Monatshefte für Chemie 124, 673–679 (1993)

Monatshefte für Chemie
Chemical Monthly

Solubility of Some Lanthanide Sulfates in Polycomponent Systems Containing H_2SO_4

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Summary. The paper presents data on the solubility of La, Ce, Pr, Nd sulfates in the polycomponent system $La_2(SO_4)_3 \cdot 8H_2O$–$Ce_2(SO_4)_3 \cdot 8H_2O$–$Pr_2(SO_4)_3 \cdot 8H_2O$–$Nd_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O (at 25 °C and 64 °C) as well as in the same polycomponent system but in the presence of $CaSO_4 \cdot 2H_2O$. The solubility of the sulfates – octahydrates of Pr at 25 °C and 64 °C and of La and Ce at 64 °C in tricomponent system $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O are also reported.

Keywords. Lanthanides; Sulfates; Solubility; Polycomponent systems.

Löslichkeit einiger Lanthanidsulfate in Mehrkomponenten-Systemen mit H_2SO_4

Zusammenfassung. Die Arbeit präsentiert Daten für die Löslichkeit von La-, Ce-, Pr- und Nd-Sulfaten in den Vielkomponenten-Systemen $La_2(SO_4)_3 \cdot 8H_2O$–$Ce_2(SO_4)_3 \cdot 8H_2O$–$Pr_2(SO_4)_3 \cdot 8H_2O$–$Nd_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O (bei 25 °C und 64 °C) sowie in den gleichen Systemen, jedoch in Anwesenheit von $CaSO_4 \cdot 2H_2O$. Über die Löslichkeit von Sulfatoctahydraten von Pr bei 25 °C und 64 °C und von La und Ce bei 64 °C in den Dreikomponenten-Systemen $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O wird auch berichtet.

Introduction

Investigations on the solubility of $Ln_2(SO_4)_3 \cdot 8H_2O$ (Ln = La, Ce, Pr, Nd) at their coexistence (including the presence of $CaSO_4 \cdot nH_2O$) in sulfuric acid solutions are of prime interest for the sulfuric acid processing of light lanthanide concentrates.

References data on the La-, Ce- and Sm-sulfate octahydrate solubility at 25 °C [1] and of the Nd-compound at different temperatures [2] in H_2SO_4 with different concentrations are reported. The system Ce_2O_3–SO_3–H_2O has been more precisely studied [3–5]. We have not found solubility data for $Pr_2(SO_4)_3 \cdot 8H_2O$ and for all of these compounds at their coexistence in H_2SO_4-containing solutions.

The presence of $CaSO_4 \cdot 0.5H_2O$ in the system creates the possibility for Ln^{3+}-ions heterovalent isomorphic inclusion, especially in the presence of alkali metals (vacancy compensators) and above 85 °C (the semihydrate crystallizes above 66 °C) [6–15]. The Ln^{3+}-coprecipitation with $CaSO_4 \cdot 2H_2O$ is negligible and mainly due to a mechanical inclusion. The coprecipitation is influenced by the solution acidity because the latter determines the Ln-chemical species in the solution [15]. Similar effects in the system $CePO_4$–$Ca_3(PO_4)_2$–H_3PO_4–H_2O [16, 17] are observed. The solubility of $CaSO_4 \cdot 2H_2O$ in the presence of other electrolytes is studied and a complicated pattern of the dependence upon the background electrolyte concentration was found [18–23].

The present work reports on the sulfate solubility (at 25 °C and 64 °C) at different H_2SO_4 concentration in the systems $La_2(SO_4)_3 \cdot 8H_2O$–$Ce_2(SO_4)_3 \cdot 8H_2O$–$Pr_2(SO_4)_3 \cdot 8H_2O$–$Nd_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O and in the same systems in the presence of $CaSO_4 \cdot 2H_2O$.

Experimental Part

The lanthanide sulfates were prepared by the method described in [24] using oxides with an assay 99.9%. The content of crystallohydrate water was controlled gravimetrically and its content fluctuated within ±2% of the stoichiometric content. Other reagents used were "puriss.p.a." grade.

The determination of La and Ca was done by means of ICP emission spectroscopy. The relative standard deviation of the results was ±5%.

For the solubility determination the solid sulfate mixture was kept in contact with the solvent, using a magnetic stirrer in a thermostatic vessel for 18 h. After separation both phases were analysed.

