Enthalpy of Mixing of the $PrCl_3$-LiCl and $NdCl_3$-LiCl Molten Salt Systems

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The molar enthalpies of mixing ($\Delta_{\text{mix}}H_{\text{m}}$) of liquid $PrCl_3$-LiCl and $NdCl_3$-LiCl mixtures have been measured at 1044 K. For both systems these enthalpies are negative in the whole composition range, with a minimum at x_{PrCl_3} and $x_{NdCl_3} \approx 0.4$. The results are compared with existing mixing enthalpy data on lanthanide chloride-alkali metal chloride systems and discussed in terms of complex formation in the melts.

Key words: Praseodymium(III) Chloride; Neodymium(III) Chloride; Alkali Metal Chlorides; Mixing Enthalpy; Interaction Parameter; Complex Formation.

1. Introduction

The mixing enthalpies of the $PrCl_3$-MCl (M = Na, K) [1] and $NdCl_3$-MCl (M = Na, K, Rb, Cs) [2] liquid systems have been investigated previously. These results were discussed in terms of $LnCl_6^{3-}$ complex formation in melts. The present work continues our systematic research program on $LnCl_3$-MCl liquid mixtures. It reports the mixing enthalpies of the $PrCl_3$-LiCl and $NdCl_3$-LiCl liquid systems.

2. Experimental

2.1. Chemicals

Praseodymium and neodymium chlorides were synthesized from Pr_6O_{11} and Nd_2O_3 oxides of 99.9% purity supplied by the Chemistry Department of the Lublin University. This synthesis included several steps: dissolution of the oxide in hot concentrated hydrochloric acid, crystallization of the $LnCl_3 \cdot 6H_2O$ hydrate, partial dehydration of $LnCl_3 \cdot 6H_2O$ to $LnCl_3 \cdot H_2O$ monohydrate, final dehydration and distillation resulting in high purity $LnCl_3$ (Ln = Pr or Nd). The details of the synthesis were described in [2].

Lithium chloride was a Merck Suprapur reagent (min. 99.9%). Before use it was progressively heated up to fusion under gaseous HCl. HCl in excess was then removed from the melt by argon bubbling.

All chemicals were handled in an argon glove box with a measured volume fraction of water of about 2×10^{-6} and continuous gas purification by forced recirculation through external molecular sieves.

2.2. Mixing Enthalpy Measurements

The mixing experiments were all of the simple liquid-liquid type, performed under pure argon at atmospheric pressure. The calorimetric apparatus, a Calvet-type high-temperature microcalorimeter, the mixing devices and the possible experimental methods have all been described in details in [3]. The so-called “break-off bubble” method was selected here. This method is both technically demanding and time-consuming since only one mixing experiment at a time can be performed after prior thermal equilibration of samples for about 2 h. However, it makes it possible to measure directly, and more accurately, the heat effect during the mixing of components, *e.g.* with no corrective term as for instance with the far easier and faster indirect drop method; the latter consists in adding a solid component to a liquid bath, and thus the mixing enthalpy, obtained from the experimental heat effect

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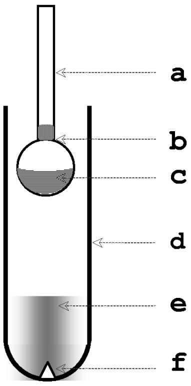

Fig. 1. Break-off bubble method: a, drop quartz tube; b, break-off quartz bubble; c, more volatile salt B; d, quartz crucible, e, less volatile salt A; f, break-off tip.

and corrected for the enthalpy increment of the added solid, is associated to a larger uncertainty. The principle of this break-off bubble method is schematized in Figure 1. Inside the quartz liner, located in the core of the high-temperature microcalorimeter, a cylindrical quartz crucible (d) contains the less volatile liquid salt A (e) while the second salt B (c) is contained in a spherical thin-walled ampoule (b). This quartz ampoule has to be thin enough to be broken with a single stroke. The mixing of the two liquids is initiated by crushing the bubble against the break-off tip on the bottom of the crucible. The thermal effect related to the ampoule break-off was evaluated in separate series of blank experiments and found very small and negligible. All this calorimetric set-up is maintained inside the quartz liner.

