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Calorimetric investigation of $PrCl_3$–NaCl and $PrCl_3$–KCl liquid mixtures

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Abstract

The present work is part of the thermodynamic research performed on the $LnCl_3$–MCl systems (where Ln is lanthanide and M is alkali metal). The molar enthalpies of mixing $\Delta_{mix}H_m$ in the NaCl–$PrCl_3$ and KCl–$PrCl_3$ liquid binary systems were measured at 1122 K over the whole composition range under argon at atmospheric pressure, 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 systems, the enthalpies of mixing values are negative, with a minimum value of about −7 and −16 kJ mol^{-1} for NaCl–$PrCl_3$ and KCl–$PrCl_3$, respectively, at $x_{PrCl_3} \approx 0.4$. These values are very similar to those relative to the systems MCl–$LnCl_3$ previously investigated. The molar enthalpies of formation $\Delta_f H_m(K_3PrCl_6, l, 1122\,K)/kJ\,mol^{-1}$, $\Delta_f H_m(Rb_3PrCl_6, l, 1122\,K)/kJ\,mol^{-1}$ and $\Delta_f H_m(Cs_3PrCl_6, l, 1122\,K)/kJ\,mol^{-1}$, according to the reaction $3MCl(l) + PrCl_3(l) = M_3PrCl_6(l)$, are equal to −55.9, −66.4, and −80.4 kJ mol^{-1}, respectively, and are almost identical (in the limits of experimental uncertainty) to those of the compounds M_3LnCl_6 (where M is K, Rb, Cs, and Ln is La, Ce, Nd) previously investigated. The least-squares coefficients *A*, *B*, *C*, *D* and *E* of the equation for the interaction parameter $\lambda = A + Bx + Cx^2 + Dx^3 + Ex^4$ (in kJ mol^{-1}) are presented.

INTRODUCTION

As part of 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 La, Ce, Pr, Nd) [1, 2], the present work reports the experimental enthalpies of mixing of the NaCl–$PrCl_3$ and KCl–$PrCl_3$ liquid systems. A comparison with the analogous $LaCl_3$- [3], $CeCl_3$- [4] and $NdCl_3$-based mixtures [2] is also presented.

In addition, the enthalpies of formation for all the liquid $PrCl_3$–MCl melts (where M is Li, Na, K, Rb, Cs) at the composition $x_{PrCl_3} = 0.25$ were determined.

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EXPERIMENTAL

Chemicals

$PrCl_3$ was synthesized from Pr_4O_{11}(99.9%) produced by Hydromet Co. (Kowary, Poland). The main steps of this synthesis are the same as for $NdCl_3$ which has been described in detail elsewhere [2]. The $PrCl_3$, obtained after 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 to fusion under gaseous HCl atmosphere; excess HCl was removed from the melt by argon. The samples were stored in a glove-box.

Procedure

The mixing experiments were all of the simple liquid–liquid type under argon at 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 [5]. The two salts were mixed by the break-off ampoule technique.

Calibration of the calorimeter was performed with NIST α-alumina [6]; known amounts of alumina were dropped directly into the melt. The surface of the thermograms was automatically integrated by a computer.

The experimental uncertainty on calibration was about 3%; the experimental uncertainty for the enthalpy of mixing data is estimated at 6%, because they were obtained from independent experiments.

RESULTS

Calorimetric experiments were carried out at 1122 K for both systems.

The experimental enthalpies of mixing $\Delta_{mix}H_m$ are given in Tables 1 and 2, and are plotted against composition in Figs. 1 and 2. In evaluating the

TABLE 1

Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the NaCl–$PrCl_3$ liquid system at $T = 1122$ K

x_{PrCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}	x_{PrCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1}	λ/kJ mol^{-1}
0.104	3.27	−35.10	0.599	6.66	−27.73
0.173	4.85	−33.90	0.675	5.37	−24.48
0.249	6.15	−32.89	0.751	4.50	−24.06
0.250	6.25	−33.33	0.800	3.59	−22.44
0.273	6.21	−31.29	0.856	2.83	−22.96
0.386	7.26	−30.63	0.900	2.02	−22.44
0.499	6.87	−27.48	0.953	0.800	−17.86

TABLE 2

Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ and interaction parameters λ of the KCl–PrCl$_3$ liquid system at $T = 1122$ K

