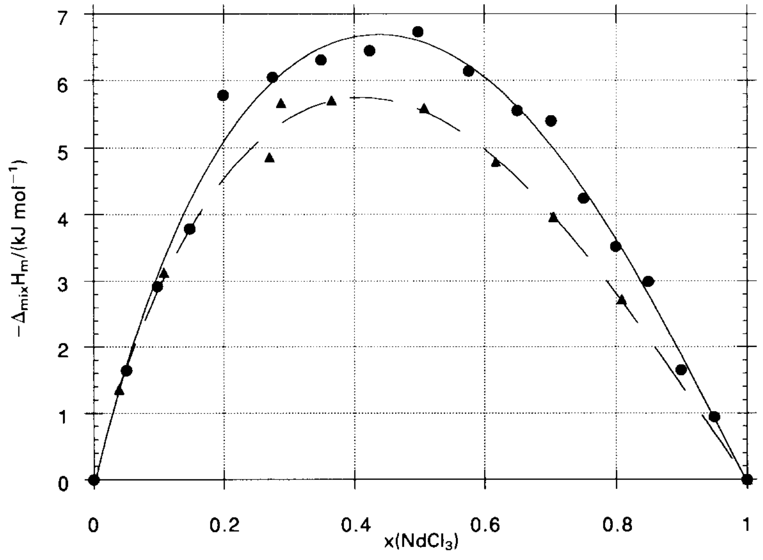

Fig. 3. Molar enthalpies of mixing $\Delta_{mix}H_m$ of the NaCl-NdCl$_3$ liquid system $T = 1124$ K: ●, this work; ◆, ref. 8.

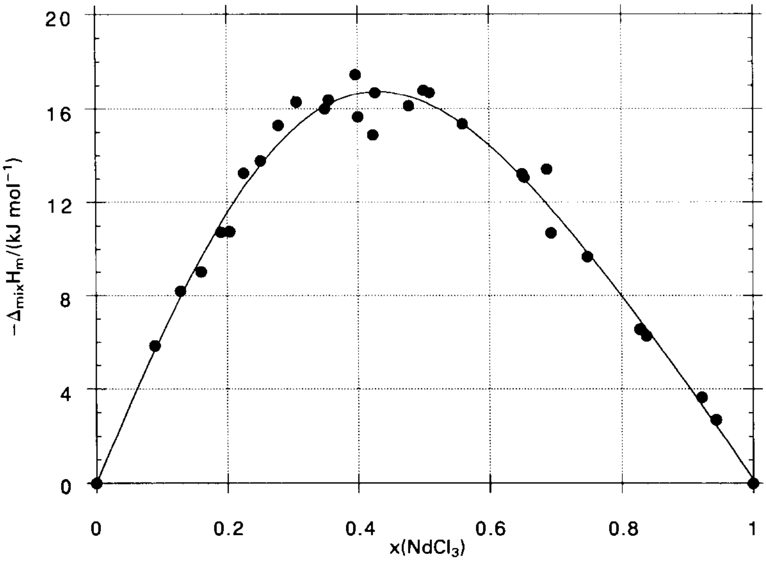

Fig. 4. Molar enthalpies of mixing $\Delta_{mix}H_m$ of the KCl–NdCl$_3$ liquid system at $T = 1065$ K.

The experimental values are reported in Table 6. The same table also includes analogous values obtained for the mixtures of alkali chlorides with CeCl$_3$ and LaCl$_3$ [9, 10]; the ionic radii used in the present work are also indicated [11].