Results and Discussion

The obtained experimental data are shown in Table 1 and are illustrated on Figs. 1 and 2. The literature data for the solubility of the sulfates in the di- (or tri-) component system $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2O, resp. $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O are given as well. The results refer the possibility to evaluate the interconnected influence of the H_2SO_4 concentration, the temperature and the presence of other sulfates on the solubility of every one of the sulfates studied.

Figures 1a, b show the dependence of the sulfate solubility on the lanthanide atomic number in the tricomponent systems $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O. The

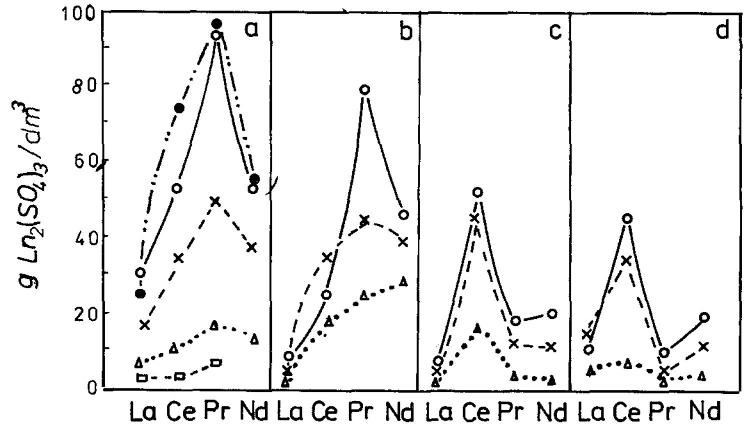

Fig. 1. Solubility of $Ln_2(SO_4)_3 \cdot 8H_2O$ according to the atomic number in the three component systems $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O at 25 °C (a) and at 64 °C (b), in the polycomponent systems $La_2(SO_4)_3 \cdot 8H_2O$–$Ce_2(SO_4)_3 \cdot 8H_2O$–$Pr_2(SO_4)_3 \cdot 8H_2O$–$Nd_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O at 25 °C (c) and at 64 °C (d); H_2SO_4 concentration (g/dm^3): 0 (●), 100 (○), 200 (×), 300 (400 for b) (△), and 600 (□)

Table 1. Solubility of some rare earth sulfates (g anhydrous salt/dm^3) in H_2SO_4

No.	System $H_2SO_4+H_2O+$	Compound	t °C	Concentration of H_2SO_4, g/dm^3					
				54.2	106.6	170.3	269.5	465.5	820.0
1	$Ce_2(SO_4)_3 \cdot 8H_2O$	$Ce_2(SO_4)_3 \cdot 8H_2O$	64	18.48	25.67	40.13	22.73	–	–
2	$La_2(SO_4)_3 \cdot 8H_2O$	$La_2(SO_4)_3 \cdot 8H_2O$	64	16.38	17.25	7.90	6.49	–	–
3	$Pr_2(SO_4)_3 \cdot 8H_2O$	$Pr_2(SO_4)_3 \cdot 8H_2O$	25	89.90	95.72	61.23	35.40	12.08	3.5
			64	71.39	70.80	60.94	35.57	9.37	1.34
4		$Ce_2(SO_4)_3 \cdot 8H_2O$	25	75.12	50.79	51.08	36.93	7.73	0.29
			64	49.10	43.85	35.96	20.47	2.75	0.91
	$Ce_2(SO_4)_3 \cdot 8H_2O+$ $La_2(SO_4)_3 \cdot 8H_2O+$ $Nd_2(SO_4)_3 \cdot 8H_2O+$ $Pr_2(SO_4)_3 \cdot 8H_2O$	$La_2(SO_4)_3 \cdot 8H_2O$	25	5.34	8.35	3.64	0.49	0.42	1.27
			64	15.85	11.06	15.89	12.02	4.26	0.26
		$Nd_2(SO_4)_3 \cdot 8H_2O$	25	26.34	20.93	15.39	4.38	0.68	2.25
			64	17.37	16.23	14.85	7.49	3.33	0.24
		$Pr_2(SO_4)_3 \cdot 8H_2O$	25	14.76	11.59	10.62	6.76	0.79	0.24
			64	9.33	5.50	3.98	4.26	2.41	0.42
		$Ln_2(SO_4)_3 \cdot 8H_2O$*	25	121.56	91.66	80.73	48.56	9.62	4.05
			64	91.65	76.64	70.68	44.24	12.75	1.83
5		$Ce_2(SO_4)_3 \cdot 8H_2O$	25	90.97	71.84	30.16	28.38	9.64	3.04
			64	62.87	49.61	37.16	18.52	3.46	–
		$La_2(SO_4)_3 \cdot 8H_2O$	25	3.07	3.58	2.44	1.71	0.79	0.144
			64	14.83	15.84	15.20	16.56	5.26	–
	The same as No. 4 $+CaSO_4 \cdot 2H_2O$	$Nd_2(SO_4)_3 \cdot 8H_2O$	25	23.95	17.91	9.14	7.78	1.76	0.081
			64	26.44	21.14	15.71	10.81	4.39	–
		$Pr_2(SO_4)_3 \cdot 8H_2O$	25	16.16	14.28	4.72	4.93	1.02	0.36
			64	9.34	6.29	4.89	3.05	0.62	–
		$CaSO_4 \cdot 2H_2O$	25	1.84	1.52	0.76	0.51	0.68	0.015
			64	2.33	0.77	1.34	4.43	0.068	–
		$Ln_2(SO_4)_3 \cdot 8H_2O$	25	134.15	107.61	46.45	42.8	13.21	4.35
			64	113.48	92.88	72.96	48.94	13.74	–

