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# MOLTEN LITHIUM SULPHATE—SODIUM SULPHATE—POTASSIUM SULPHATE EUTECTIC: REACTIONS AND ABSORPTION SPECTRA OF SOME LANTHANIDES

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## ABSTRACT

The reactions of lanthanum(III) chloride, cerium(III) chloride and sulphate, cerium(IV) sulphate, praseodymium(III) chloride and sulphate and europium(III) chloride, in molten lithium sulphate—sodium sulphate—potassium sulphate eutectic, have been studied. Lanthanum(III) chloride and cerium(IV) and praseodymium(III) sulphates reacted as acids whereas cerium(III) chloride and sulphate and praseodymium(III) and europium(III) chlorides exhibited oxidation—reduction in addition to the acid—base reaction. The stoichiometries of the reactions were established by thermogravimetry. Visible and UV absorption spectra of lanthanum(III), cerium(III), praseodymium(III), neodymium(III) and dysprosium(III) solutions, in the molten sulphate eutectic at 580°C, are presented and compared with those reported in other melts.

## INTRODUCTION

Our understanding of the inorganic chemistry of molten sulphates is by far still incomplete. Indeed, research devoted to pure inorganic chemistry in these melts is very limited and comprised of studies of the reactions and spectra of some first row transition metal compounds [1] and of the reactions of condensed phosphates [2]. Spectroscopic studies are confined to IR and Raman spectra of molten alkali metal sulphates [3,4] and visible and UV spectra of dilute solutions of transition metal ions in the ternary sulphate eutectic [5]. Some further information can be derived from electrochemical studies related to acid—base behaviour [6] and corrosion of metals by molten sulphates [7—11]. On the other hand, several studies, mainly concerned with the comparative electronic spectra of lanthanides in molten fluorides [12,13], chlorides [14—17] and nitrates [18—22], have been reported.

In the present investigation the reactions and spectra of some compounds of lanthanides in the ternary sulphate eutectic were studied and the results are now reported as a contribution to the chemistry of molten sulphates.

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## EXPERIMENTAL

### *Materials*

Pure anhydrous lanthanum(III), cerium(III), praseodymium(III) and europium(III) chlorides were prepared by dehydration of the hydrated chlorides with thionyl chloride [23]. Anhydrous cerium(III) and cerium(IV), praseodymium(III), neodymium(III) and dysprosium(III) sulphates were prepared by heating the pure hydrated sulphates to constant weights at 245, 200, 240, 290 and 200°C, respectively [24]. The ternary sulphate eutectic was prepared as previously described [2].

### *Procedure*

Reactions were carried out, using powdered reactant mixtures (0.5 g of the eutectic), in 5 ml alumina crucibles, on a Stanton-Redcroft MF-H5 mass-flow thermobalance with a heating rate of 4°C min$^{-1}$; unless otherwise stated, all runs were under a nitrogen atmosphere. Visible and UV spectra of melt solutions were measured on a Pye-Unicam SP8100 recording double-beam spectrophotometer, modified as previously described for the Pye-Unicam SP1800 [25], but using steel furnaces instead of the two copper furnaces used in the previous modification, which permits measurements up to 650°C. Gaseous products were identified by their IR bands at 520, 1150 and 1350—1360 cm$^{-1}$ for sulphur dioxide and at 485, 540 and 1395 cm$^{-1}$ for sulphur trioxide [26], measured on a Perkin-Elmer 377 spectrometer. The X-ray powder patterns were obtained on a Philips 1410 diffractometer using nickel filtered Cu$K_\alpha$ radiation.

