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IDENTIFICATION OF SATURATING SOLID PHASES IN THE SYSTEM $Ce_2(SO_4)_3$–H_2O FROM THE SOLUBILITY DATA

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Abstract

Saturating solid phases, $Ce_2(SO_4)_3 \cdot hH_2O$, with hydrate numbers h equal to 12, 9, 8, 5, 4 and 2, have been identified by critical evaluation of the solubility data in the system $Ce_2(SO_4)_3$–H_2O over the temperature range 273–373 K. The results are compared with the respective TG–DTA–DSC and X-ray data. The solubility smoothing equations, transition points and solution enthalpy estimators of the identified hydrates are given. The stable equilibrium solid phases are concluded to be only $Ce_2(SO_4)_3 \cdot 9H_2O$ at 273–310 K, $Ce_2(SO_4)_3 \cdot 4H_2O$ at 310–367 K and $Ce_2(SO_4)_3 \cdot 2H_2O$ at 367–373 K. Divergencies of up to 185% in the reported solubility data are mainly due to a variety of metastable equilibria involved in the close crystallization fields, and incorrect assignments of the saturating solid phases. Since a similar variety of the hydrate numbers exists for the analogous La(III) system, it most probably also occurs for the corresponding Pu(III), Np(III) and U(III) systems.

Keywords: cerium(III) sulfate, solubility equations

Introduction

It appears that, of all salts, cerium sulfate displays the greatest diversity in the hydrate number h, and this is why the aqueous system $Ce_2(SO_4)_3 \cdot hH_2O$ is one of the most controversial. Apart from the salts isomorphous with the respective lanthanum sulfate hydrates, i.e. the hexagonal nonahydrate ($P6_3/m$) [1], the monoclinic pentahydrate (C2/c) [2] (or B2/b [3]), and the orthorhombic octahydrate (Cmca) [4], the monoclinic tetrahydrate ($P2_1/c$) [5], in the α and β forms [6], the dihydrate [6] and the monohydrate [6] (both rhombohedral, biaxial, but optically (+) and (–), respectively [6]) have been reported. The dihydrate was also found in thermogravimetric studies [7–10], where it was reported to be amorphous [9]. The existence of the monohydrate as a distinct intermediate step before the monoclinic anhydrous $Ce_2(SO_4)_3$, (B2/b or Bb) is reached [7–10], appears to be

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doubtful [7], or at least the monohydrate is extremely unstable. Early papers also reported the occurrence of $Ce_2(SO_4)_3 \cdot 12H_2O$ [11–17] and, similarly as in the case of lanthanum sulfate hexadecahydrate, $Ce_2(SO_4)_3 \cdot 16H_2O$ [13].

To confuse the matter, further tensimetric studies [18] led to hydrate numbers h=7.5, 7, 6, 4.5, 4 and 2 being reported. All these hydrate numbers were found [18] by equilibration of $Ce_2(SO_4)_3 \cdot 6H_2O$ (an unusual water content in the starting solid phase calls into question the other h numbers) with dilute sulfuric acid.

To summarize, the papers dealing with the binary system $Ce_2(SO_4)_3$–H_2O reported h=16, 12, 9, 8, 5, 4 (α and β forms), 2 and 0, not to mention the unreliable hydrate numbers, viz. 7.5, 7, 6, 4.5 [18], 3 and 1.

In contrast with the corresponding nitrate [19] and halide [20] systems, the solubility data for cerium(III) sulfate are at variance, the difference reaching 185%, similarly as for other rare earth sulfates [21], though the experimental imprecision of the standard gravimetric determinations, e.g. by the sulfate method, is claimed to be ±2%. (Usually gravimetric analysis, e.g. by the sulfate method, was used, except for some early studies which employed not an analytical, but a synthetic method of solubility determination.) It appears that the main reason for this major disagreement in reported solubility values is the difference in the final solid phases to which the respective data refer, i.e. the occurrence of meta-stable solid phases of close crystallization fields, and incorrect identification of the saturating sulfate hydrates. These controversies cannot be eliminated by an experimental redetermination of the solubility in the aqueous cerium(III) sulfate system since there is no foundation to justify a higher statistical weight for new data.