For any mixture under investigation, one component was weighed in the glove box within 10^{-5} g and placed in the break-off ampoule (b). The other component, weighed under the same conditions, was placed in the quartz crucible (d). The break-off ampoule was evacuated under controlled argon pressure, calculated to correspond to one atmosphere at the experimental temperature, and then sealed-off. It was then welded to a quartz tube, which could move up and down in the calorimetric cell through a special gas-tight ring. Argon filled the calorimetric cell through the same quartz tube. At thermal equilibrium, the ampoule was broken off against the inner break-off tip (f) at the bottom of the quartz crucible, and the thermal effect resulting from mixing was recorded. Calibration of the calorimeter was performed with NIST α-alumina with a reproducibility of about 3%. A weighed amount of α-alumina (30 – 100 mg) was dropped directly into the melt, and the corresponding enthalpy increment was measured. The overall experimental uncertainty of molar enthalpies of mixing is ±6%.

Table 1. Molar enthalpies of mixing $\Delta_{\text{mix}}H_\text{m}$ and interaction parameters λ of the $PrCl_3$-LiCl liquid system at $T = 1044$ K.

x_{PrCl_3}	$-\Delta_{\text{mix}}H_\text{m}$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}	x_{PrCl_3}	$-\Delta_{\text{mix}}H_\text{m}$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}
0.014	0.09	6.66	0.550	1.36	5.51
0.024	0.18	7.62	0.601	1.24	5.17
0.097	0.77	8.83	0.643	1.06	4.61
0.200	0.98	6.14	0.701	0.93	4.43
0.297	1.31	6.29	0.801	0.86	5.39
0.342	1.12	4.96	0.801	0.83	5.24
0.403	1.53	6.38	0.874	0.60	5.45
0.457	1.06	4.26	0.935	0.31	5.06
0.476	1.25	5.03	0.937	0.21	3.60
0.502	1.20	4.80	0.942	0.18	3.21

Table 2. Molar enthalpies of mixing $\Delta_{\text{mix}}H_\text{m}$ and interaction parameters λ of the $NdCl_3$-LiCl liquid system at $T = 1044$ K.

x_{NdCl_3}	$-\Delta_{\text{mix}}H_\text{m}$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}	x_{NdCl_3}	$-\Delta_{\text{mix}}H_\text{m}$ kJ mol^{-1}	$-\lambda$ kJ mol^{-1}
0.031	0.24	7.99	0.499	1.10	4.39
0.045	0.34	8.05	0.554	1.13	4.56
0.067	0.49	7.75	0.602	0.91	3.78
0.102	0.61	6.63	0.640	1.02	4.41
0.250	1.03	5.47	0.697	1.03	4.88
0.291	1.12	5.42	0.958	0.14	3.52
0.396	1.23	5.14			

3. Results

The calorimetric experiments were carried out at 1044 K. According to the phase diagrams established previously for $PrCl_3$-LiCl [4] and $NdCl_3$-LiCl [5], both systems are simple-phase liquids at 1044 K over the whole composition range. Thus the thermal effects obtained during the experimental runs are direct measurements of the mixing enthalpy of liquid components. In evaluating the results of our measurements, all uncertain experimental data were disregarded when evaporation or poor homogeneity of the melt during mixing was noticed.

The experimental enthalpies of mixing are given in Tables 1 and 2 and are plotted against composition in Figs. 2 and 3. Because of the relatively modest magnitude of this enthalpy of mixing, separate determinations of the two limiting partial enthalpies were conducted, each component acting as solvent of the other, successively. The experimental mixing procedure was similar to that described above, and only the relative amount of components was chosen such that the heat effect ΔQ obtained in the related experiments be representative of the reaction

$$n_1 L_{1(\text{l})} + n_2 L_{2(\text{l})} \rightarrow (n_1 + n_2)(L_1, L_2)_{(\text{l})} : \Delta Q,$$

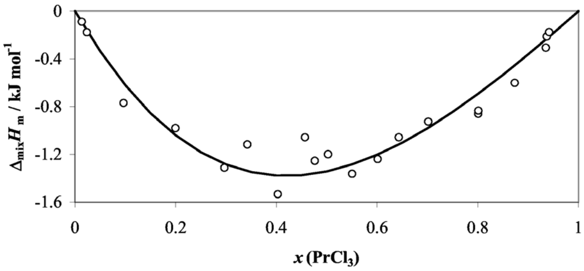

Fig. 2. Molar mixing enthalpy of the $PrCl_3$-LiCl liquid system; open circles: experimental results; solid line: polynomial fitting of experimental results.