$x_{\mathrm{PrCl_3}}$	$-\Delta_{\mathrm{mix}}H_{\mathrm{m}}/\mathrm{kJ\ mol^{-1}}$	$\lambda/\mathrm{kJ\ mol^{-1}}$	$x_{\mathrm{PrCl_3}}$	$-\Delta_{\mathrm{mix}}H_{\mathrm{m}}/\mathrm{kJ\ mol^{-1}}$	$\lambda/\mathrm{kJ\ mol^{-1}}$
0.947	2.01	−40.05	0.400	15.9	−66.35
0.897	1.23	−13.28	0.350	16.3	−71.52
0.850	3.79	−29.74	0.273	15.5	−78.22
0.801	6.49	−40.82	0.250	14.0	−74.56
0.748	7.43	−39.48	0.194	12.4	−79.00
0.711	9.74	−47.41	0.150	10.3	−81.14
0.659	12.1	−53.75	0.0896	7.89	−96.72
0.601	12.8	−53.45	0.0734	4.57	−67.19
0.548	14.3	−57.72	0.0397	2.75	−72.01
0.470	15.4	−61.80	0.0101	0.530	−53.01

results of our measurements, all experimentally uncertain data were disregarded, as when evaporation or poor homogeneity of the melt during mixing were noticed; moreover, in order to improve the overall accuracy, some experimental points were obtained as the average value of several runs.

Figures 3 and 4 indicate for both systems the composition dependence of the interaction parameter λ

$$\lambda = \Delta_{\mathrm{mix}}H_{\mathrm{m}}/x_{\mathrm{MCl}}x_{\mathrm{PrCl_3}}$$

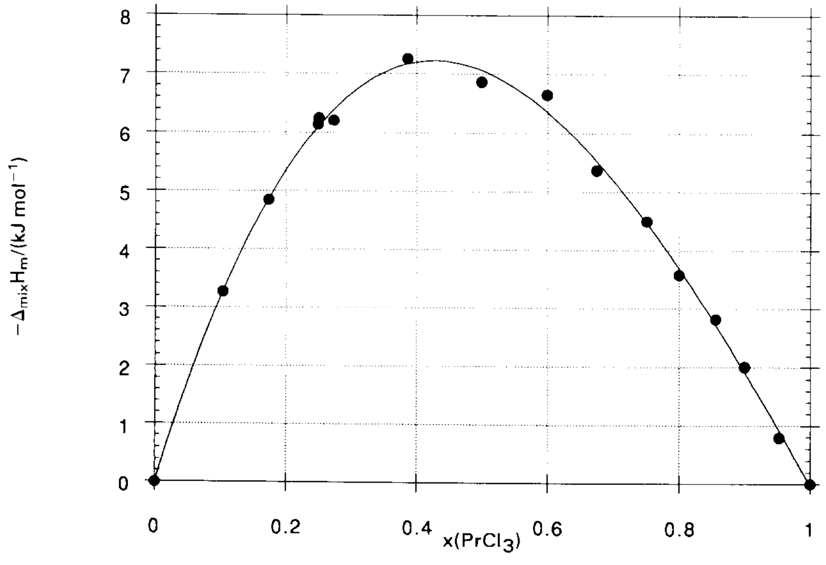

Fig. 1. Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ of the NaCl–PrCl$_3$ liquid system at $T = 1122$ K.

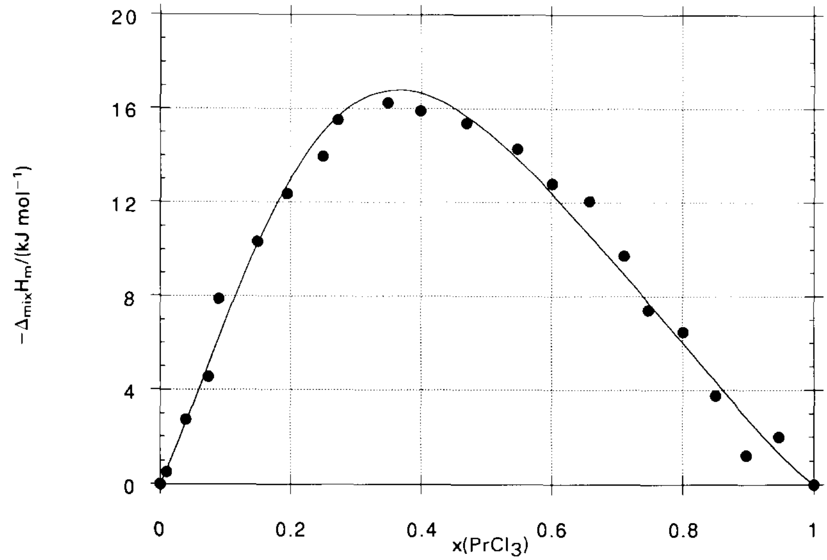

Fig. 2. Molar enthalpies of mixing $\Delta_{mix}H_m$ of the KCl–PrCl$_3$ liquid system at $T = 1122$ K.