The major objective of this paper is to clarify the actual nature of the saturating solid phases as a function of temperature in the system $Ce_2(SO_4)_3$–H_2O. This seems to be of interest not only for lanthanide fission product treatment, but also as concerns, for example, the stoichiometry of the $Pu_2(SO_4)_3 \cdot hH_2O$ and $Np_2(SO_4)_3 \cdot hH_2O$ hydrates, which should be analogous to that of $Ce_2(SO_4)_3 \cdot hH_2O$; direct studies are difficult due to the oxidizing nature of the α-radiolysis products in aqueous solutions. The present study follows the previous approach referring to the aqueous scandium and lanthanide sulfate systems [21] and to the rare earth coordination in the crystal phases *vs.* that in solution [22, 55, 56].

Results

The solubility data for the system $Ce_2(SO_4)_3$–H_2O have been reported in 39 source papers [6, 11–15, 23–54]. Most of these publications deal with ternary systems. All independently determined experimental data concerning the binary system under consideration are listed in Table 1 in molality, m, units, mol kg^{-1}, in the sequence imposed by increasing temperature T. The data cover the temperature range 273–373 K. All the data from Table 1 have been plotted in a large scale $\ln m$ *vs.* $1/T$ diagram. As previously [21], it has been found that all the data points, except for several evident outliers [11, 26, 46, 47] which must be rejected, can,

Table 1 Solubility in the system $Ce_2(SO_4)_3$–H_2O at 273–373 K

T/K	Solubility Molality (m)/ mol kg^{-1}	Ref.	Solid phases $Ce_2(SO_4)_3 \cdot hH_2O$ h assignment lit./calc.			T/K	Solubility Molality (m)/ mol kg^{-1}	Ref.	Solid phases $Ce_2(SO_4)_3 \cdot hH_2O$ h assignment lit./calc.		
273.2	0.3360	11	8	9	A	308.2	0.1117	13	9	8	B
	0.3765	11	12	12	C		0.1123	13	8	8	B
	0.2913	12	12	8	B	311.2	0.1120	15	not sp.	8	B
	0.3691	12	9	12	C		0.1065	15	8	8	B
	0.3358	26	8	9	A	313.2	0.144	11	5	5	E
	0.3358	24	not sp.	9	A		0.1046	12	5	8	B
	0.3760	13	9	12	C		0.991	13	9	4	F
	0.3313	13	8	9	A		0.1004	13	8	4	F
	0.2847	14, 44	8	8	B		0.1053	12	4	4	F
	0.2878	14	8	8	B	318.2	0.0914	12	9	4	F
	0.3299	44	8	9	A		0.0906	13	8	4	F
288.2	0.2088	12	9	9	A		0.0886	13	9	4	F
	0.1946	12	8	8	B	323.2	0.0978	11	5	5	E
	0.2736	46, 47	not sp.	outlier			0.2196	11	8	12	C
289.2	0.189	22, 23	not sp.	9	A		0.0822	12	9	9	A