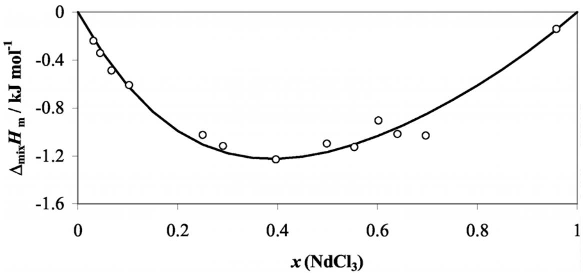

Fig. 3. Molar mixing enthalpy of the $NdCl_3$-LiCl liquid system; open circles: experimental results; solid line: polynomial fitting of experimental results.

where n_i is the mole number of the liquid component L_i with $n_1 \ll n_2$.

The limiting partial enthalpy is obtained as:

$$\Delta\bar{H}^{\infty}{}_{\mathrm{LiCl(LnCl_3)}} = \lim\left(\frac{\partial \Delta H}{\partial n_1}\right) = \lim\left(\frac{\partial \Delta Q}{\partial n_1}\right).$$

Under these conditions, the enthalpy effect did yield a direct measurement of the two limiting partial enthalpies of $\Delta\bar{H}^{\infty}{}_{\mathrm{LiCl(LnCl_3)}} = -3.71$ and -3.64 kJ mol^{-1} and $\Delta\bar{H}^{\infty}{}_{\mathrm{LnCl_3(LiCl)}} = -7.32$ and -7.60 kJ mol^{-1} for $PrCl_3$ and $NdCl_3$, respectively. Several experiments were carried out for the determination of each limiting partial enthalpy, and the results given are the average values corresponding to 4–6 individual experiments.

For every $LnCl_3$-LiCl mixture the interaction parameter

$$\lambda = \Delta_{\mathrm{mix}}H_{\mathrm{m}}/(x_{\mathrm{LiCl}} \cdot x_{\mathrm{LnCl_3}})$$

which represents the energetic asymmetry in the melt, was calculated. It was plotted against the mixture composition in Figs. 4 and 5, which also include the limiting values $\lambda_0 = \Delta\bar{H}^{\infty}_{\mathrm{LnCl_3(LiCl)}}$ and $\lambda_1 = \Delta\bar{H}^{\infty}_{\mathrm{LiCl(LnCl_3)}}$.

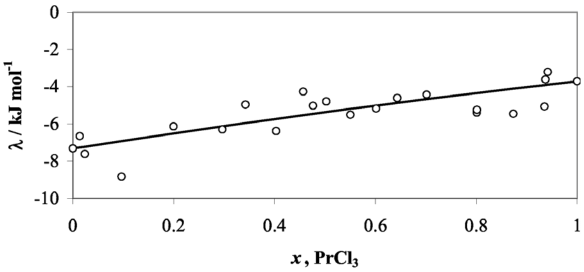

Fig. 4. Variation of the interaction parameter λ with the composition of the $PrCl_3$-LiCl liquid system; open circles: experimental results; solid line: polynomial fitting of experimental results.

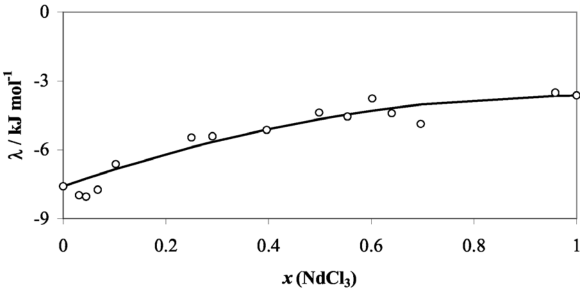

Fig. 5. Variation of the interaction parameter λ with the composition of the $NdCl_3$-LiCl liquid system; open circles: experimental results; solid line: polynomial fitting of experimental results.

