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Enthalpies of mixing in $PrCl_3$–$CaCl_2$ and $NdCl_3$–$CaCl_2$ liquid systems

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Abstract

The molar enthalpies of mixing $\Delta_{mix}H_m$ in the $PrCl_3$–$CaCl_2$ and $NdCl_3$–$CaCl_2$ liquid binary systems were measured at 1073 K over the whole composition range under argon at atmospheric pressure. The apparatus used was a Calvet-type high-temperature micro-calorimeter and mixing of the two liquid components was obtained by the break-off ampoule technique. In both systems the plots of enthalpies of mixing versus composition were "S-shaped" curves.

The enthalpy of mixing values are positive for $NdCl_3$- and $PrCl_3$-rich compositions, and negative for other compositions. These values are very small (from about -200 to about $180\ J\ mol^{-1}$). In the $PrCl_3$–$CaCl_2$ and $NdCl_3$–$CaCl_2$ liquid binary systems, $\Delta_{mix}H_m \approx 0$ at $x_{PrCl_3} \approx 0.6$ and at $x_{NdCl_3} \approx 0.4$, respectively. These results are discussed in terms of equilibrium between the $LnCl_3$ (where Ln is Pr, Nd) polymers and anionic complexes as a function of the composition of the melts.

INTRODUCTION

Mixtures of lanthanide chlorides ($LnCl_3$) with calcium chloride are formed during the reduction of $LnCl_3$ by calcium. Therefore, a knowledge of the thermodynamics of these systems is very useful in the preparation of lanthanides from molten chlorides by the calciothermic method.

As part of a general research program on the thermodynamic properties and electrical conductivities of $LnCl_3$-based liquid mixtures (where Ln is La, Ce, Pr, Nd) [1-3], the present work reports the experimental enthalpies of mixing of the $PrCl_3$–$CaCl_2$ and $NdCl_3$–$CaCl_2$ liquid binary systems.

EXPERIMENTAL

Chemicals

High grade (min. 99.9%) $PrCl_3$ and $NdCl_3$ were prepared as described previously [2, 3]. The calcium chloride was a Merck Suprapur reagent (min.

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TABLE 1

Molar enthalpies of mixing $\Delta_{mix}H_m$ and interaction parameters λ of the $CaCl_2$–$PrCl_3$ liquid system at $T = 1073$ K

x_{PrCl_3}	$\Delta_{mix}H_m$/J mol^{-1}	λ/J mol^{-1}	x_{PrCl_3}	$\Delta_{mix}H_m$/J mol^{-1}	λ/J mol^{-1}
0.100	−170.6	−1889	0.500	−103.3	−413
0.150	−183.1	−1437	0.550	−89.1	−360
0.190	−215.6	−1404	0.551	−80.1	−323
0.248	−212.1	−1138	0.609	−34.1	−143
0.295	−183.2	−881	0.649	31.5	138
0.345	−184.8	−818	0.700	47.4	226
0.398	−96.1	−401	0.725	124.0	622
0.405	−185.0	−768	0.801	141.6	889
0.418	−113.3	−466	0.850	121.0	946
0.475	−68.9	−276	0.901	106.1	1185
0.496	−76.5	−306	0.950	79.6	1685

99.9%). Before use, it was 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 [4]. Mixing of the two salts was by the break-off ampoule technique, as described previously [2].

Calibration of the calorimeter was performed with NIST α-alumina [5]; known amounts of alumina were dropped directly into the melt. Integration of the surface of the thermograms was made automatically by computer.

The experimental uncertainty on the calibration was about 3%. Because of the small values of the enthalpies of mixing (100–200 J mol^{-1}), considerable effort was made to reduce the interfering effects arising from breaking off the ampoule: the ampoule rested on a sharp tip at the bottom of the crucible and a mechanical shock was applied to achieve the mixing of the components. Because of these precautions, the experimental uncertainty on the enthalpy of mixing data was less than usual and is estimated at 10–15%.

RESULTS

The calorimetric experiments were carried out at 1073 K for both systems.

