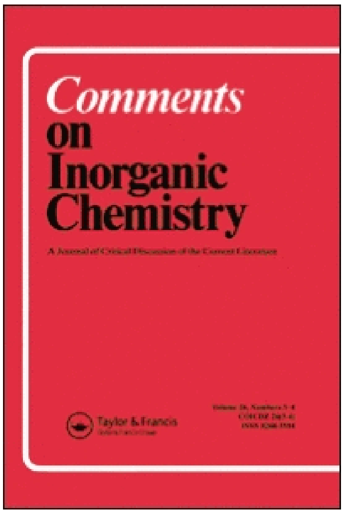

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Hydration and Covalence of the Ln^2 and An^2 Ions vs. Alkaline Earth Ions as Reflected in Solubility and Cocrystallization of Their Sulfates

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Hydration and Covalence of the Ln^{2+} and An^{2+} Ions vs. Alkaline Earth Ions as Reflected in Solubility and Cocrystallization of Their Sulfates

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Solubilities of some divalent lanthanide and actinide sulfates were evaluated and compared with the solubilities of alkaline earth sulfates. It has been concluded that the shift of the solubilities of $LnSO_4$ and $AnSO_4$ towards the solubility of $BaSO_4$ is a consequence of differences in the aquo ion structure between $[Ln(OH_2)_9]^{2+}_{aq}$, $[An(OH_2)_9]^{2+}_{aq}$, $[Ba(OH_2)_9]^{2+}_{aq}$ and $[Ra(OH_2)_9]^{2+}_{aq}$ vs. $[Sr(OH_2)_8]^{2+}_{aq}$ and $[Ca(OH_2)_8]^{2+}_{aq}$. This difference in the primary hydration number throws light on the problem of the nomadic behavior of Eu(II) which, depending on the system, migrates from Ca(II) to Ba(II) on plots of the Gibbs solution and complexation energies. The virtual absence of the covalent shortening in the Eu^{2+}_{aq} aquo ion slightly enlarges the Eu^{2+} ion, and this makes its primary hydration number higher by 1 than that of the Sr^{2+} ion. The increase in the coordination number (CN) for the Eu^{2+}_{aq} species with respect to the Sr^{2+}_{aq} species is supported by the solution enthalpy and entropy values of the respective sulfates. In particular, the difference in the primary hydration explains why the solubility product of $EuSO_4$ is about two orders of magnitude lower than that of $SrSO_4$ and close to $BaSO_4$, while the stability of the Eu(II) complexes with EDTA, DCTA and 2-picolinic acid is close to that for the respective Ca complexes. The stronger interactions in the octaaquaions(II) than in the nonaaquaions(II) is the reason why, in oposition to Sr^{2+}, the ions of Eu^{2+}, Yb^{2+} and Es^{2+} form inner sphere complexes with tetraphenylborate anions in aqueous-ethanolic solutions. The same reason elucidates why, contrary to the Ln^{2+}_{aq} and An^{2+}_{aq} species, Sr^{2+}_{aq} does not form complexes with o-phenantroline and dipirydyl.

Key Words: *lanthanides(II), actinides(II), alkaline earth ions, hydration, covalence, sulfate solubilities*