## RESULTS AND DISCUSSION

$LaCl_3$, as a white powder, dissolved in the molten ternary sulphate eutectic at 580°C to form a colourless solution. The visible and UV spectra of the melt alone (Fig. 1, curve A) showed a single band at 204 nm due to $n \rightarrow \pi^*$ transition of the sulphate ion [27], whereas spectra of the melt solution of La(III), $^1S_0$ state, (Fig. 1, curve B) showed an intense band at 240 nm with a shoulder at 264 nm which were assigned to charge transition, ligand to metal, in a soluble sulphatolanthanum(III) complex; complex species of the form $LnSO_4^+$ have been suggested in aqueous solutions of lanthanides [28]. The melt solutions reacted at around 800°C to form a white precipitate with the evolution of sulphur trioxide and sulphur dioxide; the presence of the latter is probably due to decomposition of sulphur trioxide above 400°C [29]. The white precipitate, which was separated from the melt after a reaction at 1100°C for 2 h, consisted of a white powder and a bright crystalline solid. The powder pattern of the washed and dried precipitate corresponded to those reported in the ASTM index for $La_2O_2SO_4$, $La_2O_3$ and $La(OH)_3$; the latter is probably formed by hydrolysis of the basic sulphate, $La_2O_2SO_4$. Thermogravimetry (Fig. 2, curve A) showed two stages of weight loss, overlapping with that due to decomposition of the sulphate melt (Fig. 2, curve B). Weight losses at minima (a) and (a') of the thermogram, after correction for the melt decomposition, were 31.9 and 48.2% (calcd. for loss of 1 S + 3 O

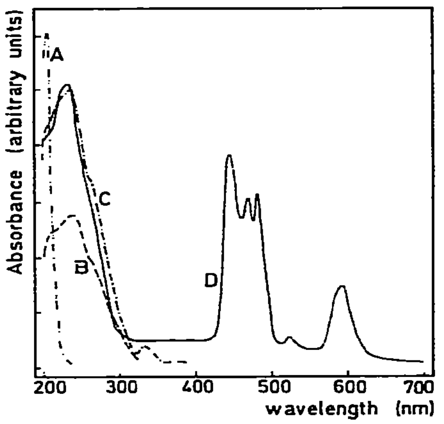

Fig. 1. Absorption spectra of molten lithium sulphate—sodium sulphate—potassium sulphate eutectic solution at 580°C. A, Pure eutectic; B, $LaCl_3$; C, $Ce_2(SO_4)_3$; D, $Pr_2(SO_4)_3$ (no absorption 700—900 nm).

and for loss of 1.5 S + 4.5 O per $LaCl_3$ are 32.6 and 49.0%, respectively). Thus, the decomposition of the La(III) solution may, be represented by the following acid—base reactions

$$2\,La^{3+} + 3\,SO_4^{2-} \rightarrow La_2O_2SO_4 + 2\,SO_3 \qquad (1)$$

and

$$La_2O_2SO_4 \rightarrow La_2O_3 + SO_3 \qquad (2)$$

and may also be compared with the decomposition of $La_2(SO_4)_3$ to $La_2O_2SO_4$ and $La_2O_3$ [30].

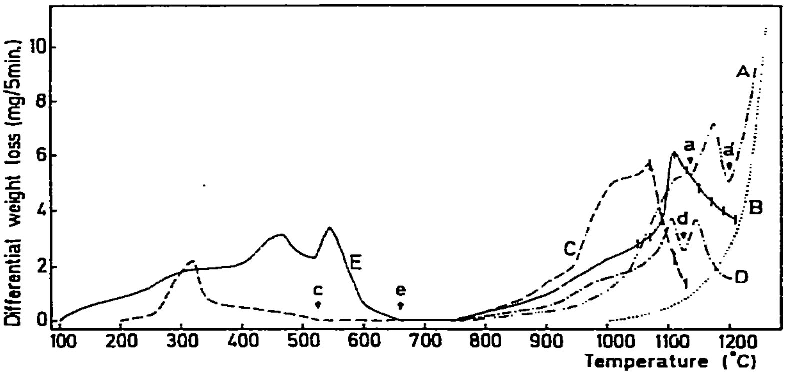

Fig. 2. Thermogravimetry of lithium sulphate—sodium sulphate—potassium sulphate eutectic. A, 0.56 m $LaCl_3$; B, 0.5 g pure eutectic; C, 0.55 m $CeCl_3$ (maintained at 1070°C for 20 min); D, 0.19 m $Ce_2(SO_4)_3$; E, 0.99 m $Ce(SO_4)_2$ (maintained at 1050°C for 40 min).