TABLE 2

Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ and interaction parameters λ of the $CaCl_2$–$NdCl_3$ liquid system at $T = 1073$ K

x_{NdCl_3}	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}/\mathrm{J\ mol^{-1}}$	$\lambda/\mathrm{J\ mol^{-1}}$	x_{NdCl_3}	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}/\mathrm{J\ mol^{-1}}$	$\lambda/\mathrm{J\ mol^{-1}}$
0.049	−84.0	−1789	0.491	68.7	275
0.094	−88.8	−1045	0.557	113	457
0.100	−147	−1645	0.571	108	441
0.150	−152	−1190	0.595	120	498
0.199	−152	−956	0.649	132	580
0.245	−153	−826	0.701	155	738
0.307	−128	−602	0.704	111	533
0.349	−95.2	−419	0.753	165	887
0.373	−69.9	−299	0.800	156	978
0.401	0.0	0.0	0.900	130	1443
0.401	−107	−448	0.926	84.1	1230
0.425	68.9	282	0.951	114	2458
0.453	34.0	137	0.978	50.1	2032

The experimental enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ are given in Tables 1 and 2 and are plotted against composition in Figs. 1 and 2. In evaluating the results of our measurements, all uncertain experimental data were discarded, as when evaporation or poor homogeneity of the melt during mixing were noticed.

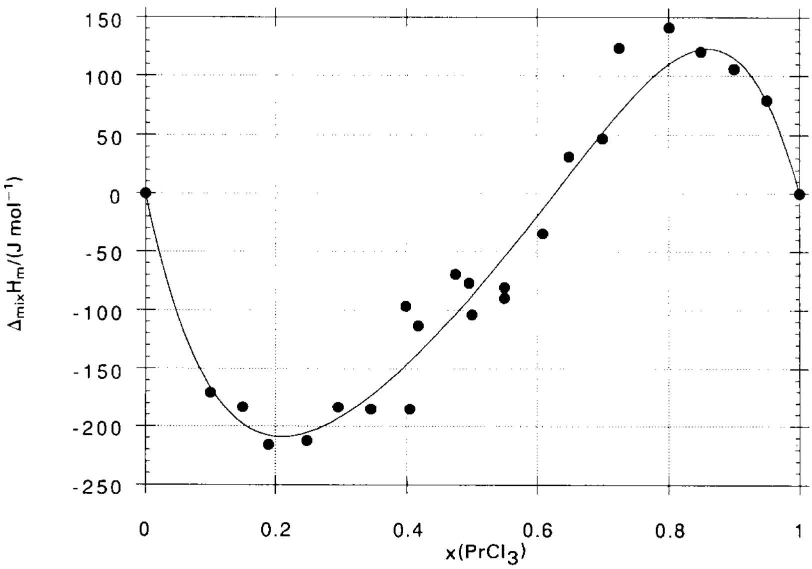

Fig. 1. Molar enthalpies of mixing $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ of the $CaCl_2$–$PrCl_3$ liquid system at $T = 1073$ K.

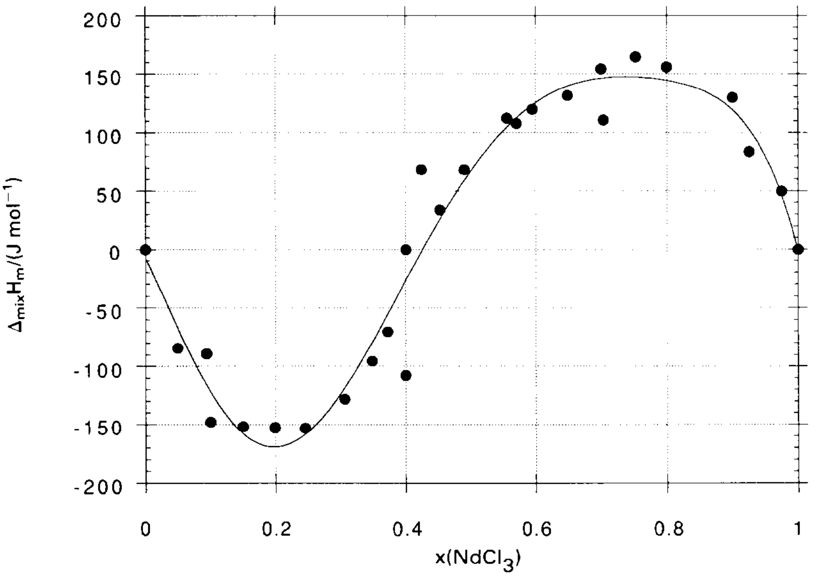

Fig. 2. Molar enthalpies of mixing $\Delta_{mix}H_m$ of the $CaCl_2$–$NdCl_3$ liquid system at $T = 1073$ K.