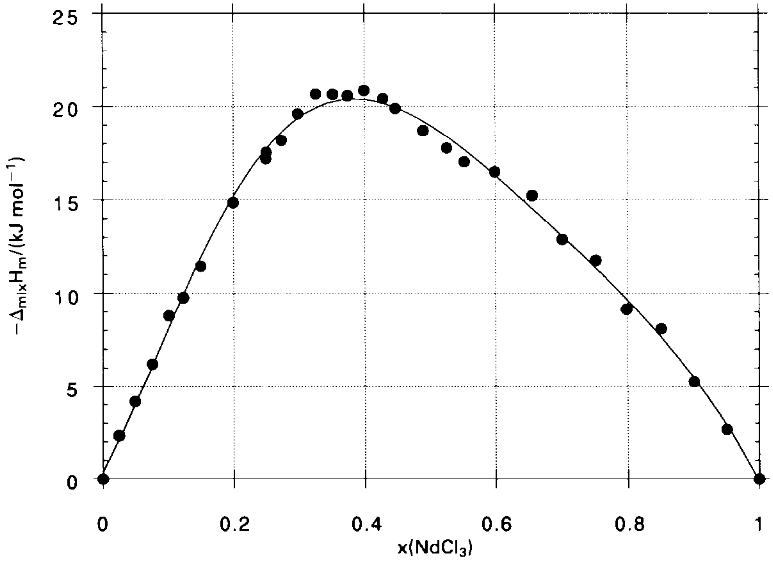

Fig. 5. Molar enthalpies of mixing $\Delta_{mix}H_m$ of the RbCl–NdCl$_3$ liquid system at $T = 1122$ K.

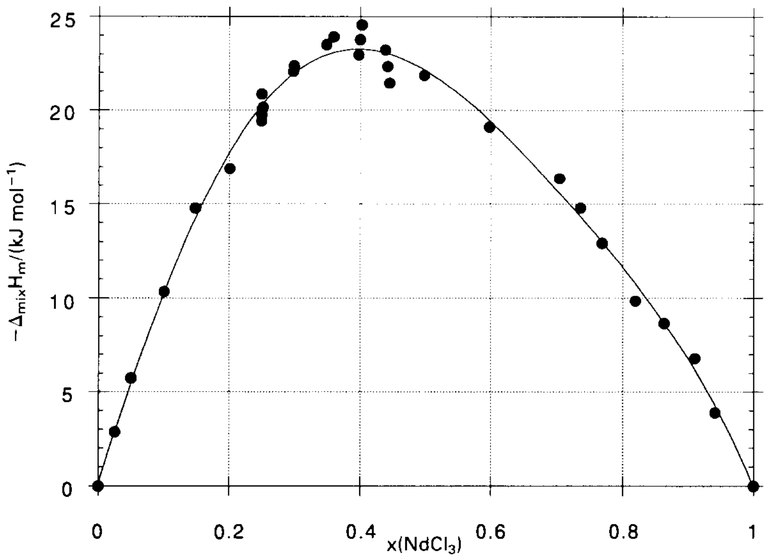

Fig. 6. Molar enthalpies of mixing $\Delta_{mix}H_m$ of the CsCl–NdCl$_3$ liquid system at $T = 1122$ K.

DISCUSSION

The melts investigated, namely NaCl–NdCl$_3$, KCl–NdCl$_3$, RbCl–NdCl$_3$ and CsCl–NdCl$_3$, are characterized by strongly negative enthalpies of mixing which decrease with the ionic radius of alkali metal. For all systems,

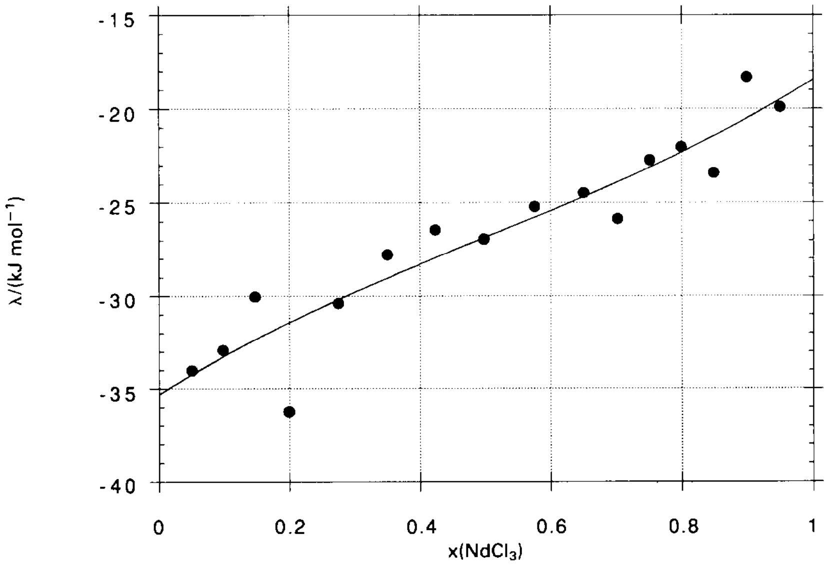

Fig. 7. Variation of the interaction parameter $\lambda = \Delta_{mix}H_m/x_{NdCl_3}(1 - x_{NdCl_3})$ with composition for the NaCl–NdCl$_3$ liquid system at $T = 1124$ K.