Table 1 Continued

T/K	Solubility Molality (m)/ mol kg^{-1}	Ref.	Solid phases $Ce_2(SO_4)_3 \cdot hH_2O$ h assignment lit./calc.			T/K	Solubility Molality (m)/ mol kg^{-1}	Ref.	Solid phases $Ce_2(SO_4)_3 \cdot hH_2O$ h assignment lit./calc.		
291.2	0.3047	11	8	12	C		0.0842	12	5	5E or 8B	
	0.3244	11	12	outlier			0.0603	12	4	4	F
292.0	0.3082	12	12	12	C		0.0841	24	not sp.	5E or 8B	
292.4	0.3114	12	12	12	C		0.08525	14	8	5E or 8B	
293.2	0.170	23	not sp.	8	B		0.06054	14	4	4	F
	0.173	13	9	9	A		0.08318	44	8	8	B
	0.1659	13	8	9	B		0.08799	44	4	5	E
	0.186	27	8	9	A		0.082	51	9	9	A
293.7	0.1676	12	8	8	B	330.2	0.0412	12	4	4	F
294.2	0.1711	12	9	8	B	333.2	0.0607	11	5	5	E
298.2	0.2854	11	12	12	C		0.1654	11	8	2	D
	0.1471	13	9	8	B		0.0683	12	9	9	A
	0.1445	13	8	8	B		0.0715	12	5	8B or 9A	
	0.08907	25	not sp.	outlier			0.0710	12	8	8B or 9A	
	0.1337	26	8	outlier		338.2	0.0632	12	9	9	A

Table 1 Continued

T/K	Solubility Molality (m) mol kg^{-1}	Ref.	Solid phases $Ce_2(SO_4)_3 \cdot hH_2O$ h assignment lit./calc.			T/K	Solubility Molality (m) mol kg^{-1}	Ref.	Solid phases $Ce_2(SO_4)_3 \cdot hH_2O$ h assignment lit./calc.		
	0.146	14	8	8	B	343.2	0.0746	11	8	2	D
	0.1644	33	8	9	A		0.0339	12	5	4	F
	0.1451	40	8	8	B		0.0243	12	4	4	F
	0.1484	44	8	8	B	348.2	0.01942	14	4	4	F
	0.143	51	9	9	A		0.0364	34	5	5	E
301.2	0.1401	15	8	8	B		0.01933	44	4	4	F
303.2	0.2838	11	8	outlier?	C	353.2	0.0299	11	5	2D or 5F	
	0.1293	12	9	8	B		0.0212	12	5	4	F
	0.1300	12	5	8	B		0.0178	12	4	4	F
	0.1274	13	9	8	B	363.2	0.01470	12	5	2D or 4B	
	0.2536	46, 47	not sp.	outlier		372.7	0.00761	44	4	2	D
	0.2158	49, 50	8	5	E	373.2	0.0136	11	5	5	E
	0.1645	41	8	4	F		0.0137	24	not sp.	5	E
303.6	0.1249	13	8	8	B	373.7	0.00825	12	5	4	F
306.2	0.122	23	not sp.	8	B		0.0076	12	4	2	D
	0.1214	15	8	8	B						

Table 2 Solubility smoothing equations in the system $Ce_2(SO_4)_3$–H_2O over the temperature range 273–373 K

$Ce_2(SO_4)_3 \cdot hH_2O$	Solubility equations [a]: $\ln m = a + b/T$ m in moles of anhyd. salt/kg H_2O and T/K	ΔH^{est}_{soln} kJ mol^{-1}
Phase A; $h=9$	$\ln m = (-9.166 \pm 0.118) + (2163 \pm 36)/T$	-90 ± 1.5
Phase B; $h=8$	$\ln m = (-9.951 \pm 0.101) + (2419 \pm 30)/T$	-100.5 ± 1.5
Phase C; $h=12$	$\ln m = (-4.365 \pm 0.344) + (926 \pm 100)/T$	-38.5 ± 4
Phase D; $h=2$	$\ln m = (-30.70 \pm 0.93) + (9627 \pm 332)/T$	-400 ± 14
Phase E; $h=5$	$\ln m = (-16.52 \pm 1.25) + (4553 \pm 418)/T$	-189 ± 17
Phase F; $h=4$	$\ln m = (-16.92 \pm 1.03) + (4567 \pm 342)/T$	-190 ± 14

