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THERMOCHEMISTRY OF MIXTURES OF LANTHANOID CHLORIDES WITH CHLORIDES OF SOME DIVALENT CATIONS

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ABSTRACT

The phase diagrams of the systems $MgCl_2 + LaCl_3(GdCl_3, YbCl_3)$, $CaCl_2 + LaCl_3(YbCl_3)$, $ZnCl_2 + GdCl_3(YbCl_3)$ and $PbCl_2 + YbCl_3$ were determined by differential thermal analysis. All systems are eutectic. Additionally, the enthalpies of mixing of the systems $MgCl_2 + LaCl_3(GdCl_3, YbCl_3)$, $CaCl_2 + LaCl_3(GdCl_3, YbCl_3)$ and $MgBr_2 + GdBr_3$ were determined in a heat flow calorimeter. In the system $CaCl_2 + LaCl_3$, exothermic enthalpies of mixing were observed; the other systems show positive enthalpies of mixing. However, the deviations from ideal behaviour are small.

INTRODUCTION

Lanthanoid halides are known to form four different series of compounds with alkali halides, namely, MLn_2X_7, $M_3Ln_2X_9$, M_2LnX_5 and M_3LnX_6 (M = Na, K, Rb, Cs; Ln = La–Lu; X = Cl, Br, I) [1–5]. The stability of these compounds increases with increasing radius of the alkali cation and decreasing radius of the lanthanoid ion. The forces acting between the ions which lead to the formation of compounds are also revealed by the enthalpies of mixing of the respective melts. These are exothermic. The values show pronounced minima at 75 mole % MCl, the depth of which depend on the differences in the ionic radii. Compound formation in the solid state [6,7] also shows a dependence on ionic radii.

The influence of the different charges of the cations on the stability of ternary lanthanoid halides is not well known. Little information has been published [8–12] on the phase diagrams of systems formed by lanthanoid halides and halides of M^{2+} ions. The present work was carried out to give a more detailed view of the thermochemical behaviour of $MCl_2 + LnCl_3$ systems.

EXPERIMENTAL

Lanthanum, gadolinium and ytterbium chloride were obtained by dissolving the respective oxides (99.99% Auer-Remy) in concentrated HCl. The

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solutions were evaporated. The residual chlorides were then purified by high-temperature reaction with NH_4Cl [13]. The melting points of $LaCl_3$, $GdCl_3$ and $YbCl_3$ were 875, 608 and 864°C, respectively. Commercial $CaCl_2$, $MgCl_2$, $ZnCl_2$ and $PbCl_2$ were dried in another way: a dried mixture of HCl and N_2 was passed through the molten salt (enclosed in a silica tube with filter), and finally the gas stream was reversed and the molten salt flushed through the filter. All salts were then handled under anhydrous conditions. The melting points of the specimens obtained were 771°C for $CaCl_2$, 707°C for $MgCl_2$, 304°C for $ZnCl_2$ and 501°C for $PbCl_2$. In the latter sample the phase transformation at 424°C could be found in the differential thermal analysis. It seems that the occurrence of the phase transformation sometimes reported in the literature depends on the purity of the sample. The samples for the differential thermal analysis were prepared from the respective anhydrous salts. The powders were mixed in the desired proportions (total mass 2.5 g) and the mixtures sealed under vacuum in silica ampoules. The mixtures were molten and afterwards annealed for 1 month. The annealing temperatures were chosen from preliminary experiments, and were normally about 30°C below the respective eutectic temperatures. The reaction of the lanthanoid chlorides with the M^{2+} chlorides were studied by DTA. The heating curves were recorded in a DTA apparatus constructed in this laboratory. The heating rate was 10° min^{-1}, and the reference material used was silicon.