The composition dependence of both interaction parameters was described properly by a second order polynomial (Tables 1 and 2)

$$\lambda_{\mathrm{PrCl_3}} = -7.32 + 4.18 \cdot x_{\mathrm{PrCl_3}} - 0.57 \cdot x^2_{\mathrm{PrCl_3}},$$
$$\lambda_{\mathrm{NdCl_3}} = -7.60 + 7.76 \cdot x_{\mathrm{NdCl_3}} - 0.38 \cdot x^2_{\mathrm{NdCl_3}}.$$

4. Discussion

For both systems, the molar enthalpies of mixing are negative over the whole composition range, with a minimum located at $x_{\mathrm{PrCl_3}}$ and $x_{\mathrm{NdCl_3}} \approx 0.4$; similar to those of several other $LnCl_3$-MCl (Ln = La, Ce, Pr, Nd, Tb; M = Na, K, Rb, Cs) systems [1, 2, 6–8]. As expected from the trends observed in those systems, the present $PrCl_3$-LiCl and $NdCl_3$-LiCl liquid systems are less exothermic than the $PrCl_3$- or $NdCl_3$-based mixtures including heavier alkali metal chlorides [1, 2]. Evidently the mixing thermicity depends on the ionic radius of the alkali metal, the smaller the ionic radius the smaller the absolute value of this enthalpy. Accordingly, the mixing enthalpy decreases (in absolute value) along the sequence CsCl > RbCl > KCl >

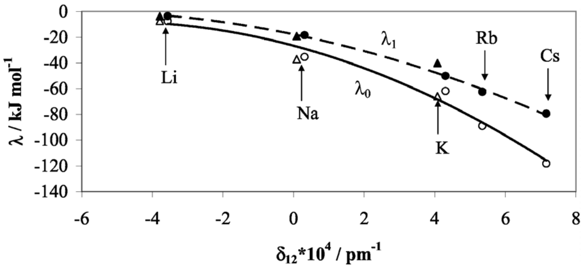

Fig. 6. Dependence of the limiting values of the interaction parameters (λ_0 and λ_1) on the size parameter δ_{12}; open circles and open triangles: λ_0 for NdCl$_3$-LiCl and PrCl$_3$-LiCl, respectively; black circles and black triangles: λ_1 for NdCl$_3$-LiCl and PrCl$_3$-LiCl, respectively.

NaCl > LiCl.

Figures 4 and 5 present the dependence of the interaction parameter λ on the molar fraction of the praseodymium and neodymium chlorides. This dependence, not very far from linear, confirms the low possibility of PrCl$_6^{3-}$ and NdCl$_6^{3-}$ complex formation in the corresponding melts. Indeed it was observed in the LnCl$_3$-MCl liquid systems with heavier alkali cations (M = K, Rb, Cs) [1, 2, 6 – 8], that complex formation was related to a minimum of the interaction parameter at the composition corresponding to the main complex stoichiometry, and thus to a less simple composition dependence.

Several approaches were made to describe complex formation in terms of physicochemical features of the salts. Except for the most simple charge-symmetrical AX-BX common anion systems, complex formation in melts occurs generally when the enthalpy interaction parameter λ varies strongly with composition, with a minimum located around $x_{\mathrm{BX_2}} \approx 0.33$ and $x_{\mathrm{BX_3}} \approx 0.25$ in the AX-BX$_2$ and AX-BX$_3$ charge-asymmetrical mixtures, respectively, and becomes more and more marked for the heaviest alkali cations A in the same series of AX-BX$_2$ and AX-BX$_3$ systems.