[a] By definition [21], $\Delta H^{est}_{soln} = [5RT_2T_1/(T_2-T_1)]\ln(m_2/m_1)$. The uncertainties in the a, b and ΔH^{est}_{soln} values are given at the confidence level $\beta=0.95$. The major transition points, as calculated from the respective solubility smoothing equations, are as follows: A↔B at 327 K, B↔C at 267 K, A↔E at 324 K, A↔F at 310 K and D↔F at 367 K

with some difficulties [11, 12], be attributed to six straight line populations: A, B, C, D, E and F, as specified in Table 1. The relation between a given data population and the solid phases assigned by the authors is, as expected, not a simple one. Therefore, the distribution of the data points had to be made somewhat arbitrarily in some cases, i.e. mostly on the basis of the $\ln m$ *vs.* $1/T$ criterion [21]. The results of the preliminary graphical data settling were confirmed, in principle, by computer-fitting the data in Table 1 to the smoothing equations. The critically evaluated solubility smoothing equations are given in Table 2 and plotted in Fig. 1. Because of the disagreement in the reported solubilities and in the solid phase assignments, and because of the variety of metastable equilibria involved, the fitting results may be expected to be tentative from several respects.

Discussion

$Ce_2(SO_4)_3 \cdot 9H_2O$ and $Ce_2(SO_4)_3 \cdot 8H_2O$

Indisputably, A and B are $Ce_2(SO_4)_3 \cdot 9H_2O$ and $Ce_2(SO_4)_3 \cdot 8H_2O$, respectively. This is indicated by the difference between the values of ΔH^{est}_{soln} (by definition [21], this solution enthalpy esimator is equal, in terms of molality, m, mol kg^{-1}, and absolute temperature, T, to $[5RT_2T_1/(T_2-T_1)]\ln(m_2/m_1)$) for A and B, viz. 10.5 kJ mol^{-1}. It can be seen in Table 1 that the authors' h assignment was incorrect in many cases, and $h=9$ and 8 were used rather interchangeably. This points to the difficulties in the appropriate determination of the water content in the saturating dry solid residues, i.e. in the final solid phases.

The major final solid phase in the discussed system is $Ce_2(SO_4)_3 \cdot 9H_2O$ (A). Its aqueous solubility, as a function of temperature, is well established by numerous source papers originating from various laboratories. The solubilities of the