* Ln – sum of the lanthanoid solubility

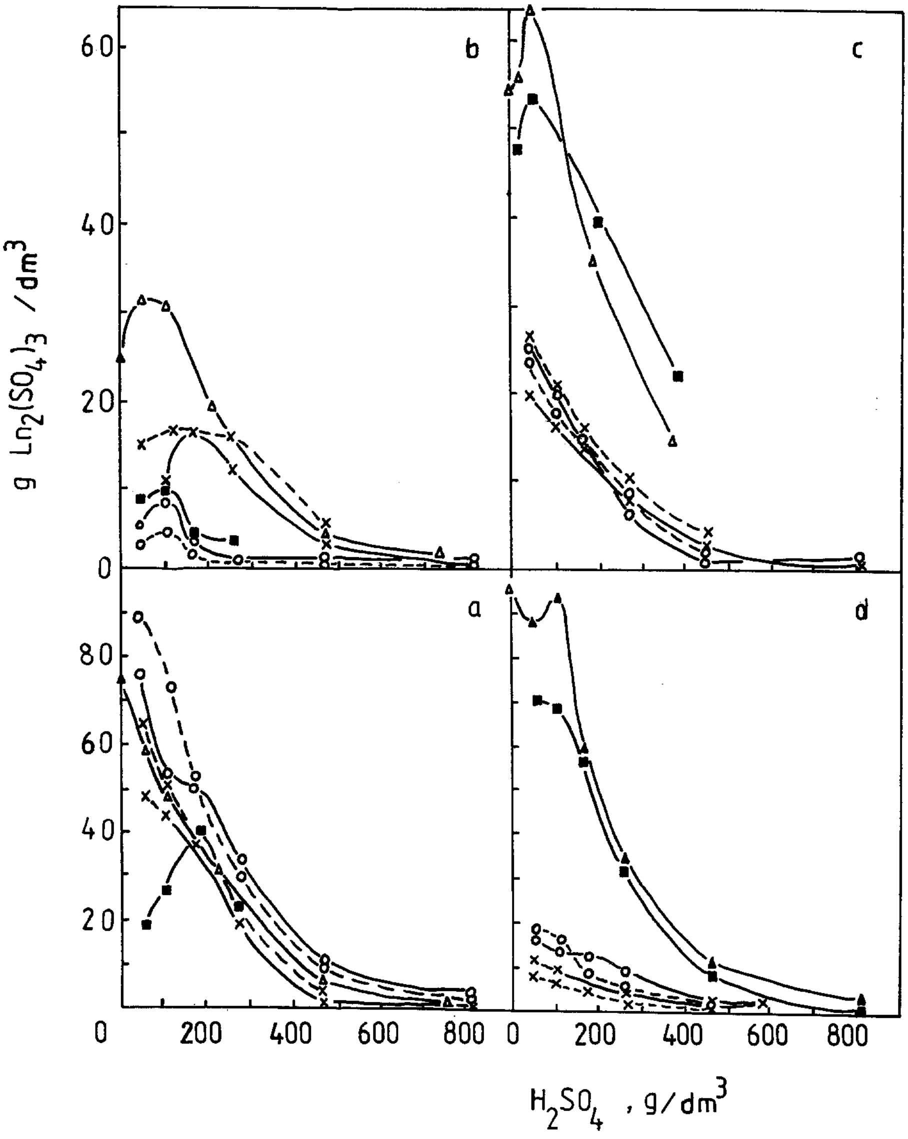

Fig. 2. Solubility of $Ln_2(SO_4)_3 \cdot 8H_2O$ [*Ln* = Ce (a), La (b), Nd (c), Pr (d)], $CaSO_4 \cdot 2H_2O$ (e) and total lanthanide solubility (f) as a function of H_2SO_4: △ – for individual compounds $Ce_2(SO_4)_3 \cdot 8H_2O$, $La_2(SO_4)_3 \cdot 9H_2O$ and $CaSO_4 \cdot 2H_2O$ at 25 °C; $Nd_2(SO_4)_3 \cdot 8H_2O$ and $Pr_2(SO_4)_3 \cdot 8H_2O$ at 25 °C in water and $Nd_2(SO_4)_3 \cdot 8H_2O$ at 30.4 °C in acid [2]; □ – the same for $CaSO_4 \cdot 2H_2O$ 43 °C [1] and for $Nd_2(SO_4)_3 \cdot 8H_2O$ at 46 °C [2]; ▲ and ■ – data for the individual compounds at 25 °C and 64 °C; ○ – the same at 25 °C in the Ca-free polycomponent system (—) and the polycomponent system in the presence of $CaSO_4 \cdot 2H_2O$ (– –) at 25 °C; × – the same for 64 °C