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

$$\lambda = \Delta_{mix}H_m/x_{MCl}x_{LnCl_3}$$

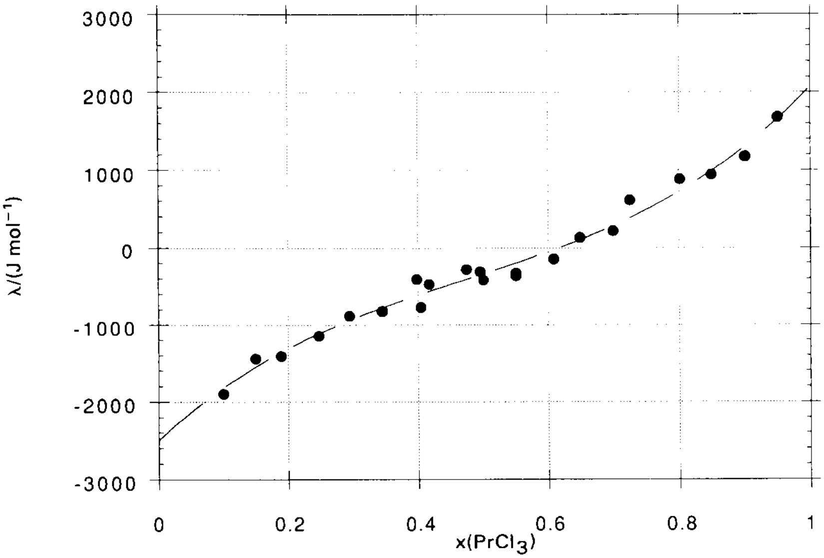

Fig. 3. Variation of the interaction parameter $\lambda = \Delta_{mix}H_m/x_{PrCl_3}(1 - x_{PrCl_3})$ with composition for the $CaCl_2$–$PrCl_3$ liquid system at $T = 1073$ K.

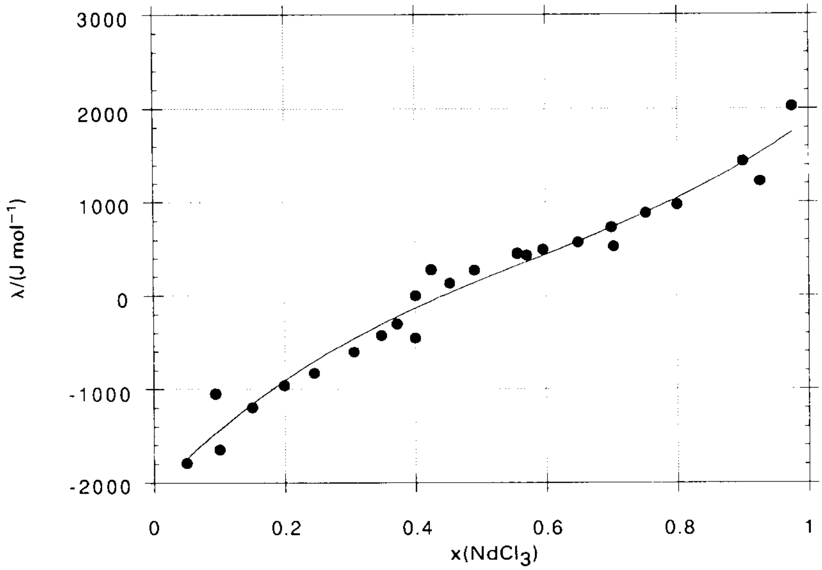

Fig. 4. Variation of the interaction parameter $\lambda = \Delta_{\text{mix}}H_m/x_{PrCl_3}(1 - x_{PrCl_3})$ with composition for the $CaCl_2$–$NdCl_3$ liquid system at $T = 1073$ K.