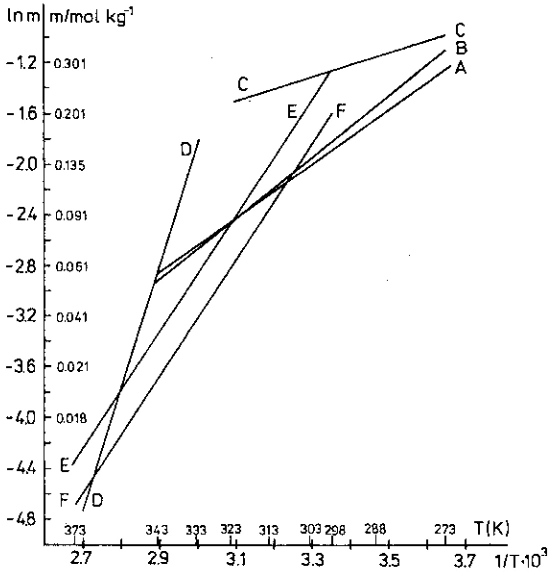

Fig. 1 Solubility in the system $Ce_2(SO_4)_3$–H_2O as ln molality *vs.* 1/*T*/K.
(A) is $Ce_2(SO_4)_3 \cdot 9H_2O$, (B) is $Ce_2(SO_4)_3 \cdot 8H_2O$, (C) is $Ce_2(SO_4)_3 \cdot 12H_2O$, (D) is $Ce_2(SO_4)_3 \cdot 2H_2O$, (E) is $Ce_2(SO_4)_3 \cdot 5H_2O$ and (F) is $Ce_2(SO_4)_3 \cdot 4H_2O$. Uncertainties in the ln*m* values, at the confidence level $\beta=0.95$, are as follows: ±0.034 (A), ±0.034 (B), ±0.057 (C), ±0.097 (D), ±0.253 (E) and ±0.201 (F). The A↔B transition point is calculated with a poor accuracy of ±20 K, and it must differ slightly from that of A↔E since the specious equilibrium A↔B↔E is forbidden by the phase rule. The stable equilibrium solid phases are $Ce_2(SO_4)_3 \cdot 9H_2O$ at 273–310 K, $Ce_2(SO_4)_3 \cdot 4H_2O$ at 310–367 K and $Ce_2(SO_4)_3 \cdot 2H_2O$ at 367–373 K. All the other final saturating solid phases, as more soluble at a given temperature, exhibit metastable equilibria

nonahydrate calculated from the ln*m* *vs.* 1/*T* smoothing equation given in Table 2 are only slightly higher than those calculated from the smoothing equation given by de Saja *et al.* [51]. According to the present paper, the nonahydrate is stable, i.e. the least soluble, solid phase over the temperature range 273–310 K. At 310 K, which is almost the same as the temperature reported by Voogd [13], the transition of $Ce_2(SO_4)_3 \cdot 9H_2O$ (A) into F, designated as $Ce_2(SO_4)_3 \cdot 4H_2O$, is concluded. The tetrahydrate F is presumed to be the stable solid phase in the range 310–367 K. Above 367 K, the stable solid phase is D, which appears to be the dihydrate rather than the less stable [10] monohydrate or anhydrous sulfate, which seems to be reached at a higher temperature.

The solubility of the octahydrate (B) is only slightly higher than that of the nonahydrate (A) below 310 K. Above 310 K, the difference in solubility between the nona- and octahydrates is within the experimental accuracy limits. Due to the close crystallization fields of the nona- and octahydrates of cerium(III) sulfate and, on the other hand, a small number of data which can be attributed reliably to the octahydrate, the A↔B transition point at 326 K could be evaluated in Table 2 with only a poor overall uncertainty of ±20 K. This point can even be lowered as much as by 23 K, and the actual A↔B transition point may be at 303 K, as reported by Voogt [13]. In such a case, at 303–310 K the stable equilibrium solid phase would be the octahydrate, and at 273 K the octahydrate B would be slightly more soluble and, consequently, less stable, than the still metastable (with respect to the nonahydrate) solid phase C of the dodecahydrate. Moreover, the A↔B transition could not be accompanied by that of E at around 325 K, which is forbidden by the Gibbs phase rule. It results from the present evaluation that the octahydrate is often present at ambient temperature if the system is not seeded with the nonahydrate crystal and vice versa.

$Ce_2(SO_4)_3{\cdot}12H_2O$

Surprisingly, it appears that the solid phase C, which must be assigned as the dodecahydrate (since the respective ΔH^{est}_{soln} value is 51.5 kJ mol^{-1} higher than that of the nonahydrate and 62 kJ mol^{-1} higher than that of the octahydrate), is less stable even at 273 K than both the nona- and the octahydrate. In addition, in the present critical evaluation no evidence has been found for the existence of the hexadecahydrate, reported [13] in both the corresponding lanthanum and cerium systems.