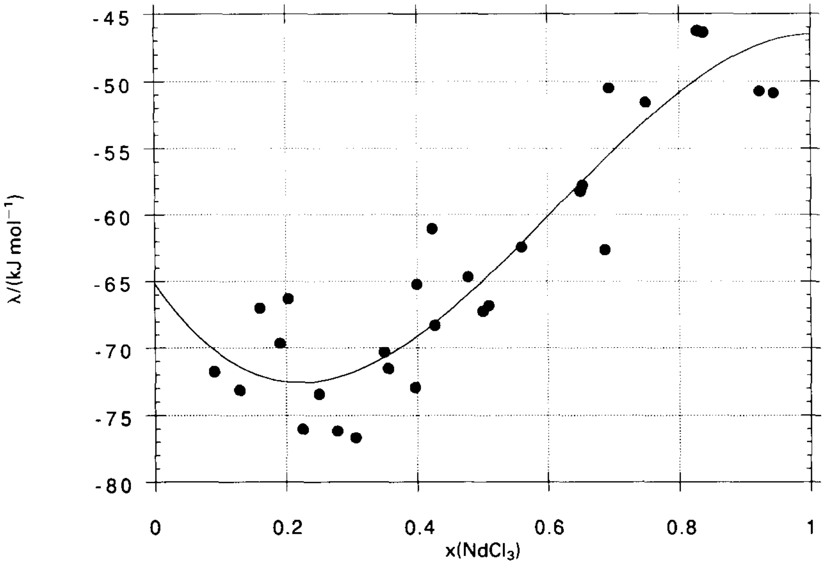

Fig. 8. Variation of the interaction parameter $\lambda = \Delta_{mix}H_m/x_{NdCl_3}(1 - x_{NdCl_3})$ with composition for the KCl–NdCl$_3$ liquid system at $T = 1065$ K.

the minimum of the enthalpy of mixing is shifted toward alkali-chloride-rich compositions and is located in the vicinity of $x_{NdCl_3} = 0.4$.

These results are very similar to those obtained by Papatheodorou and Kleppa [10] and Papatheodorou and Østvold [9] for the analogous mixtures

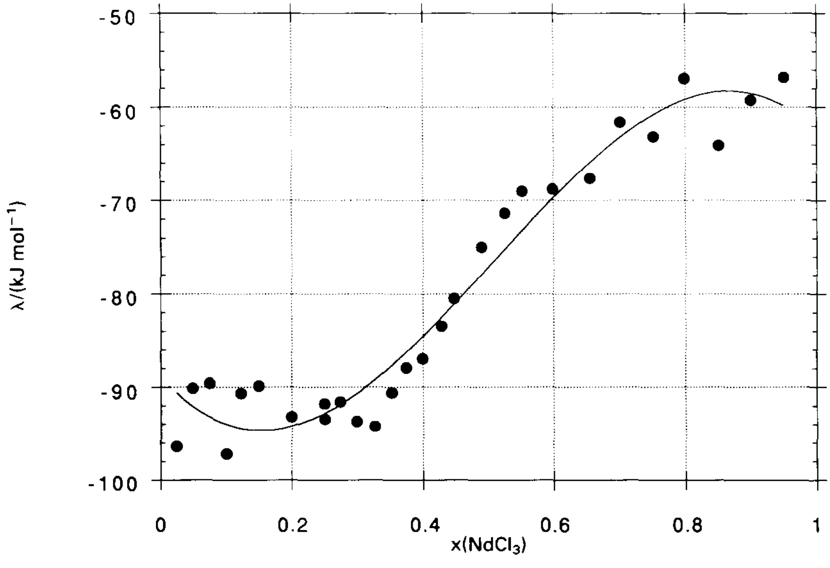

Fig. 9. Variation of the interaction parameter $\lambda = \Delta_{mix}H_m/x_{NdCl_3}(1 - x_{NdCl_3})$ with composition for the RbCl–NdCl$_3$ liquid system at $T = 1122$ K.