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 listed in Table 3, the values of λ were fitted by the method of least squares of polynomials of x_{LnCl_3}.

DISCUSSION

The melts investigated, namely $PrCl_3$–$CaCl_2$ and $NdCl_3$–$CaCl_2$, are characterized by very small enthalpy of mixing values which are positive for $NdCl_3$- and $PrCl_3$-rich compositions and negative for other compositions. For both systems, $\Delta_{\text{mix}}H_m \approx 0$ at $x_{PrCl_3} \approx 0.6$ and at $x_{NdCl_3} \approx 0.4$, respectively. Some results have been obtained for the enthalpies of formation of the liquid $PrCl_3$–$CaCl_2$ [6] and $NdCl_3$–$CaCl_2$ [7] systems by Savin et al. These authors have indicated that the formation of the mixtures is only

TABLE 3

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

System	*A*	*B*	*C*	*D*
$CaCl_2$–$PrCl_3$	−2495.3	7736.3	10483.5	7308.8
$CaCl_2$–$NdCl_3$	2144.7	8070.7	10175.5	6436.8

endothermic; furthermore, the values obtained are very different from those obtained in the present work. For instance, from the data of Savin et al. [7] for the $NdCl_3$–$CaCl_2$ system, the following values of $\Delta_{mix}H_m$ are obtained: 5.2 and 5.8 kJ mol^{-1} at $x_{NdCl_3} = 0.5$ and 0.333, respectively, while we found 55 and -120 J mol^{-1} for the same compositions.

The composition dependence of the interaction parameter λ for $PrCl_3$–$CaCl_2$ and $NdCl_3$–$CaCl_2$ is close to linear and it is evident that λ also has positive and negative values.

The phase diagrams of the $PrCl_3$–$CaCl_2$ [8] and $NdCl_3$–$CaCl_2$ [9–11] systems exhibit a simple eutectic point. There is little difference between the literature data published for these systems. In the $PrCl_3$–$CaCl_2$ system, the eutectic is located at $x_{PrCl_3} = 0.42$ and 880 K [8]. In the $NdCl_3$–$CaCl_2$ system, the eutectic is located at $x_{NdCl_3} = 0.43$ according to Morozov et al. [9], at $x_{NdCl_3} = 0.41$ according to Igarashi et al. [10] and Sharma and Roger [11]. The melting temperature is reported as 858 K [9], 860 K [10] and 873 K [11].

The enthalpy of mixing is so low that the systems under investigation might be considered quasi-ideal. Other properties such as superficial tension [12] and molar volume [13] show little deviation from additivity. In fact, the structure of these melts is complex. $PrCl_3$ and $NdCl_3$ are associated in the liquid state. Investigations by X-ray diffractometry have shown that the $Pr_2Cl_{11}^{5-}$ and $Nd_2Cl_{11}^{5-}$ species may exist in the liquid [14, 15]. The values of the electrical equivalent conductivity, at a fixed temperature, are very small and may suggest the existence of clusters in the liquid state [16]; they are smaller for $NdCl_3$, however, indicating more complexation for $NdCl_3$ than for $PrCl_3$.

The heat capacity values for these compounds in the liquid state and close to the melting temperature are very high [7, 17]; this may confirm the possible existence of clusters in the liquid state. Our experimental enthalpy of mixing results may be explained as the superposition of two opposite effects, one endothermic and the other exothermic. The addition of $CaCl_2$ to molten $PrCl_3(NdCl_3)$ leads to the destruction of the clusters and corresponds to endothermic effects. However, at high $CaCl_2$ compositions, exothermic effects of formation of anionic complexes, e.g. $PrCl_6^{3-}$ or $NdCl_6^{3-}$ and $CaCl_6^{4-}$, in the liquid mixture is dominant and results in negative $\Delta_{mix}H_m$ values. The formation of these complexes is possible even if the corresponding compounds do not exist in the solid state. For the composition range corresponding to negative $\Delta_{mix}H_m$ values, the equilibria

$$2Ln^{3+} + 3CaCl_6^{4-} \rightleftharpoons 3Ca^{2+} + 6Cl^- + 2LnCl_6^{3-}$$

may be considered to be a function of x_{LnCl_3}.