$Ce_2(SO_4)_3{\cdot}5H_2O$ vs. $Ce_2(SO_4)_3{\cdot}4H_2O$

There is a difficulty as concerns a clear interpretation of the E solubility line. It results from Fig. 1 that the solid phase E is metastable over the entire temperature range. It is unlikely that E is the same saturating solid phase as F, since a positive systematic error by 44% [11] is unbelievable. It is possible that E is β-$Ce_2(SO_4)_3{\cdot}4H_2O$, in perfect accordance with the reported parallel solubilities of the E and F saturating solid phases presented in Fig. 1 and, consequently, with the calculated solution enthalpy estimators ΔH^{est}_{soln} of –189 and –190 kJ mol^{-1}, respectively. However, the occurrence of the α and β forms of the tetrahydrate was reported only by Belokoskov *et al.* [6]. Moreover, in such an evaluation the well-established pentahydrate would be missing. Therefore, it appears that E is the pentahydrate, a slight slope error of the E solubility line possibly resulting in a lowered ΔH^{est}_{soln} value of –189 kJ mol^{-1}. The expected ΔH^{est}_{soln} value for $Ce_2(SO_4)_3{\cdot}5H_2O$ is about –155 kJ mol^{-1}. The respective values have been evaluated to be –169 kJ mol^{-1} for $Nd(SO_4)_3{\cdot}5H_2O$ and –176 kJ mol^{-1} for $Sm_2(SO_4)_3{\cdot}5H_2O$ [21]. The tetrahydrate does not occur for lanthanide sulfates, except for cerium(III). The parallel course of the tetrahydrate line F with respect to that of the pentahydrate E in Fig. 1 can be related with the water location in the respective crystal structures. It should be noted that, generally, the cerium(III) ion forms nonacoordinate polyhedra, CeO_9, in a distorted tricapped trigonal prismatic arrangement, D_{3h}, both in the aqua ion [55, 56], $[Ce(OH_2)_9]^{3+}_{aq}$, and in $Ce_2(SO_4)_3\cdot hH_2O$, where h=9 (for Ce_I CN=12, but for Ce_{II} CN=9), 8, 5 and 4 [2, 57]. Within the coordination sphere of the Ce(III) ion in the sulfate pentahydrate, $Ce_2(SO_4)_3\cdot 5H_2O$, four aqua molecules are coordinated inner-spherically, $[(H_2O)_2CeO_7]_2$, while the fifth crystallization water molecule is not coordinated to either of the cerium atoms or to the anion. The fifth water molecule is stoichiometric lattice water, statistically distributed in a cavity of the structure and held there tightly by the hydrogen-bonds [2, 3, 57]. In contrast with the sulfates of bivalent lanthanides [55], and as for all other rare earth(III) sulfates [21], the dissolution of all cerium sulfates is exothermic (Table 2). The exothermic effect of dissolution of the cerium sulfate hydrates roughly corresponds to the difference between the aquation of Ce^{3+} in the saturated solution and in the crystal phase of the hydrate. Therefore, the ΔH^{est}_{soln} value is a sensitive measure of the hydrate number [21] of saturating solid phases. The exothermic effect is due to the removal of rigid bonds of different lengths between cerium and oxygen atoms in the bi- and tetradentate sulfato groups [2, 57, 58]. The anions SO_4^{2-} join two cerium polyhedra into pairs (the bidentate SO_4^{2-} group), and four cerium atoms into a three-dimensional network (tetradentate SO_4^{2-} group). These bridging bonds are replaced by flexible and generally shorter [2, 57, 58], i.e. enthalpically more stable [17], bonds with water oxygens, producing the exothermic effect. In the pentahydrate, the odd, noncoordinated, water molecule does not participate in such a substitution of the $Ce^{3+}-OSO_3^{2-}$ bonds. This is why the standard molal enthalpy of solution, and consequently the ΔH^{est}_{soln} value, of $Ce_2(SO_4)_3\cdot 5H_2O$ may be more or less the same as for $Ce_2(SO_4)_3\cdot 4H_2O$.

However, such an explanation cannot be directly applied in the case of $Ce_2(SO_4)_3\cdot 9H_2O$ *vs.* $Ce_2(SO_4)_3\cdot 8H_2O$. In the former hydrate, with the highly asymmetric coordination, Ce_I, with CN=12, is coordinated by the twelve oxygen atoms of the sulfate ions only. The nonacoordinate Ce_{II} ion is coordinated by six water molecules and three oxygens of the sulfato groups, while the remaining three aquas are bound by hydrogen-bonds in suitable holes of the structure. In the symmetrically coordinated $Ce_2(SO_4)_3\cdot 8H_2O$, eight of the eighteen coordination sites are occupied by water molecules, viz. all the water molecules are coordinated in the inner coordination sphere.