which is representative of the energetic asymmetry in these melts. The corresponding values of λ are also given in Tables 1 and 2. For each system, the values of λ were fitted by the method of least squares to polynomials of x_{PrCl_3}; the results are given in Table 3.

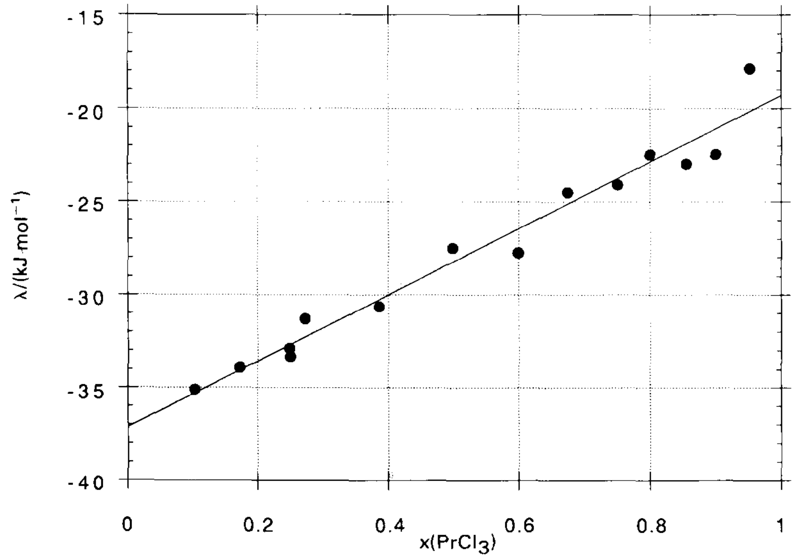

Fig. 3. Variation of the interaction parameter $\lambda = \Delta_{mix}H_m/x_{PrCl_3}(1 - x_{PrCl_3})$ with composition for the NaCl–PrCl$_3$ liquid system at $T = 1122$ K.

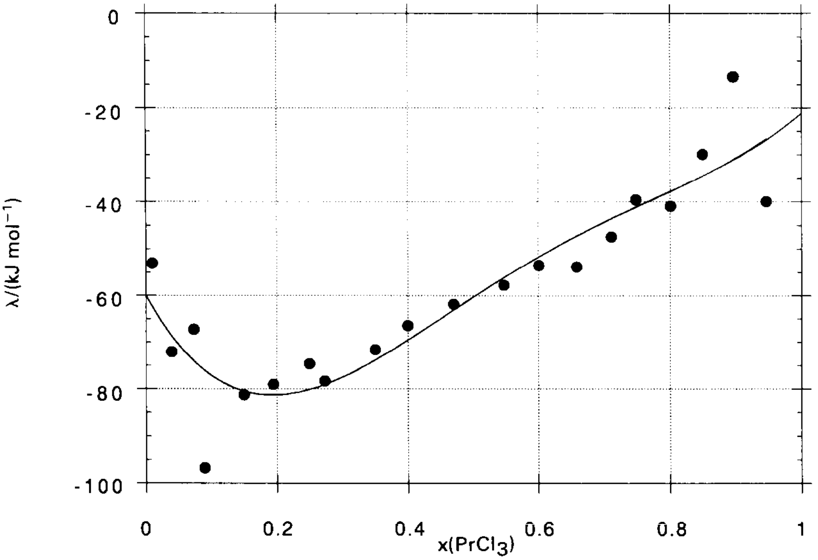

Fig. 4. Variation of the interaction parameter $\lambda = \Delta_{\text{mix}}H_m/x_{\text{PrCl}_3}(1 - x_{\text{PrCl}_3})$ with composition for the KCl–PrCl$_3$ liquid system at $T = 1122$ K.