$CeCl_3$ reacted with the melt in two stages commencing at 200 and 760°C (Fig. 2, curve C), to form a pale yellow precipitate, with the evolution of sulphur trioxide and sulphur dioxide. The powder pattern of the washed and dried pale yellow precipitate corresponded to that of $CeO_2$. The overall weight loss, after correction for melt decomposition, of 48.5% corresponded to that expected from the stoichiometry

$$2\,Ce^{3+} + 3\,SO_4^{2-} \rightarrow 2\,CeO_2 + 2\,SO_3 + SO_2 \qquad (3)$$

(calcd. for loss of 1.5 S + 4 O per $CeCl_3$ is 45.5%).

Aqueous solutions of solid mixtures obtained at the end of the first stage contained a pale yellow precipitate. The powder pattern of the pale yellow precipitate corresponded to that of both $Ce_2(SO_4)_3$ and $CeO_2$. The weight loss at the end of this stage (at c) of 12.7% was attributed to reaction on the surface of the powder particles of the $CeCl_3$ to form a coating of $CeO_2$, which prevented completion of the reaction; the remaining precipitated as $Ce_2(SO_4)_3$ when the reaction mixture was dissolved in water.

$Ce_2(SO_4)_3$ dissolved in the melt at 580°C forming a colourless solution. Its spectra (Fig. 1, curve C) showed an intense band at 236 nm and a shoulder at 264 nm, assigned to charge transitions of the type ligand to metal in a soluble sulphatocerium(III) complex, and an *f—f* band at 325 nm similar to that obtained for Ce(III) in molten chloride [16], and was likewise assigned to the transition $^2F_{5/2} \rightarrow {}^2D_5$. The melt solution was stable up to 760°C. Above this temperature decomposition produced a pale yellow precipitate of $CeO_2$ with the evolution of sulphur trioxide and sulphur dioxide. Thermogravimetry (Fig. 2, curve D) showed two stages of weight loss. The overall weight loss, after correction for the decomposition of the melt, was 39.1% which corresponded to eqn. (3) (calcd. for loss of 3 S + 8 O per $Ce_2(SO_4)_3$ is 39.4%). The minimum (d) at 31.0% was not far from that expected from the formation of $Ce_2O_3 \cdot SO_3$(28.2%), although attempts to separate such an intermediate were unsuccessful. The similarity between the thermogram of $Ce_2(SO_4)_3$ solution and the second stage of that of $CeCl_3$ solution may indicate the presence of similar complex species in both solutions, although the latter exhibited a lower stability.

$Ce(SO_4)_2$ reacted with the melt in two stages (Fig. 2, curve E) commencing at 100 and 750°C, respectively, forming pale yellow products in both stages, with the evolution of sulphur trioxide. The powder patterns of the washed and dried first stage and final products corresponded to those of $CeOSO_4 \cdot H_2O$ and $CeO_2$, respectively. The weight loss at the end of the first stage (at e) and the overall weight loss averaged 22.9 and 49.5%, respectively, corresponding to the reactions

$$Ce(SO_4)_2 \rightarrow CeOSO_4 + SO_3 \qquad (4)$$

$$CeOSO_4 \rightarrow CeO_2 + SO_3 \qquad (5)$$

(calcd. for loss of 1 S + 3 O and for loss of 2 S + 6 O per $Ce(SO_4)_2$ are 24.1 and 48.2%, respectively).