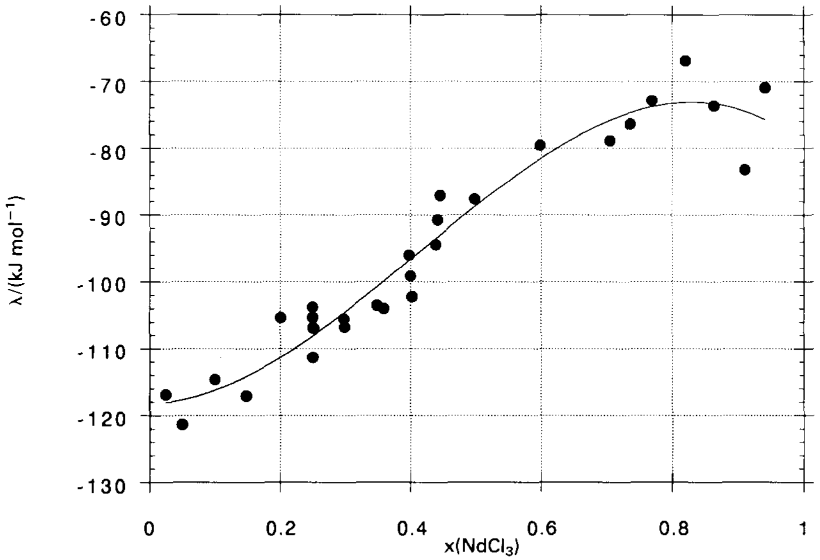

Fig. 10. Variation of the interaction parameter $\lambda = \Delta_{mix}H_m/x_{NdCl_3}(1 - x_{NdCl_3})$ with composition for the CsCl–NdCl$_3$ liquid system at $T = 1122$ K.

MCl–CeCl$_3$ and MCl–LaCl$_3$, and also to our preliminary results for MCl–PrCl$_3$ [12]. The corresponding numerical values are also very similar. This is not surprising in view of the great similarity between the physicochemical properties of LaCl$_3$, CeCl$_3$ and NdCl$_3$ [10].

The only results to compare with our experimental data are those read from a graph obtained for the NaCl–NdCl$_3$ mixture [8]. The agreement is within the experimental uncertainty.

The composition dependence of the interaction parameter λ for NaCl–NdCl$_3$ is close to linear. For the systems involving KCl, RbCl and CsCl, the composition dependence of λ is somewhat more complicated: a broad minimum appears to exist at $x_{NdCl_3} = 0.2$ to 0.3; the relative changes of λ are smaller in the alkali-chloride-rich region than in the neodymium-chloride-rich region. Similar variations in λ were also observed for the corresponding

TABLE 5

Least-squares coefficients for the equation of λ for the liquid alkali chloride–neodymium, chloride mixtures, $\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4$, in kJ mol^{-1}

System	A	B	C	D	E
Na–Nd	−35.34	22.48	−16.43	10.88	—
K–Nd	−65.12	−16.43	200.44	109.23	—
Rb–Nd	−89.04	−83.65	342.85	−281.57	51.99
Cs–Nd	−118.29	3.28	188.70	−153.14	—

TABLE 6

Molar enthalpy of formation $\Delta_f H_m(M_3LnCl_6, l, T)/(kJ\,mol^{-1})$ of the liquid mixtures according to the reaction: $3\,MCl(l) + LnCl_3 =$ "M_3LnCl_6"(l) (M is Li, Na, K, Rb, Cs; Ln is La, Ce, Nd)

MCl	$\Delta_f H_m$ in kJ mol^{-1} $LaCl_3$ [a] 1173 K	$\Delta_f H_m$ in kJ mol^{-1} $CeCl_3$ [b] 1118 K	$\Delta_f H_m$ in kJ mol^{-1} $NdCl_3$ [c] 1122 K	r_{M^+} in pm [d]
LiCl	−6.7	−5.8	−6.9 (1065 K)	74
NaCl	−27.6	−26.7	−24.8	102
KCl	−52.0	−55.7	−55.2 (1065 K)	138
RbCl	−65.7	−68.2	−68.8	149
CsCl	−83.7	−80.8	−80.8	170

[a] Calculated from ref. 9. [b] Calculated from ref. 10. [c] This work. [d] From ref. 11.

MCl–$LaCl_3$ and MCl–$CeCl_3$ mixtures [9, 10]; in both cases it was attributed to the formation of $LnCl_6^{3-}$ complexes in the alkali-chloride-rich mixtures.

The systems under investigation, however, all exhibit compounds which differ in number and composition.

In the NaCl–$NdCl_3$ system, only the $Na_3Nd_5Cl_{18}$ compound is reported, with an incongruent melting point at about 813 K [13].

Three compounds have been found in the KCl–$NdCl_3$ system: K_3NdCl_6 which melts congruently (955 K [14], 972 K [13]), K_2NdCl_5 which decomposes peritectically (863 K [14], 883 K [13]), and KNd_2Cl_7 which also decomposes peritectically (783 K [13]). According to ref. 13, solid K_3NdCl_6 only exists from 719 K (formation) up to 972 K (melting), while KNd_2Cl_7 forms at 742 K and decomposes at 883 K.