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1. INTRODUCTION

Contrary to the lanthanides(III) and actinides(III),[1] hydration and covalence effects for the divalent f-block elements have not yet been discussed in detail. It is well-known that except trapping all the Ln^{2+} ions in alkaline earth matrices, e.g., in place of Ca in CaF_2, monochalcogenides of all Ln, LnA, where A = S, Se and Te have been prepared.[2] The diiodides, LnI_2, of almost all Ln, several $LnBr_2$ and $LnCl_2$, besides LnF_2, $LnCO_3$ and $LnSO_4$, where Ln = Sm, Eu and Yb, are known as well. The established aqueous chemistry exists only for Eu^{2+}_{aq} since Nd^{2+}_{aq}, Sm^{2+}_{aq}, Tm^{2+}_{aq}, and to a lesser degree Yb^{2+}_{aq}. are rapidly oxidized even in the solid phase by protons of the crystallization water. Aqueous chemistry is developing for No(II) and Md(II) available in ultramicrotrace amounts. For the former +2 is the most stable oxidation state, the stability of which generally decreases from No(II) with decreasing Z.[3] In the An(II) series an analogue of Eu(II), i.e., Am(II), is highly unstable in spite of the $[Rn]5f^7$ configuration, and it is only minutely more stable than its neighbors in the An series, Cm(II) and Pu(II). Almost all actinides(II) have been obtained, Pu^{2+}. U^{2+} (both in molten salts with $NdCl_2$[4]), Pa^{2+} and Ac^{2+} included. The existence of the latter in aqua, proved by radiopolarography,[5] is still in question.[6] Several unsuccessful attempts[7] to obtain Lr^+, relativistically stabilized by the $7s^2$ shell shrinkage, $[Rn]5f^{14}7s^2$, do not exclude the existence of Lr^{2+}, if the relativistic effect is insufficient, and, contrary to some calculations, it is not the $7p^1_{1/2}$ but the $6d^1$ orbital which is occupied. Chemistry of the Ln(II) and An(II) species is studied in aqueous-alcoholic solutions of a lowered, with respect to pure water, H^+ concentration, in THF[8] (LnI_2, Ln = Nd, Sm, Eu, Dy, Tm, Yb, and several dibromides and dichlorides), in some other ethers (e.g., $LnI_2[O(CH_2CH_2OCH_3)_2]_2$ with CN = 8 for Sm and 7 for Eu), in some other aprotic solvents[8,9] and in solid phases.[4] Diversified solvation and crystal lattice Gibbs energies are more favorable for anomalous oxidation states than hydration energy is. Besides, in aprotic media the stability of low oxidation states is not limited by the oxidation potential of the H^+ ion.

In principle, the Ln^{2+} and An^{2+} ions are supposed to be analogues to the alkaline earth elements, and the chemistry of, e.g., Eu(II) should be more or less the same as that of Sr(II) due to the similarity of their effective crystal radii, viz. 117 pm and 118 pm, respectively.[10] However, the Eu(II) complexes with 2-picolinic acid, DCTA and EDTA are more stable[11] than expected. For the latter ligand $\log K_{Eu(II)EDTA}$ is 10.18 at 298 K[11] while the respective values are 10.59 for Ca and 8.63 for Sr.[12] Such a displacement of Eu towards Ca may indicate[1,13] a more covalent behavior of Eu(II) than the alkaline earth ions when hard oxygen σ-donor from water molecules of the aquo ions(II) is substituted by softer nitrogen of the amino acids. Furthermore, such an inner sphere complexation may be accompanied by a decrease in coordination number (CN) compared to that in aquo ions, and, in consequence, by a decrease in ionic radius of the central ion. This would make effective an orbital overlap of deeply buried, by the external octet, $5s^25p^6$, $4f^7$ orbitals with ligand orbitals, and the nephelauxetic effect.[1] It results in a covalent shortening of the central ion-ligand bonding. In this respect, it would be of interest to discuss the least covalent dodeca-coordinating sulfate system with six bidentate sulfate ions of a short bite, i.e., with 12 hard oxygen donor atoms (CN = 12), making the orbital overlaps negligible. The sulfates of $EuSO_4$, $SmSO_4$, $SrSO_4$, $BaSO_4$, and presumably also of $RaSO_4$, and of all $LnSO_4$ and $AnSO_4$, are isostructural and crystallize as orthorhombic bipyramids in the barite structure of the Pnma space group.[14]

The major objective of this paper is a better comprehension of the hydration, covalence and Gibbs solution and complexation energy variations and of the shifts of the Ln(II), An(II) species with regard to the alkaline earth series as reflected in the solubility of their sulfates vs. reciprocal cationic radius, $1/r$.

