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Note

ENTHALPIES OF MIXING OF SOME BINARY LIQUID MIXTURES OF RARE EARTH HALIDES

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In recent publications we have reported the enthalpies of mixing, H^E, for the charge-unsymmetrical fused-salt mixtures $ACl-MCl_3$ and BCl_2-MCl_3 [1–3], where A is an alkali metal, B an alkaline earth metal and M a rare earth element. In the case of the $ACl-MCl_3$ systems the enthalpy of mixing data could be interpreted by the aid of the Davis–Rice theory of fused salts [4] with the basic assumption that the Coulombic forces should determine the total enthalpy of mixing. The theory predicts exothermic H^E values and a linear relationship between the interaction parameter $\alpha = H^E(x_1x_2)^{-1}$ and a size parameter $\delta_{1,2} = d_1 - d_2(d_1d_2)^{-1}$ at constant temperature and composition. x_1 and x_2 are the mole fractions of the two components, d_1 and d_2 are the cation–anion distances for the two salts. The behaviour of the curves obtained by plotting α vs. the mole fraction suggests that in these melts an octahedral $LnCl_6^{3-}$ complex stabilizes the melt. Octahedral complexes in

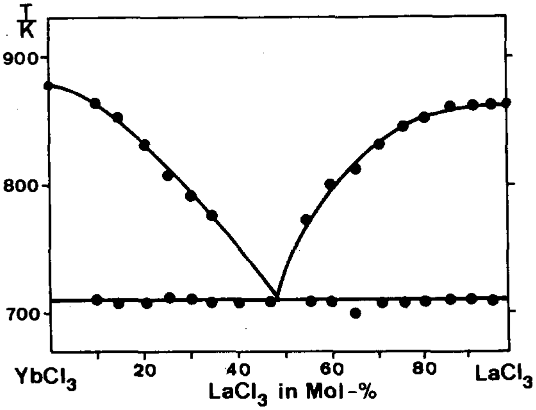

Fig. 1. Phase diagram $YbCl_3-LaCl_3$.

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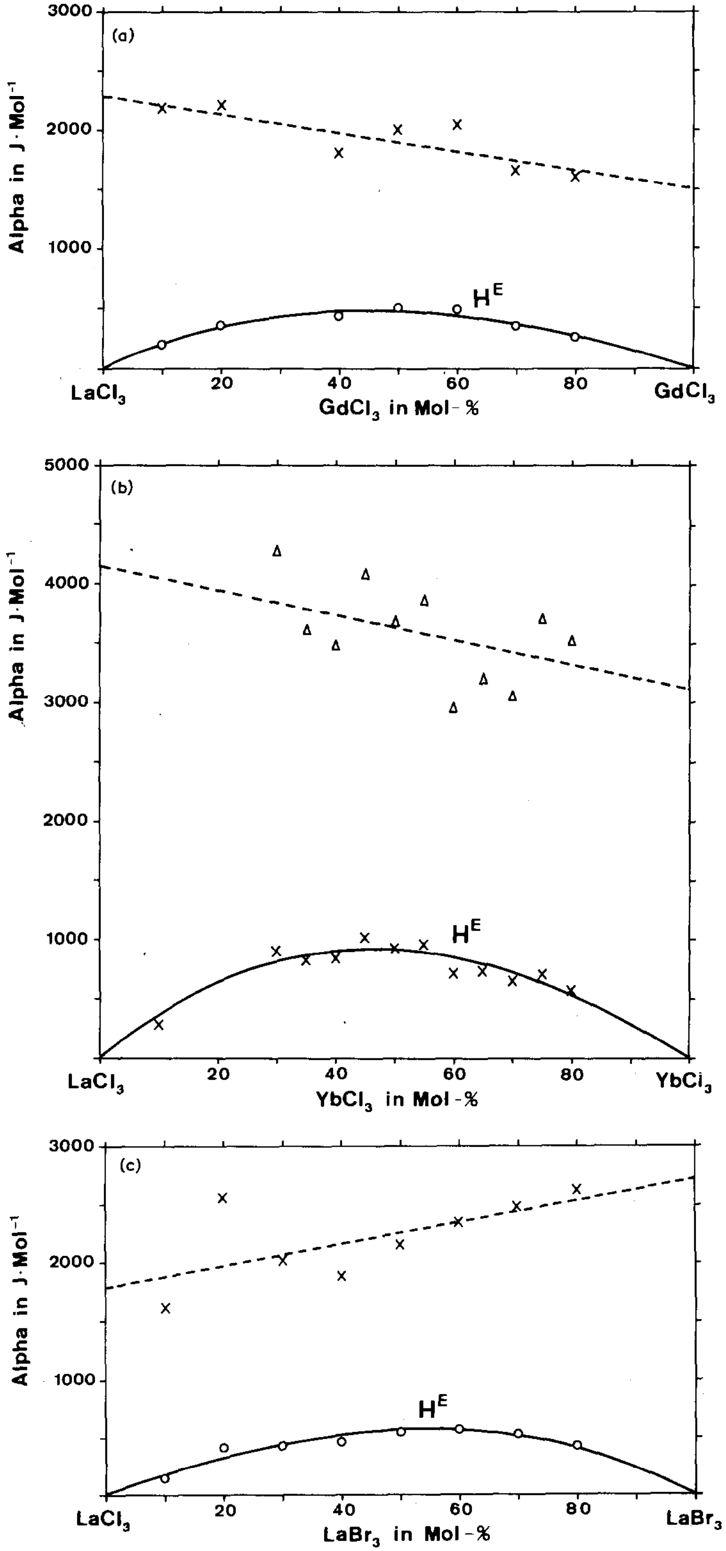