In an extension of this work we have determined the enthalpies of mixing at 1173 K for some of the systems presented in this paper. The apparatus and the method [6] have already been described. An atmosphere of purified argon was used. The apparatus was calibrated with gold. The enthalpies were taken from the tabulated data of Hultgren et al. [14]. The experiments were aimed at getting a rough idea of the correlation between the phase diagram and thermodynamic data of the melts, and not to get very precise measurements. Thus the error in these first measurements is high, probably in the range +5 to −15%, though the reproducibility was better. Precise measurements of these systems are difficult, due to the small heat effects, but are in progress.

RESULTS

The systems $MgCl_2 + LaCl_3(GdCl_3, YbCl_3)$, $CaCl_2 + LaCl_3(YbCl_3)$, $ZnCl_2 + GdCl_3(YbCl_3)$ and $PbCl_2 + YbCl_3$ are of the eutectic type. The phase diagrams are presented in Figs. 1–4. In DSC experiments on the samples of the system $MgCl_2 + GdCl_3$, some very small thermal effects at temperatures below the eutectic temperature were observed (305°C, max. at ~ 50 mole % $MgCl_2$; 504°C, max. at ~ 50 mole % $MgCl_2$; 518°C, max. at ~ 80 mole % $MgCl_2$). This may be an indication of the existence of new

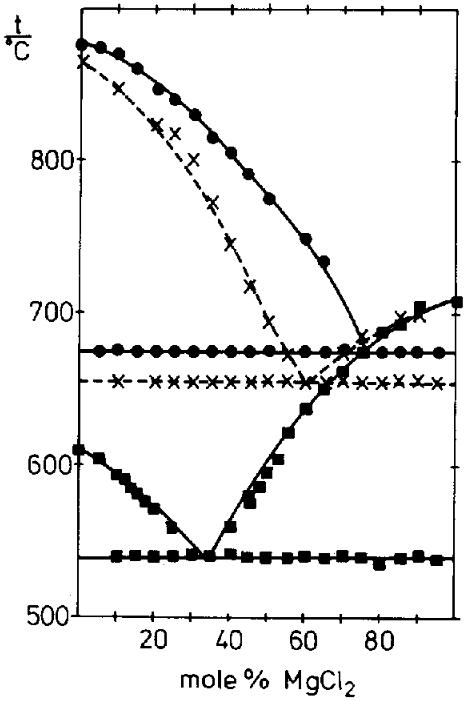

Fig. 1. Phase diagrams for the systems: ●, $LaCl_3 + MgCl_2$; ■, $GdCl_3 + MgCl_2$; ×, $YbCl_3 + MgCl_2$.

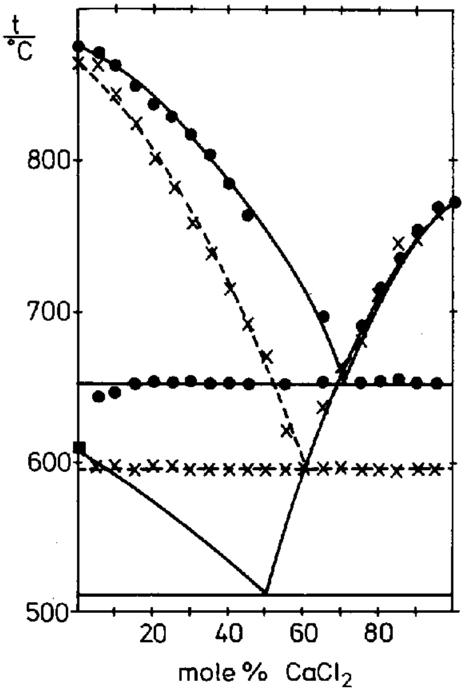

Fig. 2. Phase diagrams for the systems: ●, $LaCl_3 + CaCl_2$; ■, $GdCl_3 + CaCl_2$ calculated; ×, $YbCl_3 + CaCl_2$.