2. SOLUBILITY OF $EuSO_4$ IN WATER: CRITICAL EVALUATION

The solubility of $EuSO_4$ in pure water, given always in mol/dm^3, has been reported to be: 7.7×10^{-4} at 20°C as determined gravimetrically,[15] 7.5×10^{-5} at 20°C as determined radiometrically,[16] 3.9×10^{-5} at 20°C, 7.2×10^{-5} at 48° and 1.03×10^{-4} at 69° as determined electrochemically and confirmed by potentiometric redox titration,[17] 7.3×10^{-5} at 20°C as calculated from the Ilkovič equation[18] and 1.08×10^{-4} at 25°C as found by oxidimetric titration.[19]

The early value of 7.7×10^{-4},[15] as an evident outlier, must be rejected. [The residual error $|\sigma_{mean} - \sigma_{repd}|$ exceeds by over twice the standard deviation of the mean (a possible misprint in the original paper), and instead of 19 mg/100 cm^3, it should be 19 mg/1000 cm^3 which is exact]. The value calculated by applying the Ilkovič equation,[18] although a very reasonable one, cannot be taken into account in averaging since it is not the independent value experimentally determined. Besides, the authors did not specify the method of the limiting current determination. The value of 7.5×10^{-5} at 20°C corresponds to 8.5×10^{-5} at 25°C as results from the temperature coefficient of solubility.[17] The latter value, when averaged with 3.9×10^{-5} and 1.08×10^{-4}, yields the mean of 7.7×10^{-5} mol/dm^3 at 298 K with $\sigma_{n-1} = 3.5 \times 10^{-5}$ mol/dm^3. Rard[20] recommended a somewhat lower value of $(6.7 \pm 4.6) \times 10^{-5}$ mol/dm^3. Following his approach[20] to estimating the unknown mean ionic activity coefficients for the europous and sulfate ions in the saturated solution of $EuSO_4$ from the $MgSO_4$ and $MnSO_4$ data, one obtains at 298 K, and at 7.7×10^{-5} mol/dm^3, $\gamma_\pm = 0.905$. The solubility product constant, $K_{sp} = c^2\gamma_\pm^2$, which corresponds to equation of dissolution and a complete aqueous dissociation of the insoluble, or rather hardly soluble, sulfate,

$$EuSO_{4,c} \Leftrightarrow Eu^{2+}_{aq} + SO^{2-}_{4,aq} \tag{1}$$

is a 4.86×10^{-9} (mol/dm^3)^2 with the Gibbs solution energy, $\Delta G^o_{soln} = -RT \ln K_{sp}$, equal to 47.5 kJ/mol. The solubility smoothing equation for $EuSO_4$ in the binary $EuSO_4$–H_2O system at $273 < T(K) < 343$ is equal to

$$c\ (\text{mol/dm}^3) = \exp\,[-1.851 - 2272/T]$$

or

$$\ln c = -1.851 - 2272/T. \tag{2}$$

The slope parameter of -2272 ± 300 was calculated by the least squares method[21] from the $EuSO_4$ solubilities reported by Kozmin *et al.*[17] This slope parameter corresponds to the solution enthalpy of $EuSO_4$ equal to +37 ± 5 kJ/mol.

Hence, contrary to the sparingly soluble rare earth(III) sulfates, the solubility of which decreases with T, $EuSO_4$ is hardly soluble in water, and its temperature coefficient of solubility is positive. All the other sulfates discussed in this paper must resemble $EuSO_4$ in this respect.

3. AQUEOUS SOLUBILITY OF $EsSO_4$ AND OF SOME SIMILAR SULFATES

Einsteinium is, and it will remain, the last element available in weighted microgram quantities, indispensable, e.g., for spectral studies. The solubility of $EsSO_4$ in pure water can be evaluated from the exact data reported by Mikheev *et al.*[22] for cocrystallization in the $Sr(Sm)SO_4$–

C_2H_5OH–H_2O–Es^{2+} (Eu^{2+}, Yb^{2+}) system. At the water concentration in ethanol exceeding 6–10 mol/dm^3, the first coordination sphere of the Eu^{2+}, Yb^{2+} and Es^{2+} ions was concluded[22] to be established and it consisted of the water molecules only. This break point corresponds to about 0.3–0.4 water mole fraction while in the rare earth(III) salts–CH_3OH–H_2O systems this coordination saturation by aqua occurs at the water mole fraction of 0.2 as found by ultrasonic measurements.[23]

The present case is similar to that employed for determination "from matrix" of the solubility of Pm, Pu, Am and Cm.[24]