The existence of three compounds was also reported for the RbCl–$NdCl_3$ system: Rb_3NdCl_6 which melts congruently (1046 K [15], 1060 K [13]), Rb_2NdCl_5 which decomposes peritectically (843 K [15], 828 K [13]), and $RbNd_2Cl_7$, also with peritectic decomposition (857 K [15], 864 K [13]). According to ref. 13, the Rb_3NdCl_6 solid compound only exists from 547 K (formation) up to 1060 K (fusion).

In the CsCl–$NdCl_3$ system, the authors of ref. 14 found only the congruently melting compound Cs_3NdCl_6 (1086 K) while ref. 13 reports three compounds: Cs_3NdCl_6 and $CsNd_2Cl_7$, which melt congruently at 1108 K and 906 H, respectively, and Cs_2NdCl_5, existing up to 606 K (decomposition in the solid phase without formation of liquid).

The melting temperature of the M_3NdCl_6 compounds increases from the potassium to caesium compounds and, for Cs_3NdCl_6 is far higher than the melting temperature of the components CsCl and $NdCl_3$ (915 and 1037 K, respectively [13]). The enthalpy of mixing decreases in the same order and has the largest absolute value for the CsCl–$NdCl_3$ system. It is well known that the stability of ionic complexes in melts increases with cationic radius M^+, for example, in MCl–$MeCl_n$ mixtures (M is alkali metal, Me is multivalent metal) [16, 17].

The existence of ionic complexes is very likely in the systems investigated here. Raman spectroscopic investigations $LaCl_3$–KCl [18] melts, of the solid and liquid $Cs_2NaLaCl_6$, Cs_3LaCl_6 and K_3LaCl_6 compounds [19], of the YCl_3–MCl systems (where M is alkali metal), and of Cs_2NaYCl_6 and YCl_3 compounds [20], clearly evidenced the existence of octahedral $LaCl_6^{3-}$ and YCl_5^{3-} ionic complexes in the corresponding mixtures. The formation of AX_6^{3-} and $A_3X_{10}^-$ ionic complexes (A is trivalent metal) was also investigated by molecular dynamics [21]. Mochinaga and coworkers [22, 23], using X-ray diffraction and Raman spectroscopy, confirmed that the ACl_6^{3-} complex octahedral anion does exist in $NdCl_3$ and in other molten compounds of the ACl_3 type. The same authors also reported the existence of polymeric complex anions, for instance $A_2Cl_{11}^{5-}$, in the ACl_3 molten chlorides.

Recently Mochinaga et al. [24] determined the electrical conductivity of the $NdCl_3$–KCl, $NdCl_3$–NaCl and $NdCl_3$–$CaCl_2$ systems; the results were discussed in terms of the formation of octahedral complex ions and in terms of clustering. The same point was also addressed very recently by Tosi et al. [25] who reported 4- and 6-coordinated complex ions in AX_3–MX melts.

We also examined the evolution of the enthalpy of formation of liquid M_3NdCl_6 mixtures. The conformal solution theory of Davis [26] predicts that the interaction parameter λ, or the enthalpy of formation of the liquid mixture, should, to a second-order approximation, be a function of the size parameters δ_{12}

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

where a, b and c are complicated integral functions of T, P and x, and $\delta_{12} = (d_1 - d_2)/d_1 d_2$ where d_1 is the sum of the cationic and anionic radii for each salt $d_1 = r_{\mathrm{Ln}^{3+}} + r_{\mathrm{Cl}^-}$ and $d_2 = r_{\mathrm{m}^+} + r_{\mathrm{Cl}^-}$).

In Fig. 11 we test the dependence of the enthalpy of formation of the liquid mixtures at the composition $x_{\mathrm{NdCl_3}} = 0.25$ by plotting $\Delta_f H_m$ against δ_{12}. In the same figure, we have included the corresponding values for the MCl–$LaCl_3$ and MCl–$CeCl_3$ systems. The figure shows that, for each series of MCl–ACl_3 systems, the theoretical equation can be fitted to the data and that the coefficients a, b and c are not very different. Of course, this is not very surprising because the physical and chemical properties of the reference salts $LaCl_3CeCl_3$ and $NdCl_3$ are very similar.