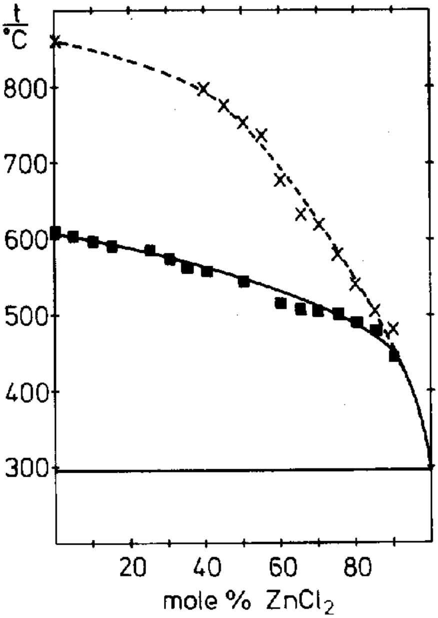

Fig. 3. Phase diagrams for the systems: ■, $GdCl_3 + ZnCl_2$; ×, $YbCl_3 + ZnCl_2$.

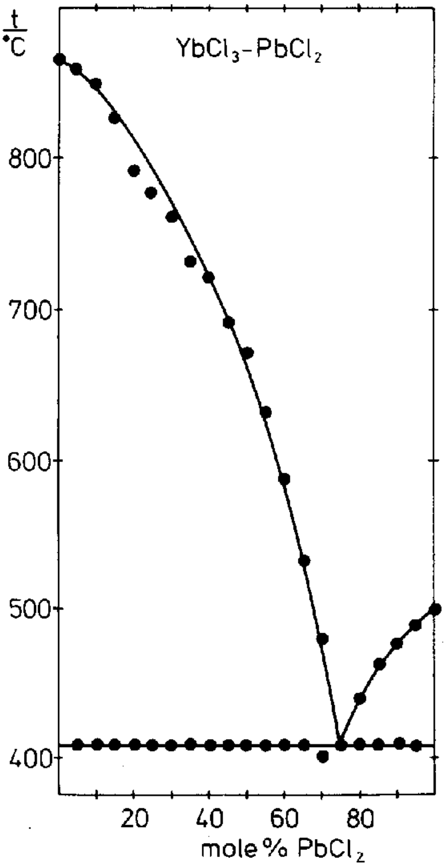

Fig. 4. Phase diagram for the system $YbCl_3 + PbCl_2$.

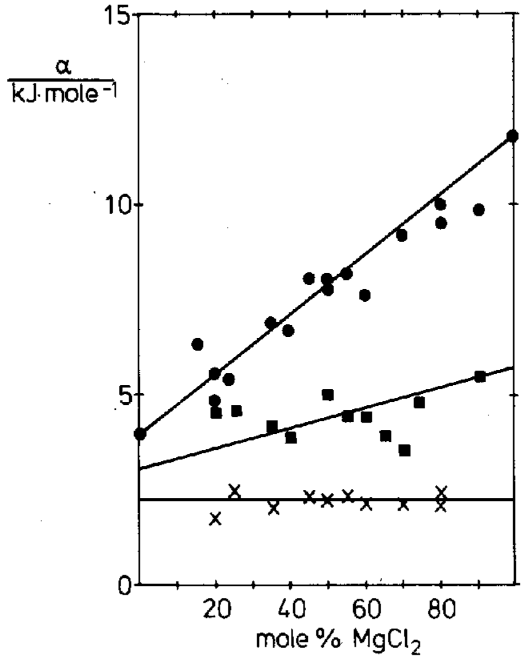

Fig. 5. Concentration dependence of the interaction parameter, H^E/x_1x_2, for the molten mixtures with $MgCl_2$. ●, $LaCl_3$; ■, $GdCl_3$; ×, $YbCl_3$.