The solubilities of a macrocomponent (host, matrix) MSO_4 and of a microcomponent $M'SO_4$ are correlated[24] with the homogeneous cocrystallization coefficient D by the Ratner equation:

$$D = \mathrm{SP_M}/\mathrm{SP_{M'}} \times (\gamma_{\pm M}/\gamma_{\pm M'})^2 \times (\bar{\gamma}_{\pm M'}/\bar{\gamma}_{\pm M})^2 \times \mathrm{f_M}/\mathrm{f_{M'}} \qquad (3)$$

where the stoichiometric solubility product ratio is followed by the activity terms. The mean molar activity coefficients at a molarity c concern saturated solutions of pure salts in pure water, when without bars, and they deal with the cocrystallization liquid phase, when with bars, i.e., for saturated ethanolic-aqueous solutions.[22]

Equation (3) can be rearranged into the form

$$D = K_{sp} / K'_{sp} \times (\bar{\gamma}_{\pm M'}/\bar{\gamma}_{\pm M})^2 \times \mathrm{f_M}/\mathrm{f_{M'}} \qquad (4)$$

and

$$\boldsymbol{D} = K_{sp}/K'_{sp} \times A \qquad (5)$$

where the stoichiometric solubility products, SP = c^2, from Eq. (3), are replaced by the solubility product constants, i.e., thermodynamic solubility products of the macro- K_{sp} and microcomponent K'_{sp}, and the activity term A.

Assuming that the term A is constant, which appears to be justified for the twin f-block ions of Eu^{2+}, Es^{2+} and Yb^{2+}, and for the truly isomorphous cocrystallization, it is possible to determine aqueous solubilities of $EsSO_4$ and $YbSO_4$.

Inserting, in Eq. (4), $D_{Eu} = 3.0$[22] and K'_{sp} for $EuSO_4$ evaluated in this paper to be equal 4.86×10^{-9} (mol/dm^3)^2 and K_{sp} for $SrSO_4$ equal to 3.44×10^{-7} (mol/dm^3)^2,[14] A is 4.24×10^{-2}, K'_{sp} for $EsSO_4$ is 1.74×10^{-8} (mol/dm^3)^2 at $D_{Es} = 0.84$, and the solubility constant for $YbSO_4$ is $7.29 \times$

10^{-8} $(\text{mol/dm}^3)^2$ since D_{Yb} is 0.2.[22] It should be recalled that the D values lower than unity for Es and Yb do not indicate that the solubilities of $EsSO_4$ and $YbSO_4$ are lower than the solubility of the macrocomponent of $SrSO_4$. In the case of the aqueous systems of, e.g., (Ba, Ra) $(NO_3)_2$, (Rb, K)Cl, (K, Rb)I, (Cs, Rb)Cl and K(Br, I), and when the Ratner equation is being obeyed, the correlation between the D value and solubilities of the salt components is reversed.[24] This is also the present case as results from the A value of 0.0424.

The solubility product constants for the sulfates of interest evaluated in this paper, as compared to those taken from the literature for the alkaline earth cations, are listed in Table I and plotted in Fig. 1 vs. Shannon's effective ionic radii[10] at the standard coordination number 6.

4. DISCUSSION

As for the nitrates, iodides, bromides, chlorides, and contrary to the fluorides of a small anion size, the solubility of the sulfates in question gener-

TABLE I

Solubility product constants of MSO_4 at 298 K.

M	$r_{M^{2+}}$ CN = 6 (pm)	K_{sp} $(\text{mol/dm}^3)^2$	$\Delta G^\circ_{\text{soln}}$ $-RT \ln K_{sp}$ (kJ/mol)	$\Delta H^\circ_{\text{soln}}$ ±5 (kJ/mol)
Ca	100	7.10×10^{-5a}	23.7^{g}	
Yb	102	7.29×10^{-8b}	40.7	
Tm	103	5.23×10^{-8c}	41.0	
Fm	108^{e}	2.60×10^{8c}	43.3	
Es	110^{e}	1.74×10^{-8b}	44.3	
Am	115	6.47×10^{-9c}	46.3	
Eu	117	4.86×10^{-9b}	47.5	37
Sr	118	3.44×10^{-7a}	36.9	8
Sm	119	6.99×10^{-10c}	48.2	
Nd	121	7.22×10^{-10c}	49.0	
Ba	135	1.07×10^{-10a}	56.9	43
Ra	141^{f}	4.02×10^{-11d}	59.4	