Thus, one must definitely choose the pentahydrate over the alternative option of the dimorphous tetrahydrate. However, to be guarded, and taking into account the lack of the respective pentahydrate solubility data for Pr and h equal rather to 6 than to 5 (as based only on the ln$m$ *vs.* 1/T slope) for lanthanum sulfate hydrate [21], the absence of the real pentahydrate in the system $Ce_2(SO_4)_3$–H_2O and the possibility of dimorphous $Ce_2(SO_4)_3\cdot 4H_2O$ cannot be entirely excluded. The observation [13] that $Ce_2(SO_4)_3\cdot 5H_2O$ is metastable with regard to $Ce_2(SO_4)_3\cdot 4H_2O$ over the entire temperature range supports the present general conclusion illustrated by lines E and F in Fig. 1.

$Ce_2(SO_4)_3{\cdot}2H_2O$

The solid phase D, which is the stable solid phase above 367 K (Table 2), may be either anhydrous $Ce_2(SO_4)_3$, as indicated by its extra exothermic ΔH^{est}_{soln} value of -400 kJ mol^{-1}, or the relatively stable dihydrate $Ce_2(SO_4)_3{\cdot}2H_2O$. The latter option was supported to a certain extent by the results of thermogravimetric studies [6–10], TG and DTA techniques confirming the existence of $Ce_2(SO_4)_3{\cdot}2H_2O$ at 423–473 K [6] or at 363–413 K [7] (the anhydrous salt was not reached until 518 K) or at 435 [8] or at 420–440 K [59] (dehydration was reported to be complete at 650 K) or at 370–430 K [9]. The anhydrous sulfate alternative must be rejected as based only on the ΔH^{est}_{soln} criterion, which evidently does not work properly at h lower than 6, for which the solution enthalpy estimator does not decrease by about 10–15 kJ mol^{-1} [21], but it probably does not change for h increasing from 4 to 5, and it decreases by about 100 kJ mol^{-1} for h increasing from 2 to 4. It was reported by Niinistö *et al.* [10] that, although the thermal dehydration of the octacoordinate monoclinic $Ln_2(SO_4)_3{\cdot}8H_2O$ series (Ln=Pr–Lu, Cc or C2/c space group) proceeded in a single step with smaller samples and a low heating rate, the dehydration became a 2–3-step process when larger samples and a higher heating rate were employed. The dihydrate $Pr_2(SO_4)_3{\cdot}2H_2O$ was the most stable intermediate hydrate, and it existed at around 380–440 K, as found thermogravimetrically [10] by dehydration in air under quasi-isothermal conditions of a 200 mg sample of $Pr_2(SO_4)_3{\cdot}5H_2O$. Anhydrous $Pr_2(SO_4)_3$ was reached only at 530 K [10]. Other possible intermediate hydrates, e.g. with h=1 and 3, or still less stable ones with half hydrate number [18], were considered [10] to be highly unstable, and the respective apparent plateaus did not correspond to phases of well-defined composition. It is worthy of mention that in the discussed case the half hydrate numbers seem rather unlikely. Since it exhibits two lone electron pairs on the oxygen atom, one water molecule forms two hydrogen-bonds in ice (i.e. two donor and two acceptor hydrogen-bonds), and it can be shared by two central ions in the stoichiometric (but not the zeolite type) hydrates, e.g. in $LnF_3{\cdot}0.5H_2O$, $CaSO_4{\cdot}0.5H_2O$, $Ce_2(SO_4)_3{\cdot}5H_2O$ or $Ce_2(SO_4)_3{\cdot}9H_2O$. Therefore, it seems that in the aqua complex salts of the $Ln_2(SO_4)_3{\cdot}hH_2O$ type the h value must be an integer.