In a number of monovalent-divalent mixtures [9 – 14], the limiting interaction parameter λ for $x_2 \to 0$ (*i.e.* λ_0) was found to depend linearly on the size parameter $\delta_{12} = (d_1 - d_2)/d_1 d_2$, which accounts for ionic radii (cationic: r_{A^+}, $r_{\mathrm{B}^{2+}}$; anionic: r_{X^-}) and distances of ionic species $d_1 = r_{\mathrm{A}^+} + r_{\mathrm{X}^-}$ and $d_2 = r_{\mathrm{B}^{2+}} + r_{\mathrm{X}^-}$. Measurements on a series of lanthanide halide-alkali halide binary melts [6, 7, 15] and of certain binary fluoride melts [16 – 18] have indicated that a quadratic term [6] should be added to this linear equation:

$$\lambda_0 = a(T,P,x) + b(T,P,x)\delta_{12} + c(T,P,x)\delta_{12}^2,$$

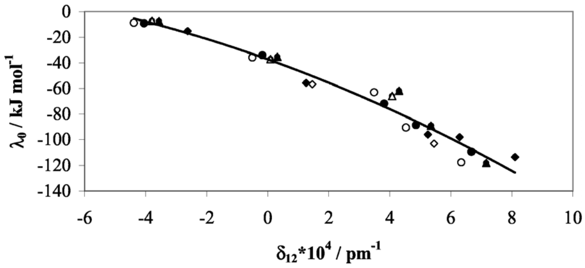

Fig. 7. Global dependence of the limiting interaction parameter (λ_0) on the size parameter δ_{12} of the LnCl$_3$-MCl liquid system series; open circles: LaCl$_3$-MCl (M = Li, Na, K, Rb, Cs); black circles: CeCl$_3$-MCl (M = Li, Na, K, Rb, Cs); open triangles: PrCl$_3$-MCl (M = Li, Na, K); black triangles: NdCl$_3$-MCl (M = Li, Na, K, Rb, Cs); open diamonds: DyCl$_3$-MCl (M = Na, K); black diamonds: TbCl$_3$-MCl (M = Li, Na, K, Rb, Cs).

where the parameters *a*, *b* and *c* are functions of temperature T, pressure P, and composition x.

Prior to the present work, systematic calorimetric investigations were conducted on the systems PrCl$_3$-NaCl, PrCl$_3$-KCl [1] and NdCl$_3$-MCl (M = Na, K, Rb, Cs) [2]. The corresponding partial limiting enthalpy of each component, $\Delta\overline{H}^{\infty}_{\mathrm{PrCl_3(MCl)}}$ and $\Delta\overline{H}^{\infty}_{\mathrm{NdCl_3(MCl)}}$ (λ_0), and $\Delta\overline{H}^{\infty}_{\mathrm{MCl(PrCl_3)}}$ and $\Delta\overline{H}^{\infty}_{\mathrm{MCl(NdCl_3)}}$ (λ_1), respectively, was calculated from these enthalpy of mixing data. They were plotted against the size parameter $\delta_{12} = (d_1 - d_2)/d_1 d_2$ in Figure 6. The ionic radii of Ln^{3+}, M$^+$ and Cl$^-$ were taken from [19]. A smooth dependence of λ_0 and λ_1 on the size parameter was found both for the NdCl$_3$-MCl and PrCl$_3$-MCl liquid mixtures. As the ionic radii of Pr^{3+} and Nd^{3+} are very similar (101.3 and 99.5 pm, respectively), this dependence is almost identical for both systems.

All the existing mixing enthalpy data of lanthanide chloride-alkali metal chloride systems [1, 2, 6 – 8, 20] were analyzed. Figure 7 clearly shows that all the corresponding partial limiting enthalpies of lanthanide chlorides, $\Delta\overline{H}_{\mathrm{LnCl_3(MCl)}}$ (λ_0) lie on a single curve, which is a quadratic function of the size parameter δ_{12}. This size parameter is influenced mostly by the ionic radius of the alkali metal cation, changing from 74 pm (Li$^+$) to 170 pm (Cs$^+$). The change of the cationic radius of the lanthanide (Ln^{3+}) is significantly smaller [from 106.1 pm (La^{3+}) to 90.8 pm (Dy^{3+})], and the influence of this radius on the size parameter is also significantly smaller. Generally, the larger the ionic radius of the alkali cation, the larger is the size parameter and accordingly the absolute value of the interaction parameter λ. For the small lithium cation ($r_{\mathrm{Li}^+} = 74$ pm), the size parameter δ_{12} is negative, resulting in small interaction parameters (λ_0, λ_1) and mixing enthalpies in the LiCl systems. These small mixing enthalpies can be interpreted as low possibility of complex formation.