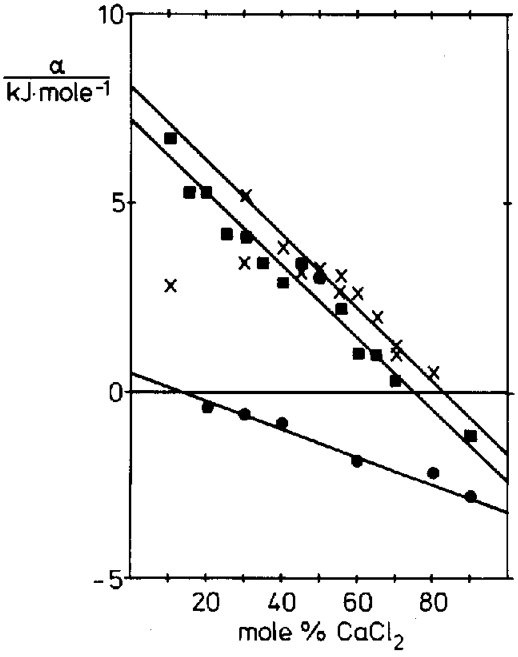

Fig. 6. Concentration dependence of the interaction parameter, α, for the molten mixtures with $CaCl_2$. ●, $LaCl_3$; ■, $GdCl_3$; ×, $YbCl_3$.

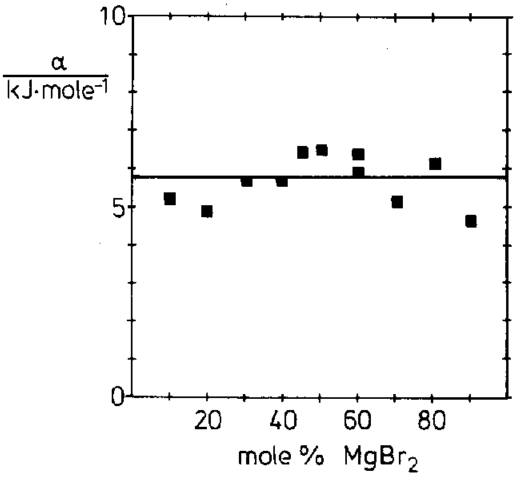

Fig. 7. Concentration dependence of the interaction parameter, α, for the molten mixtures of $GdBr_3$ with $MgBr_2$.

compounds of the peritectoid and/or high-temperature type in this system. No systematic search for these compounds was made as we were primarily interested in the course of the liquidus and solidus lines.

The preliminary data of the enthalpies of mixing are shown in Figs. 5–7 for the systems $MgCl_2 + LaCl_3(GdCl_3, YbCl_3)$, $CaCl_2 + LaCl_3(GdCl_3, YbCl_3)$ and $MgBr_2 + GdBr_3$, respectively. The data are given as usual in form of the function $\alpha = H^E/x_1x_2$.

DISCUSSION

From Figs. 1 and 2 it can be concluded that the systems behave identically on the side of the M^{2+} halide. This contrasts with the behaviour observed in the $MCl + LnCl_3$ systems in which the curvature of the liquidi on the MCl side of the systems depends on the size of the M^+ ion [15] which has been explained by assuming the existence of $LnCl_6^{3-}$ ions in these melts.

The liquidus curves in the systems presented here could be calculated on the assumption of ideal or nearly ideal solutions using the van't Hoff equation for the freezing point depression. The enthalpies of fusion used in the calculations were taken from the tabulated data of Barin et al. [16].