a. Ref. 14, b. This evaluation, c. Inter- and extrapolations based on Fig. 1, d. Ref. 24, e. Ref. 22, f. Estimated from the Shannon's radii[10] for higher CN, g. This value corresponds to the solubility of orthorhombic anhydrite, space group Amma, soly ≅ 1 g/dm^3, while for α-$CaSO_4$, which as more soluble is metastable, soly ≅ 6.3 g/dm^3 (SP = 3.68×10^{-3} $(\text{mol/dm}^3)^2$ and $\Delta G^\circ_{\text{soln}}$ is about 14 kJ/mol), and for the metastable hemihydrate $CaSO_4 \cdot 0.5H_2O$, called plaster of Paris, soly ≅ 7.2 g/dm^3.[27]

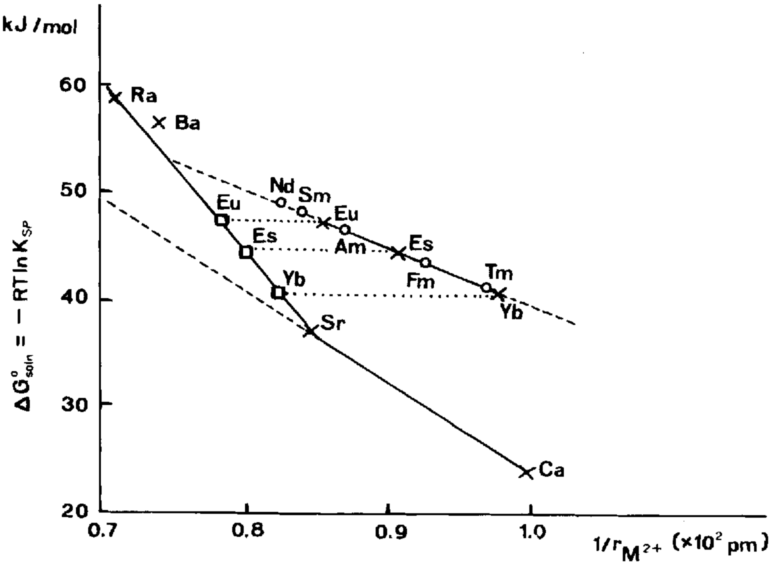

FIGURE 1 Gibbs solution energy of the sulfates of some Ln(II), An(II) and alkaline earth elements as a function of reciprocal effective cationic radius at CN = 6. ×—direct solubility and co-crystallization data. ○—inter- and extrapolated values. □—a shift of the Ln(II) and An(II) series from the Ca–Sr into the Sr–Ba range.

ally decreases with increasing cation size. This means that with the cation size increasing from Ca to Ra, the hydration Gibbs energies decrease more rapidly than the lattice energies. It can be seen in Fig. 1 that the Gibbs energy of solution of the Eu(II), Es(II) and Yb(II) sulfates, corresponding to Eq. (1) for $EuSO_4$, is a linear function of $1/r$. Thus, as expected, in this system with high CN (i.e., 12 in the solid phase vs. unknown in the liquid phase) and hard oxygen donor atoms, both in the sulfate crystal lattice and in the liquid phase, the electrostatic interactions of the Coulomb and ion-dipole type are virtually the only ones. Therefore, within the experimental precision, there is no difference between the 4f ions (Eu^{2+}, Yb^{2+}) and the 5f ion (Es^{2+}) behavior. Due to the linearity observed, this part of the tetrad effect[1,25] for the europous ion, which is called the half-filled shell effect, is absent as well. A covalent shortening implied by the Shannon[10] radii at CN = 6 in the LnO and AnO oxides of the short M–O distance is removed. The 4f and 5f divalent series are shifted from the Ca–Sr range into the Sr–Ba range. In