It appears that, by analogy, in aqueous solutions the option of the stoichiometric and relatively most stable dihydrate is also valid at about 370 K, at least for the respective Y, La, Pr, Nd and Sm systems [21].

The hydrate number in $Pu_2(SO_4)_3{\cdot}7H_2O$ [60] must be false, if it is assumed that the hydrate numbers of uranium(III), neptunium(III) and plutonium(III) sulfates are analogous with those for the lanthanum(III) and cerium(III) sulfates. This can be verified, for example, by co-crystallization [58, 61] of microamounts of Pu(III), Np(III) and U(III) with a strong reducing agent in the system $Ce_2(SO_4)_3$–H_2O, seeded with cerium(III) sulfate hydrates with well-established hydrate numbers and structures [1–5].

Conclusions

This critical evaluation of the solubility data, which cover the temperature range 273–373 K, has led to the conclusion that the only stable equilibrium solid phases in the system $Ce_2(SO_4)_3$–H_2O are $Ce_2(SO_4)_3 \cdot 9H_2O$ at 273–310 K, $Ce_2(SO_4)_3 \cdot 4H_2O$ at 310–367 K and $Ce_2(SO_4)_3 \cdot 2H_2O$ at 367–373 K. It cannot be entirely excluded (as within the accuracy limits) that $Ce_2(SO_4)_3 \cdot 8H_2O$ (rather not isomorphous with the monoclinic $Ln_2(SO_4)_3 \cdot 8H_2O$ series, where *Ln*=Pr–Lu with CN=8, although *Ln*=Ce and the cerium sulfate octahydrate dimorphism, e.g. compelled by seeding, cannot be rejected either, (as within the accuracy limits of the solubility determinations) is the stable solid phase at around 303–310 K. The remaining saturating solid phases, viz. $Ce_2(SO_4)_3 \cdot 12H_2O$ and $Ce_2(SO_4)_3 \cdot 5H_2O$, are metastable over the entire temperature range 273–373 K. The smoothing solubility equations, transition points and solution enthalpy estimators, all given with the uncertainty limits at $\beta=0.95$, for the six saturating hydrates, clearly elucidate the general disagreement in the reported solubilities. This is mainly due to the variety of metastable equilibria involved and to erroneous assignments of the hydrate numbers in the final solid phases. A similar situation arises for all the respective rare earth(III) systems [21], and particularly the analogous lanthanum system. The Shannon [62] radius of La^{3+} for a standard coordination number of 6 is 103.2 pm and that for Ce^{3+} is 101 pm. Since the respective values are [62] 102.5 pm for U^{3+}, 101 pm for Np^{3+} and 100 pm for Pu^{3+}, it appears that the sulfate hydrates of U(III), Np(III) and Pu(III) must be analogous with those of Ce(III) and La(III). All these aqueous sulfate systems are highly ionic, with generally nonacoordinate Ln(III) and An(III) ions surrounded by nine oxygen atoms of water molecules and of the sulfato ligand. In such systems of central ions with high coordination number and, consequently, relatively long M–O distances and small cation-ligand orbital overlaps, the ionic radius [62] becomes a predominant factor, and it is a good measure of all coordination properties. The information on $U_2(SO_4)_3 \cdot 8H_2O$, $Np_2(SO_4)_3 \cdot hH_2O$, $Pu_2(SO_4)_3 \cdot 5H_2O$ and $Pu_2(SO_4)_3 \cdot 7H_2O$ [60] is neither complete (presumably h is at least 9, 8 and 5) nor exact (h=7?). The dodecahydrate appears to be very likely, as reported even for the smaller Cf^{3+} (970 pm [62]), viz. $Cf_2(SO_4)_3 \cdot 12H_2O$ [63].

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