Fig. 2. Interaction parameter α and excess enthalpies vs. mole fraction $LaCl_3$ of the systems $LaCl_3$–$GdCl_3$ (a), $LaCl_3$–$YbCl_3$ (b), and $LaCl_3$–$LaBr_3$ (c).

melts could be confirmed by Raman spectroscopic measurements [5].

Mixtures formed among alkaline earth halides and rare earth halides show a deviating behaviour. The enthalpies of mixing with $MgCl_2$ and $CaCl_2$ are endothermic, however, in the $SrCl_2$ systems with the formation of compounds in the solid state exothermic H^E values were observed, with minima at the composition of the compounds.

In the present work the studies were extended to the binary mixtures of the type MCl_3–$M'Cl_3$. Phase diagrams for rare earth chloride–rare earth chloride mixtures have recently been published [6,7]. Within the isotypic series $LaCl_3 \rightarrow GdCl_3$ complete solid solubility was found. Phase diagrams involving members from non-isotypic series show eutectic behaviour. This type of phase diagram thus excludes exothermic contributions to the enthalpy of mixing from the formation of compounds in the solid state. Due to the similarity of the ionic radii and polarizabilities of the cations the coordination and the bonding in the different rare earth chloride melts should be very similar. In those charge-symmetrical mixtures, for which $\delta_{1,2}^2$ is small positive or negative, deviations from ideality are predicted by the conformal solution theory [8].

We have measured the enthalpies of mixing in the systems $LaCl_3$–$GdCl_3$, $LaCl_3$–$YbCl_3$ and $LaCl_3$–$LaBr_3$ at 1200 K. The experimental procedure was the same as described previously [9]. It is estimated that the experimental values are associated with an error of ±8%.

The phase diagram $LaCl_3$–$YbCl_3$ has so far not been investigated; our results are shown in Fig. 1. The system is of eutectic type. The results of the calorimetric experiments are plotted in Fig. 2 also in form of the interaction parameter, α, vs. the mole fraction of $LaCl_3$. The enthalpies of mixing for the three systems are positive, the interaction parameters vs. composition curves give straight lines. The type of phase diagram has no important influence. In transition metal chloride mixtures small positive deviations from ideality were explained by Papatheodoru and Kleppa [10]. They assumed, in the mixtures, a change in the covalent bridging interactions (M–Cl–M) between the ions as compared with the pure salts. On the basis of the electronegativity differences [11] between M and Cl the covalent character of the M–Cl bond should increase in the sequence La < Gd < Yb. The magnitude of the change in the covalent bridging interactions will depend on the covalent character of the melts and increases as expected: $H^E(LaCl_3\text{–}GdCl_3) < H^E(LaCl_3\text{–}YbCl_3)$. The positive enthalpy of mixing in the $LaCl_3$–$LaBr_3$ systems, on the other hand, reflects the change in polarizabilities of the anions.

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