TABLE 3

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

System	*A*	*B*	*C*	*D*
NaCl–PrCl$_3$	−37.143	17.865	–	–
KCl–PrCl$_3$	−59.812	−257.221	953.361	−1107.106

TABLE 4

Molar enthalpies of formation $\Delta_f H_m(\text{M}_3\text{LnCl}_6, \text{l}, T)$/(kJ mol^{-1}) of the liquid mixtures according to the reaction 3MCl(l) + LnCl$_3$ = "M$_3$LnCl$_6$"(l) (where M is Li, Na, K, Rb, Cs; Ln is La, Ce, Pr, Nd)

	$\Delta_f H_m$/kJ mol^{-1} LaCl$_3$ [a] 1173 K	$\Delta_f H_m$/kJ mol^{-1} CeCl$_3$ [b] 1118 K	$\Delta_f H_m$/kJ mol^{-1} NdCl$_3$ [c] 1122 K	$\Delta_f H_m$/kJ mol^{-1} PrCl$_3$ [d] 1122 K	r_{M^+}/pm [e]
LiCl	−6.7	−5.8	−6.9 (1065 K)	−6.1	74
NaCl	−27.6	−26.7	−24.8	−25.0	102
KCl	−52.0	−55.7	−55.2 (1065 K)	−55.9	138
RbCl	−65.7	−68.2	−68.8	−66.4	149
CsCl	−83.7	−80.8	−80.8	−80.4	170

[a] Calculated from ref. 3. [b] Calculated from ref. 4. [c] Calculated from ref. 2. [d] This work. [e] From ref. 7.

Several experiments were also conducted in order to determine accurately the enthalpy of formation at $x_{PrCl_3} = 0.25$ for all the MCl–PrCl$_3$ systems (M is Li, Na, K, Rb, Cs), i.e. the enthalpy variation related to the reactions

$$3MCl(l) + PrCl_3(l) \rightarrow \text{“}M_3PrCl_6\text{”}(l)$$

The notation “M$_3$PrCl$_6$” was adopted because there is no compound of the type M_3PrCl_6 with LiCl and NaCl.

The experimental values are reported in Table 4. The same table also includes analogous values obtained for the mixtures of alkali chlorides with CeCl$_3$ [4], LaCl$_3$ [3] and NdCl$_3$ [2]. The values of the ionic radii used are also indicated [7] in Table 4.

DISCUSSION

The melts investigated, namely NaCl–PrCl$_3$ and KCl–PrCl$_3$, are characterized by negative enthalpies of mixing. For both systems, the minimum of the enthalpy of mixing is shifted toward alkali-chloride-rich compositions and is located in the vicinity of $x_{PrCl_3} \approx 0.4$.

These results are almost identical, within experimental uncertainty, to those found previously for the NaCl–NdCl$_3$ and KCl–NdCl$_3$ molten salt mixtures [2]. They are also very similar to those obtained by Papatheodorou and Østvold [3] and Papatheodorou and Kleppa [4] for the analogous mixtures MCl–CeCl$_3$ and MCl–LaCl$_3$. This is not surprising in view of the great similarity between the physicochemical properties of LaCl$_3$, CeCl$_3$, PrCl$_3$ and NdCl$_3$.

However, our results were also compared with those obtained for the KCl–PrCl$_3$ system by Savin et al. [8]. The comparison is reported in Table 5: their enthalpy values obtained indirectly at 3 compositions by the drop method differ from ours by 10–15%.

The composition dependence of the interaction parameter λ for the NaCl–PrCl$_3$ system is almost linear. For the KCl–PrCl$_3$ system, the compo-

TABLE 5

Molar enthalpies of mixing $\Delta_{mix}H_m$ of the KCl–PrCl$_3$ system: comparison with the data of Savin et al. [8]

x_{PrCl_3}	$-\Delta_{mix}H_m$/kJ mol^{-1} $T = 1143$–1163 K Savin et al. [8] [a]	$-\Delta_{mix}H_m$/kJ mol^{-1} $T = 1122$ K This work
0.500	−13.6	−15.1
0.333	−13.9	−16.1
0.250	−11.9	−14.0

[a] Data recalculated for one mole of mixture in kJ mol^{-1}.