The reaction of $Ce(SO_4)_2$ with the sulphate eutectic may be considered as an acid—base reaction rather than merely a simple decomposition of the

$Ce(SO_4)_2$, since the latter has been reported to commence decomposition at a higher temperature (at 300°C) forming $CeO_2 \cdot 4\,SO_3$ [31].

$PrCl_3$, as a green powder, reacted as soon as it touched the surface of the melt at 560°C, forming a small amount of black residue. However, the reaction ceased when the remaining $PrCl_3$ started to dissolve in the melt, forming a green solution. When the addition of the $PrCl_3$ to the melt was carried out under a nitrogen atmosphere, only a few black particles were observed. The powder pattern of the washed and dried black residue corresponded to that of $Pr_6O_{11}$. The green melt solution containing the black residue was unstable, but it was not until 810°C that an observable rate of reaction was attained. The melt at 1100°C contained a green residue only, the powder pattern of which corresponded to that of $Pr_2O_3$. Thermogravimetry (Fig. 3, curves A and B) showed two stages of weight loss under both air and nitrogen atmospheres. The weight losses at the end of the first stage, at (a) and (b), averaged 9.3 and 2.0%, respectively, very far from that expected for the completion of the reaction

$$6\,Pr^{3+} + 9\,SO_4^{2-} \rightarrow Pr_6O_{11} + 7\,SO_3 + 2\,SO_2 \tag{6}$$

(calcd. for loss of 1.5 S + 4.17 O per $PrCl_3$ is 46.4%).

The higher weight loss and the larger amount of $Pr_6O_{11}$ obtained when the reaction was carried out in air may be due to aerial oxidation of Pr(III) according to the reaction

$$6\,Pr^{3+} + 9\,SO_4^{2-} + O_2 \rightarrow Pr_6O_{11} + 9\,SO_3 \tag{7}$$

The loss at (a′) for thermogram (A) and the overall loss from thermogram (B), after corrections for decomposition of the melt, averaged 51.2 and

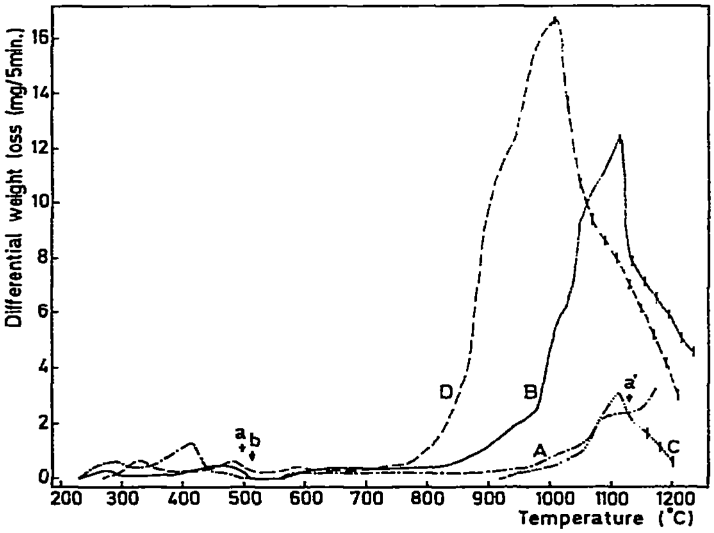

Fig. 3. Thermogravimetry of lithium sulphate—sodium sulphate—potassium sulphate eutectic. A, 0.29 m $PrCl_3$ (in air); B, 1.26 m $PrCl_3$ (maintained at 1115°C for 30 min); C, 0.55 m $Pr_2(SO_4)_3$ (in air; maintained at 1160°C for 10 min); D, 2.25 m $EuCl_3$ (maintained at 1010°C for 50 min).

53.9%, respectively, close to that expected for the acid—base reaction

$$2\,Pr^{3+} + 3\,SO_4^{2-} \rightarrow Pr_2O_3 + 3\,SO_3 \qquad (8)$$

(calcd. for loss of 1.5 S + 4.5 O per $PrCl_3$ is 48.6%).