As discussed earlier [1, 2, 6–8], the formation of $LnCl_6^{3-}$ complexes takes place in $LnCl_3$-MCl liquid mixtures. The mixing enthalpy becomes more negative with increase of the amount of complexes formed in the melt. The role of the alkali chlorides is to provide additional chloride ions to enable Ln^{3+} to expand its coordination shell. But there is a competition between M^+ and Ln^{3+} for Cl^- ions in the ionic environment. The result of this competition depends on the relative attracting power of the alkali ion. Li^+ is the most chloride attracting ion and Cs^+ the least. The radius of the alkali metal ion will therefore govern the complex ion formation in $LnCl_3$-MCl binary systems. Thus the addition of CsCl to $LnCl_3$ favors complex ion formation more than addition of RbCl and results in larger negative values of the mixing enthalpy. Indeed, in the $LnCl_3$-MCl systems the mixing enthalpy becomes more negative from lithium to caesium. It is quite small in the presence of the small highly polarizing Li^+ ion, which is sufficiently polarizing to distort the complexes that would be formed and to make them unstable.

[1] M. Gaune-Escard, L. Rycerz, W. Szczepaniak, and A. Bogacz, Thermochim. Acta **236**, 59 (1994).
[2] M. Gaune-Escard, A. Bogacz, L. Rycerz, and W. Szczepaniak, Thermochim. Acta **236**, 67 (1994).
[3] M. Gaune-Escard, Thermochemical methods. In: Molten Salts: From Fundamentals to Applications, Proceedings of the NATO Advanced Study Institute (Kas, Turkey, May 4 – 14, 2001), NATO Science Series, 375, Vol. 52, (Ed. M. Gaune-Escard), Kluwer Academic Publishers, Dordrecht 2001.
[4] I. Kim, Y. Okamoto, and T. Ogawa, Proceedings of the Seventh China-Japanese Bilateral Conference on Molten Salt Chemistry and Technology (Xian, China, October 26 – 30, 1998).
[5] K. Igarashi, M. Kosaka, and Y. Iwadate, Denki Kagaku **58**, 469 (1990).
[6] G. N. Papatheodorou and T. Østvold, J. Phys. Chem. **78**, 181 (1974).
[7] G. N. Papatheodorou and O. J. Kleppa, J. Phys. Chem. **78**, 176 (1974).
[8] L. Rycerz and M. Gaune-Escard, High Temp. Material Processes **2**, 483 (1998).
[9] G. N. Papatheodorou and O. J. Kleppa, J. Inorg. Nucl. Chem. **33**, 1249 (1971).
[10] G. N. Papatheodorou and O. J. Kleppa, J. Inorg. Nucl. Chem. **32**, 889 (1970).
[11] T. Østvold, High Temp. Sci. **4**, 51 (1972).
[12] O. J. Kleppa, J. Phys. Chem. **66**, 1668 (1962).
[13] F. G. McCarty and O. J. Kleppa, J. Phys. Chem. **68**, 3846 (1964).
[14] O. J. Kleppa and F. G. McCarty, J. Phys. Chem. **70**, 1246 (1966).
[15] F. V. Dienstbach and R. Blachnik, Inorg. Allg. Chem. **412**, 97 (1975).
[16] K. C. Hong and O. J. Kleppa, J. Phys. Chem. **82**, 176 (1978).
[17] E. W. Dewing, J. Electrochem. Soc. **123**, 1289 (1976).
[18] K. C. Hong and O. J. Kleppa, J. Phys. Chem. **83**, 2589 (1979).
[19] A. G. Sharpe, Inorganic Chemistry, Longman, New York 1986, pp. 146 and 659.
[20] M. Gaune-Escard, L. Rycerz, and A. Bogacz, J. Alloys Comp. **204**, 185 (1994).