dependences preserve the trend (with a maximum at Pr), known for the dicomponent systems $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2O [25]. In the polycomponent system, however, this maximum moves from Pr to Ce (Figs. 1c, d). At 64 °C some tendency could be revealed for a polyextremal pattern with maxima at the elements with even atomic number. This tendency may be checked studing the solubility of other lanthanide sulfates.

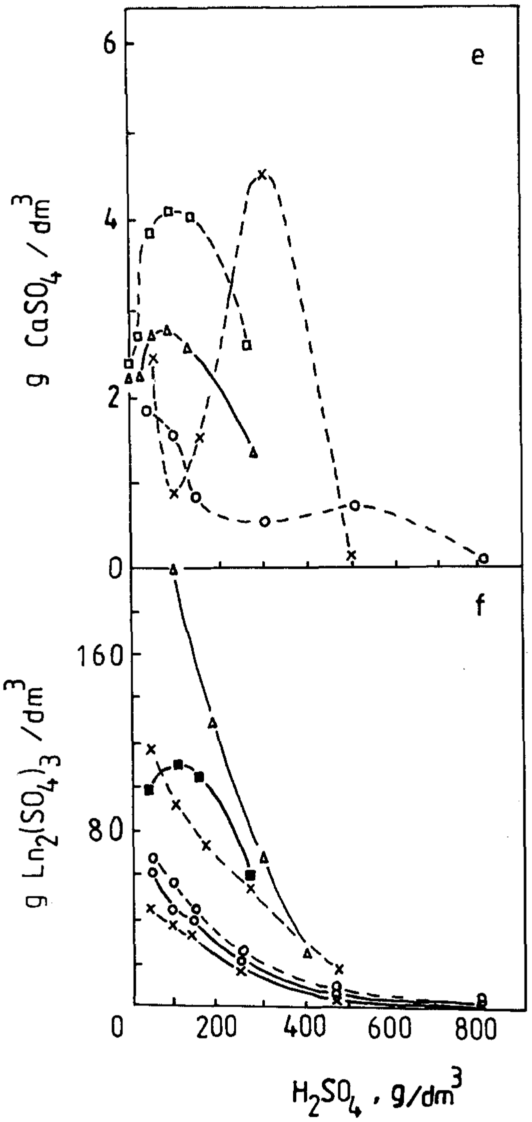

Fig. 2e and f

The solubility dependences on the H_2SO_4 concentration have a similar pattern in the studied systems-individual compounds, lanthanide mixture without and with $CaSO_4 \cdot 2H_2O$ (Fig. 2).