The sulphur dioxide formed by the decomposition of sulphur trioxide above 400°C is probably responsible for the reduction of $Pr_6O_{11}$ to $Pr_2O_3$ according to the reaction

$$Pr_6O_{11} + 2\,SO_2 \rightarrow 3\,Pr_2O_3 + 2\,SO_3 \qquad (9)$$

$Pr_2(SO_4)_3$ dissolved in the melt at 580°C to form a green solution. Its visible and UV spectra showed an intense band at 232 nm, assigned to charge transition (ligand to metal) in a sulphatopraseodymium(III) complex, and four *f—f* bands at 444, 470, 481 and 592 nm similar to those reported for Pr(III) in molten chloride [14,16], fluoride [12,13] and nitrate [18], and were likewise assigned to the transitions $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ and $^3H_4 \rightarrow {}^1D_2$ [32]. The nature of the extremely weak band at 523 nm is not definitely known but may be attributed to thermal effect since its presence has also been indicated in the molten fluorides [12,13] and chloride [14,16] but not in the lower melting nitrate [18]. Thermogravimetry (Fig. 3, curve C) showed that solutions of $Pr_2(SO_4)_3$ in the melt were stable up to 920°C, when they started to react slowly. The overall weight loss of 6.0% was very far from that calculated (42.1%) for a complete reaction of the $Pr_2(SO_4)_3$ according to eqn. (8). The similarity between the thermogram of $Pr_2(SO_4)_3$ solution and the second stage of those of $PrCl_3$ solutions and the lower stability of the latter, is analogous to the behaviour of the Ce(III) melt solutions. This behaviour, although not easy to rationalize, indicates that the presence of chloride ions lowers the stability of the Ln(III) complex species present in solution.

$Nd_2(SO_4)_3$ dissolved in the melt at 580°C to form a purple solution. Its absorption spectrum (Fig. 4) showed several *f—f* bands at 798, 742, 682, 655, 583, 525, 513(sh), 474, 460(sh), 430, 384, 357, and 352(sh) nm, similar to those reported for Nd(III) in the molten fluoride [13], chloride [14,16] and molten nitrate [19] and were assigned to transitions from $^4I_{9/2}$ to various $J$ components of the excited multiplet levels [33]. The spectrum shows a relative increase in the intensity of the 583 nm band when compared to that of Nd(III) in aqueous perchlorate solutions [14,19] which demonstrates this band's sensitivity to changes in anion environment [34]. Similar effects on this particular band have been reported in the molten nitrate [19] and can be noted in the fluoride [13] and chloride [14,16] melts.

$EuCl_3$ (Fig. 3, curve D) commenced reaction slowly with the sulphate eutectic in the solid state around 270°C but it was not until 750°C that a considerable rate was attained. The overall weight loss was 49% (calcd. for loss of 1.5 S + 4.5 O and for loss of 1.5 S + 4.67 O per $EuCl_3$ are 46.5% and 47.5%, respectively). The powder pattern of a mixture of a pale pink precipitate and bright white crystals, separated from aqueous solutions of solidified reacted melts, corresponded to those of $Eu_2O_3$ and $Eu_3O_4$. The reaction may