Fig. 1, the Eu^{2+} ion behaves as of radius of 128 pm and Yb^{2+} as of 121 pm. Thus, e.g., the Eu^{2+}_{aq} ion is less strongly hydrated than the Sr^{2+}_{aq} ion of r = 118 pm, and the SP of $EuSO_4$ is about two orders of magnitude smaller than for $SrSO_4$ (Table I). This shift is opposite to that mentioned in the introduction for the Eu(II) complexes with DCTA, EDTA and 2-picolinic acid. However, such nomadic behavior of the Ln^{2+} and An^{2+} series with respect to the "more ionic" heavy alkaline earth ions cannot be discussed as that of Y(III)[13] and Sc(III),[1,26] resulting from the shifts of the softer f-electron Ln(III) and An(III) series, unless the aquo ion structure of the cations under discussion is proved to be the same. In particular, in order to discuss the effect of the covalent shortening, the coordination number in the Sr^{2+}_{aq} and Eu^{2+}_{aq} species should be the same. (It is 12 for Sr(II) and Eu(II) in the crystal lattice of the barite structure.)

A question worthy of discussion in Fig. 1 is the slope of the ΔG^{o}_{soln} variation. A small divergence of the lines in the Yb–Eu and Ca–Sr segments is followed by a slope change for the Sr–Ra segment. The Gibbs energy of solution, $\Delta G^{o}_{soln} = \Delta G^{o}_{hydr} - \Delta G^{o}_{latt}$, for reactions of the Eq. (1) type, is a small difference (i.e., 20–60 kJ/mol) between the large Gibbs energies of hydration and crystal lattice (around 2000 kJ/mol each, and therefore even the solubility of NaCl cannot be calculated, and experimental measurements are indispensable). Both the hydration and lattice Gibbs energies are monotonic functions of the A/R ratio where R is the central ion–ligand distance. A here is the Madelung constant which characterizes packing forces, i.e., electrostatic interactions in coordination polyhedra and these of a long distance in the aqueous (A_{aq}—the Madelung constant sensu largo) and crystal phase (A_c—the Madelung constant sensu stricto) (viz. $R_{aq} = {}^{n}r + {}^{n}r_{O^{2-}}$), where n is the unknown CN in the aquo ions, and $R_c = {}^{XII}r + {}^{XII}r(SO_4^{2-})$. The A_c/R_c value must change linearly for the isomorphous MSO_4 sulfates, and the respective ΔG^{o}_{latt} values should display a smooth linear correlation with $1/r$. In conclusion, the more rapid change in the ΔG^{o}_{soln} (being a distance between roughly parallel, and close to each other, lines of hydration and crystal lattice energies) vs. $1/{}^{VI}r$ variations for the Sr–Ra segment gives evidence that it is the change in hydration and in the A_{aq}, R_{aq} and ${}^{n}r$ values (r increases with CN) for the respective aquo ions which is responsible for this slope rise.

The structure of the alkaline earth aquo ions is unknown except for the tetrahedral covalent $[Be(OH_2)_4]^{2+}_{aq}$ (${}^{VI}r_{Be^{2+}}$ = 45 pm, but of the largest radius of the total hydration sphere of all the alkaline earth ions), and much less covalent octahedral $[Mg(OH_2)_6]^{2+}_{aq}$ (${}^{VI}r_{Mg^{2+}}$ = 72 pm) species.

The present analysis of the sulfate solubilities and cocrystallizations leads to a conclusion that in the discussed aquo ions the CN value must increase by 1 (an increase by 2 from Sr to Eu is improbable since these ions, as Ca(II) and Yb(II), are almost of the same size) from n for $[Ca(OH_2)_n]^{2+}_{aq}$ and $[Sr(OH_2)_n]^{2+}_{aq}$ to $n + 1$ for $[M(OH_2)_{n+1}]^{2+}_{aq}$, where M = Ra, Ba, Ln and An. So, a removal of the covalent shortening for the f-block ions in the almost "purely ionic" aqueous sulfate system makes these ions slightly larger than the Sr^{2+} ion. This gives an increase in CN of the Ln^{2+}_{aq} and An^{2+}_{aq} species by one, compared to Sr^{2+}_{aq}, and a further increase of the ionic radii due to the CN increase and bond lengthening. It is of interest that in Fig. 1 Ra and Ba roughly belong to the same straight line population as Ln(II) and An(II) do. An increase in CN from 7 to 8 is accompanied[10] by an increase in crystal radii from 108 to 114 pm for Yb^{2+}_{aq}, from 120 to 125 pm for Eu^{2+} and from 138 to 142 pm for Ba^{2+}. That from 8 to 9 implies an increase in the r value from 114 to 120 for Yb^{2+}_{aq}, from 125 to 130 pm for Eu^{2+} and from 142 to 147 pm for Ba^{2+}. It appears that n is 8 rather than 7 although there are some X-ray data supporting the $n = 7$ value, viz. CN = 7 in $Sr(OH)_2$;[28] $[Ca(OH_2)_7]Cr_2O_7$. $[(CH_2)_6N_4]_2$, $[Ca(OH_2)_7]Cl_2$ or in the analogous bromide system when crystallized from lactose solutions.[29]