In most cases the sulfate solubility in the polycomponent systems is lower than the one of the individual compounds (Fig. 2). Some deviations for $La_2(SO_4)_3 \cdot 8H_2O$ at 64 °C are observed. For $Ce_2(SO_4)_3 \cdot 8H_2O$ this effect is observed up to a certain acid concentration. The latter decreases with an increase of the temperature.

The solubilities of the La- and Nd-sulfates increase with the temperature increasing from 25 °C to 64 °C. $Nd_2(SO_4)_3 \cdot 8H_2O$ shows that effect in the systems containing over 200 g H_2SO_4/dm^3.

The influence of $CaSO_4 \cdot 2H_2O$ is closely related to the influence of the temperature, the acid concentration and to the *Ln* nature. So, the presence of

$CaSO_4 \cdot 2H_2O$ decreases the $La_2(SO_4)_3 \cdot 8H_2O$ solubility at 25 °C (comparing with the same system but without calcium). Most frequently the presence of $CaSO_4 \cdot 2H_2O$ increases the "anomalous" effects:

- The solubility of $Ce_2(SO_4)_3 \cdot 8H_2O$ continues to increase relatively to the individual compound. This effect is observed up to a relatively low acid concentration. This concentration decreases with the temperature increasing.
- The solubility of the La- and Nd-sulfates at 64 °C increases compared with the Ca-free system. A similar tendency is also expressed for the Nd-salt at 25 °C.

It is hardly to expect a complete explanation of the effects observed in such a complicated system. Nevertheless, some hypothesis could be considered.

The increasing of $Ce_2(SO_4)_3 \cdot 8H_2O$ solubility in the presence of other lanthanide sulfates could be connected with the formation of an isomorphic series of mixed crystals between the La- and Ce-sulfates [26]. The cerium distribution coefficient (the ratio of its concentrations in the solid and liquid phases) is 0.43. This leads to an enrichment of the solution with Ce^{3+}-ions. The disposition of the rare earth sulfates to form supersaturated solutions will favour the formation of such solid solutions.

The interpretation of the experimental data for the processes at 64 °C is complicated because at this temperature tetra- and penta-hydrates of $Ce_2(SO_4)_3$ are formed [27].

In the same time, the formation of $CeSO_4{}^+$ in the solution decreases the $Ce_2(SO_4)_3 \cdot 8H_2O$ solubility. The stability of this complex decreases with the ionic strength increasing. From this point of view the presence of other rare earths (which contribute to the ionic strength considerably till the acid concentration 200–300 g/dm^3) will lead to an increase of the solubility of $Ce_2(SO_4)_3 \cdot 8H_2O$. However, the effect of $CaSO_4 \cdot 2H_2O$ could not be explained in a such a way.

The temperature dependence of the sulfate solubility in the tricomponent systems $Ln_2(SO_4)_3 \cdot 8H_2O$–H_2SO_4–H_2O (Ln = Nd or Pr) shows that the acidity and the temperature have opposite effects. Accordingly, in solutions containing over 200 g/dm^3 H_2SO_4, the solubilities of $Pr_2(SO_4)_3 \cdot 8H_2O$ (the most soluble between the studied compounds) at 25 °C and 64 °C are very close. The solubility of the less soluble $Nd_2(SO_4)_3 \cdot 8H_2O$ at the same H_2SO_4-concentration at 64 °C becomes even higher than at 25 °C. The reference data [2] point out that at this acid concentration the $Nd_2(SO_4)_3 \cdot 8H_2O$ solubility does not change in the temperature region 0–80 °C.

In the polycomponent systems this pattern remains while the $La_2(SO_4)_3 \cdot 8H_2O$ solubility at 64 °C becomes higher than the same one at 25 °C in the whole studied interval of H_2SO_4 concentrations. The presence of $CaSO_4 \cdot 2H_2O$ increases that effect.

The explanation of the observed facts has to be looked for in the changes of the forms of the Ln-ion existence in the solutions at different temperatures and acid concentrations (the change in the degree of hydration, formation of sulfate and hydrogen sulfate complexes) as well as in the role of the acid [28] and other electrolytes for a suppressing of hydrolyses and formation of less soluble basic salts.

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Received June 16, 1992. Accepted June 29, 1992