A comparison of the ionic potential values, z/r, for Ln^{3+} (where Ln is Pr, Nd) and Ca^{2+} indicates that the $LnCl_6^{3-}$ ion is more stable than $CaCl_6^{4-}$ and the above reaction is shifted toward the right-hand side.

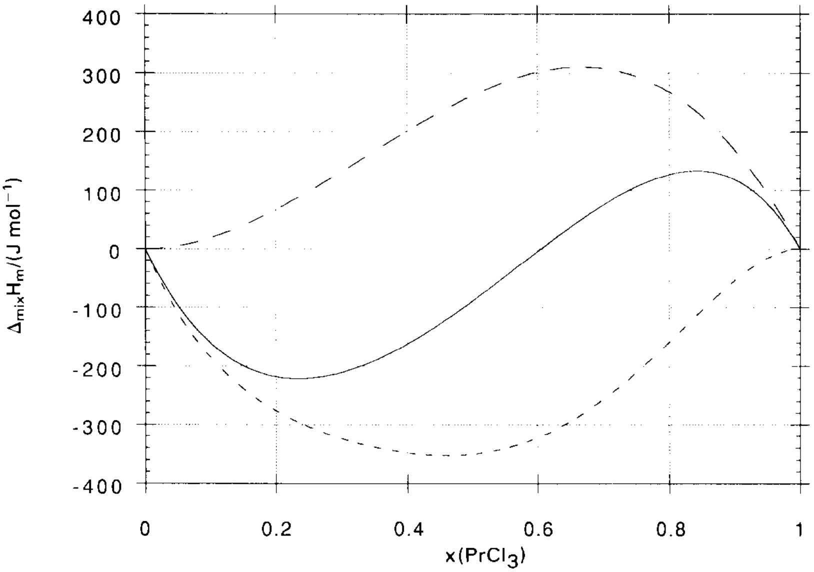

Fig. 5. Dependence of the molar enthalpy of mixing (in J mol^{-1}) of the liquid mixtures on the composition: ——, total $\Delta_{mix}H_m$; –·–·–, complexation $\Delta_{mix}H_{mc}$; —··—··—, destruction of polymers $\Delta_{mix}H_{mp}$.

The composition range in which the $\Delta_{mix}H_m$ values are positive is larger for the $NdCl_3$–$CaCl_2$ system than for $PrCl_3$–$CaCl_2$: this is consistent with the electrical conductivity data [16] which indicate that liquid $NdCl_3$ has a more polymeric structure.

With the very simple assumption that interactions in the melt are the destruction of polymers and the formation of anionic complexes, the interaction parameter λ can be written

$$\lambda = \lambda_p + \lambda_c$$

where λ_p is related to the destruction of polymers and λ_c to the formation of anionic complexes. The limiting value of λ at $x_{PrCl_3} = 1$, calculated from the polynomial given in Table 3, is about 2100 J mol^{-1}. With the same assumption, this value corresponds to the destruction of the $PrCl_3$ polymers. Therefore

$$\lambda_p = x_{PrCl_3} \times 2100$$

$$\lambda_c = \lambda - (x_{PrCl_3} \times 2100)$$

and

$$\Delta_{mix}H_{mp} = x_{PrCl_3} \times 2100 x_{PrCl_3}(1 - x_{PrCl_3})$$

$$\Delta_{mix}H_{mc} = (A + Bx_{PrCl_3} + Cx^2_{PrCl_3} + Dx^3_{PrCl_3})x_{PrCl_3}(1 - x_{PrCl_3}) - \Delta_{mix}H_{mp}$$

The composition dependences of $\Delta_{mix}H_{mp}$ and $\Delta_{mix}H_{mc}$ are given in Fig. 5 which also includes the dependence of the (total) $\Delta_{mix}H_{m}$.

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