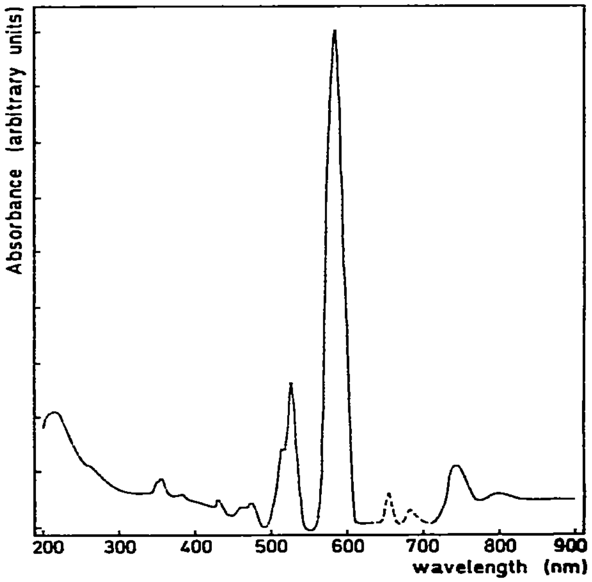

Fig. 4. The absorption spectrum of $Nd_2(SO_4)_3$ solution in molten lithium sulphate—sodium sulphate—potassium sulphate eutectic at 580°C. (Absorbance scale for the broken line is 10 times that of the solid line.)

thus be represented by the acid—base reaction

$$2\ Eu^{3+} + 3\ SO_4^{2-} \rightarrow Eu_2O_3 + 3\ SO_3 \qquad (10)$$

followed by reduction of the $Eu_2O_3$

$$3\ Eu_2O_3 + SO_2 \rightarrow 2\ Eu_3O_4 + SO_3 \qquad (11)$$

which is analogous to the reduction of $Pr_6O_{11}$ to $Pr_2O_3$.

The absorption spectrum of the yellow melt solution of $Dy_2(SO_4)_3$ at 580°C (Fig. 5) showed a charge transfer band at 216 nm and several *f*—*f* bands at 300(sh), 352, 365, 387, 428, 453, 478, 748(sh) and 792 nm, assigned to transitions between various *J* components of the ground states $^6H$ and $^6F$ and those of the excited multiplet levels [35]. The positions of these bands are close to those obtained in aqueous perchlorate solution [14] and molten chloride [14,16]. Comparison between the spectra in the three media, however, showed many variations in the relative intensities of the bands. For example, an interesting observation can be made by noting the change in the relative intensities of the two bands at 352 and 453 nm. While the second band is the strongest *f*—*f* band in the sulphate melt at 580°C, it has about the same intensity as the first band in the chloride melt at 450°C [16], but it becomes much weaker in the same melt at 400°C [14] and even weaker in the aqueous solution at 25°C [14], where the first band becomes the strongest band. These variations may be attributed to changes in the population of the ground state components. The presence of three new bands at 568(sh), 616 and 671 nm in the spectrum of the sulphate melt solution that were not observed in the aqueous [14] and chloride melt [14,16] solutions may be attributed to a thermal effect.

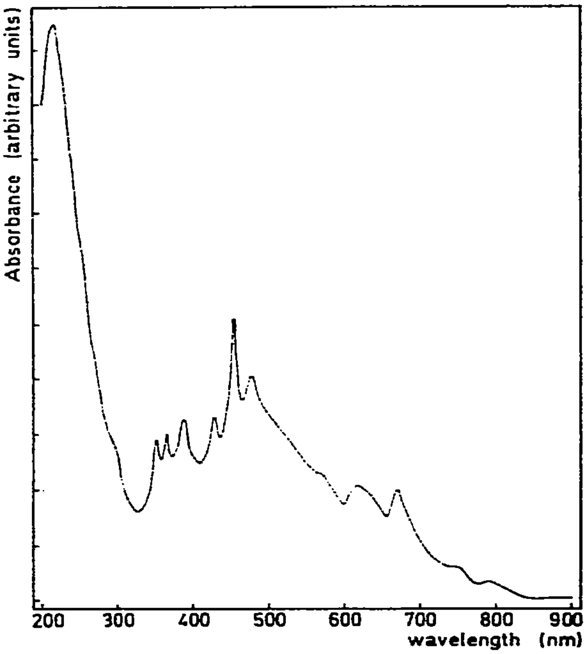

Fig. 5. The absorption spectrum of $Dy_2(SO_4)_3$ solution in molten lithium sulphate—sodium sulphate—potassium sulphate eutectic at 580°C.

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