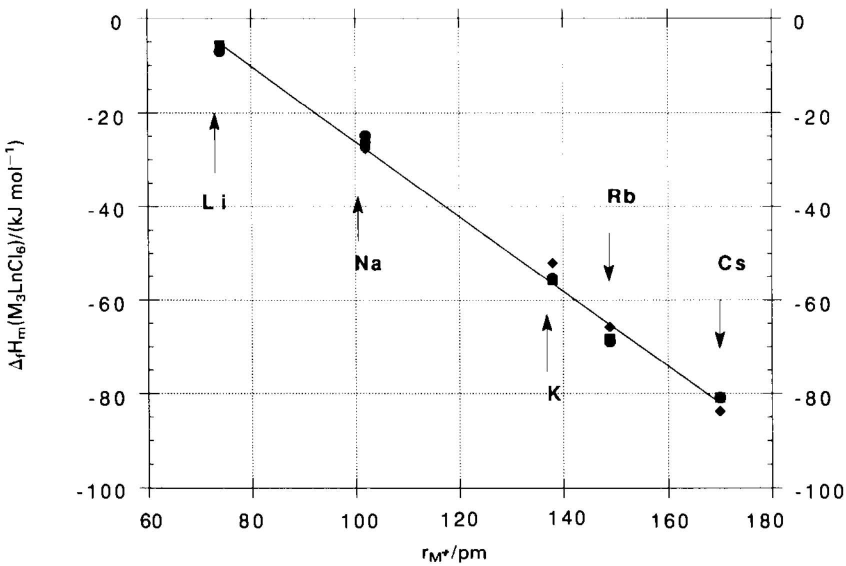

Fig. 5. Dependence of the molar enthalpy of formation $\Delta_f H_m(M_3LnCl_6, l, T)/(kJ\ mol^{-1})$ of the liquid mixtures M_3LnCl_6 on the alkali metal ionic radius r_{M^+}: ◆, $LaCl_3$–MCl at $T = 1173$ K; ■, $CeCl_3$–MCl at $T = 1118$ K; ●, $PrCl_3$–MCl at $T = 1122$ K; ▲, $NdCl_3$–MCl at $T = 1122$ K and $T = 1065$ K (where M is Li, K).

sition dependence of λ is somewhat more complicated: a broad minimum appears to exist at $x_{PrCl_3} \approx 0.2–0.3$; the relative changes in λ are smaller in the alkali-chloride-rich region than in the praseodymium-chloride-rich region. Similar variations in λ were also observed for the corresponding MCl–$LaCl_3$, MCl–$CeCl_3$ and MCl–$NdCl_3$ mixtures; for all the KCl–$LnCl_3$ systems, the minimum in λ was attributed to the formation of $LnCl_6^{3-}$ complexes in the alkali-chloride-rich mixtures.

The systems under investigation all exhibit different compounds in the solid state. For NaCl–$PrCl_3$, neither Novikov et al. [9] nor Shevtsova et al. [10] reported any compound; this was confirmed by Desyatnik et al. [11]. However, Mochinaga et al. [12] and Hattori et al. [13] found $3PrCl_3 \cdot NaCl$, which melts incongruently at 860 K. Seifert et al. [14] reported only the compound $Na_3Pr_5Cl_{18}$, with an incongruent melting at about 873 K.

Two or three compounds have been found in the KCl–$PrCl_3$ system: $3KCl \cdot 2PrCl_3$ which melts incongruently at 888 K [9]; $2KCl \cdot PrCl_3$ which melts incongruently at 893 K [9], 898 K [11], 890 K [14]; K_3PrCl_6 which melts congruently at 948 K [9], 963 K [11], 945 K [14]. According to ref. 14, solid K_3PrCl_6 only exists from 762 K (formation) up to 945 K (melting).

In spite of the above contradictions, the phase diagrams of the NaCl–$PrCl_3$ and KCl–$PrCl_3$ systems exhibit many similarities with the analogous NaCl–$NdCl_3$ and KCl–$NdCl_3$ systems.

$PrCl_3$ and $NdCl_3$ are probably associated in the liquid state [15] and values of the equivalent electrical conductivity, at a fixed temperature, are very similar [16].

These results show that the systems under investigation behave like the analogous mixtures with $NdCl_3$. Figure 5, which displays the dependence of the enthalpy of formation $\Delta_f H_m(M_3LnCl_6, l, T)$ on the ionic radius of the alkali metal r_{M^+}, clearly indicates that the same behaviour can be observed with the $LaCl_3$–MCl and $CeCl_3$–MCl systems.

The enthalpy of formation changes linearly with the ionic radius of the alkali metal and is the same for the four series of mixtures.

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