The corresponding calculated and observed liquidi indicate the absence of anionic complexes, $[LnX_n]^{(+3-n)}$, in these melts. As an example, the system $LaCl_3 + CaCl_2$ is given in Fig. 8. The unknown phase diagrams can thus be calculated on the same assumptions. The differences between calculated and observed eutectic temperatures and compositions in the system $LaCl_3 + CaCl_2$ were 11°C, and 3 mole %, respectively. In the system $YbCl_3 + CaCl_2$,

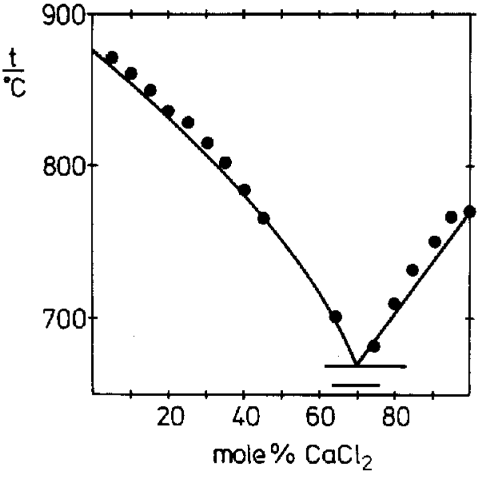

Fig. 8. Liquidus data of the system $LaCl_3 + CaCl_2$ (ideal solution model). ————, Calculated; ●, observed.

the model of the regular solution gave a better fit; the A parameter of the equation $H^E = Axx_2$ was 6250 J mole^{-1}.

The most successful approach for a correlation of enthalpies of mixing in charge-unsymmetrical molten salts with the ionic parameters is the conformal solution theory. This theory was developed for molten salt systems by Davis [17]. Davis postulated that the enthalpies of mixing should vary linearly with the parameter $\delta_{1,2}$ according to the equation $\delta_{1,2} = (d_1 - d_2)/d_1 d_2$, where $d_1 = r_{Ln^{3+}} + r_{Cl^-}$ and $d_2 = r_{M^{2+}} + r_{Cl^-}$. Østvold [18], in a thermodynamic study of fused mixtures containing alkali and alkaline earth halides, has found a satisfactory agreement between the theoretical predictions and the experimental results. Some general statements could be made by Østvold.

(1) When a halide of an alkaline earth cation is mixed with the corresponding alkali halide the system shows increasing negative deviation from ideal behaviour with increasing size of the alkali cation.

(2) For a given alkali metal cation the negative deviations from ideality in the excess enthalpies increase as the size of the M^{2+} ion becomes smaller. These observations can be explained by the competition of the two different cations for the common anion which leads in many cases to the formation of complex anionic species.

Though our values are not the results of measurements with high precision, the trends revealed are not consistent with the statements based on Østvold's work. All the mixtures investigated do not deviate largely from ideal behaviour. However, the deviations are mainly positive and not negative, as one would have expected. The magnitude of these deviations decreases with decreasing size difference between the cations. In the Ca^{2+}

ion-containing systems, small negative enthalpies of mixing in the $CaCl_2$ + $LaCl_3$ system were observed. Kleppa [19] has shown that the ionic potential of the cation, Z/r, is a rough quantitative measure of the complex-forming ability of the cation. The concentration dependence of our interaction parameter, α, reflects the influence of the ionic potential. In the presence of Ca^{2+} ions, the formation of $LnCl_6^{3-}$ would be supported by the higher ionic potential of Ln^{3+}. The α parameters are more negative on the $CaCl_2$ side of the systems. In systems with magnesium chloride one would expect, from the comparison of the ionic potentials of Mg^{2+} and Ln^{3+}, a preference for $MgCl_4^{2-}$. This corresponds to the smaller endothermic values of the enthalpies of mixing on the $MgCl_2$ side of the respective systems. From the slope of the α function, one can conclude that there is a small influence of the ability to form anionic complexes on the thermodynamic data of the melts. However, these forces are so small that they do not lead to the formation of solid compounds.

No influence of the common anion on the enthalpy of mixing was found as is evident from a comparison of the data of $GdCl_3$ + $MgCl_2$ and $GdBr_3$ + $MgBr_2$.

It seems that for a complete understanding of molten salt mixtures, precise measurements of the enthalpies of mixing of charge-unsymmetrical mixtures containing cations of higher valencies are necessary.

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