Finally, a very simple correlation was observed between the enthalpies of formation of the same mixtures and the size of the alkali cation. Figure 12 shows that the enthalpy of formation changes linearly with the ionic radius of the alkali metal for the three series of mixtures.

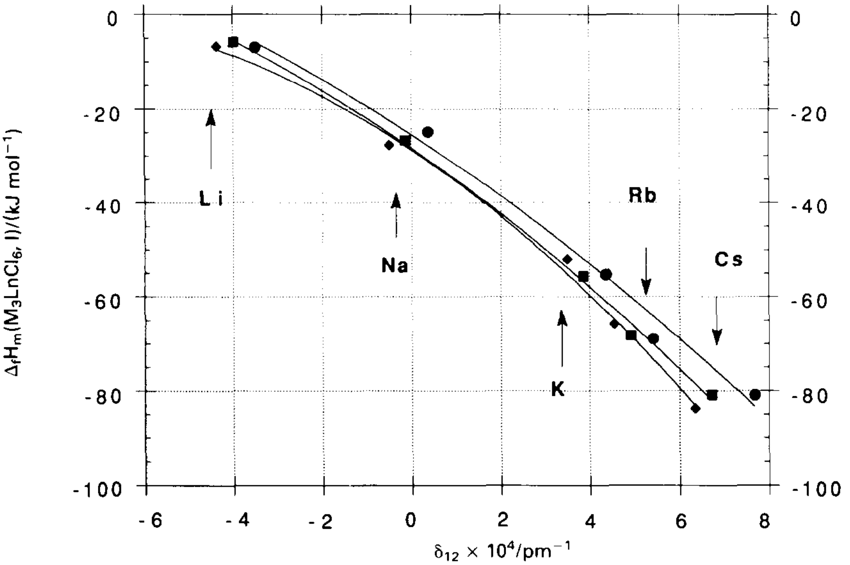

Fig. 11. Dependence of the molar enthalpy of formation $\Delta_f H_m(M_3LnCl_6, l, T)/(kJ\ mol^{-1})$ of the liquid mixtures M_3LnCl_6 on the size parameter $\delta_{12} = (d_1 - d_2)/d_1 d_2$: ◆, $LaCl_3$–MCl at $T = 1173$ K; ■, $CeCl_3$–MCl at $T = 1118$ K; ●, $NdCl_3$–MCl at $T = 1122$ K and $T = 1065$ K (where M is Li, K).

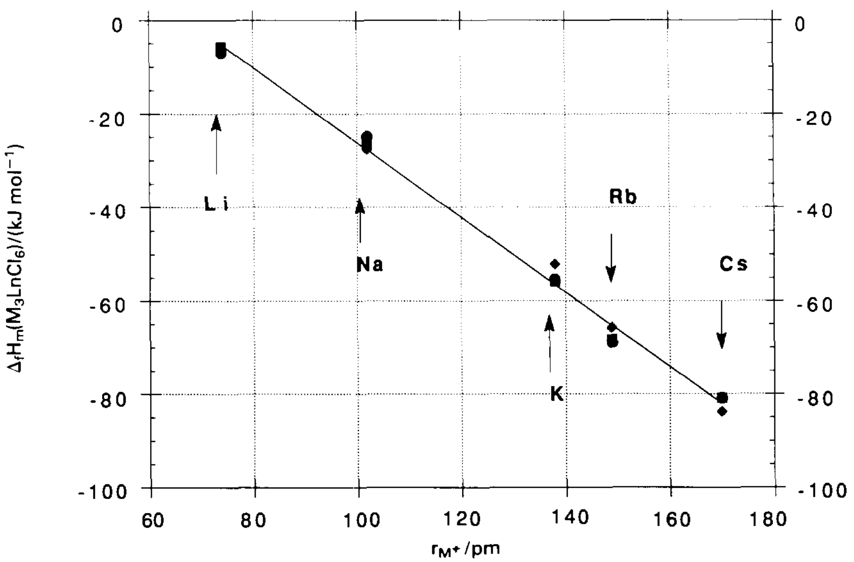

Fig. 12. Dependence of the molar enthalpy of formation $\Delta_f H_m(M_3LnCl_6, l, T)/(kJ\ mol^{-1})$ of the liquid mixtures M_3LnCl_6 on the alkali metal ionic radius r_{M^+}: ◆, $LaCl_3$–MCl at $T = 1173$ K; ■, $CeCl_3$–MCl at $T = 1118$ K; ●, $NdCl_3$–MCl at $T = 1122$ K and $T = 1065$ K (where M is Li, K).

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