Generally, in a great majority of cases, aqua molecules for Ca(II) occur in the eight- and sevenfold coordination polyhedra.[29]

Mikheev *et al.*[30] ask the question: What is the reason for much lower solubility of $EuSO_4$ than that of $SrSO_4$ (similarly with $YbSO_4$ vs. $CaSO_4$, $r_{Yb^{2+}} = 102$ pm, $r_{Ca^{2+}} = 100$ pm), if both hydration and crystal lattice energies are related to ionic radii by the Born equation, and this radius is virtually the same, i.e., 117 pm vs. 118 pm? Any covalent f-electron effects are stronger in the aquo ions than in the crystal lattice where CN = 12. Therefore, the hydration should be rather stronger for the Eu^{2+} ion, resulting in a higher solubility of $EuSO_4$ than $SrSO_4$ (and of $YbSO_4$ than $CaSO_4$). There is enough evidence to ascribe a definite reason for this behavior. The answer is as follows: In the assumed $[Eu(OH_2)_9]^{2+}_{aq}$ species the ionic radius of Eu^{2+} is about 130 pm, and in $[Sr(OH_2)_8]^{2+}_{aq}$ the r of Sr^{2+} is about 126 pm.[10] In consequence of the larger surface charge density or of charge/radius ratio, i.e., ionic potential, the primary hydration of the Sr^{2+} ion is stronger and the solubility of $SrSO_4$ higher. In contrast, in the crystal lattice at CN = 12, the radii (and consequently the interactions) are almost the same for Eu(II), 142 pm and for Sr(II), 143 pm. In other words, the ΔG^0_{hydr} value is a monotonic function of $1/r$, but the straight line coefficient resulting from the A_{aq}/R_{aq} ratio slightly varies as the CN in the aquo ions changes. Generally, for coordination polyhedra of lower CN, the Gibbs energies vary more rapidly with $1/r$, and this is why ΔG^o_{soln} increases more rapidly, viz. the ΔG^o_{hydr} and ΔG^o_{latt} roughly parallel lines become more divergent at the Sr–Ra segment. For the same reason the solubility and cocrystallization of the isomorphous ethylsulfates,[31] $[Ln(OH_2)_9](C_2H_5SO_4)_3$, decreases from La to Pm, then slightly increases in the Pm–Gd range, and faster in the Gd–Lu range. This reflects the CN change in the lanthanide aquo ions from $[Ln(OH_2)_9]^{3+}$ in the La–Pm range to the stronger hydration and higher solubility in the Gd–Lu range of the octaaquaions(III).[31]

Summarizing, in nearly infinitely dilute solutions, the aquo ions of the discussed divalent cations, which must be both thermodynamically and kinetically unstable, viz. labile ones in comparison with those of M^{3+}_{aq}, are believed to be as follows: $[Ca(OH_2)_8]^{2+}_{aq}$, $[Sr(OH_2)_8]^{2+}_{aq}$, $[Ra(OH_2)_9]^{2+}_{aq}$, $[Ba(OH_2)_9]^{2+}_{aq}$, $[Eu(OH_2)_9]^{2+}_{aq}$, $[Yb(OH_2)_9]^{2+}_{aq}$, $[Md(OH_2)_9]^{2+}_{aq}$ and $[No(OH_2)_9]^{2+}_{aq}$. All the other Ln^{2+}_{aq} and An^{2+}_{aq} species, if they only exist for a while in aqueous-alcoholic solutions to make them real and not virtual ones, justifying the inter- and extrapolations listed in Table I, must be nonaaquaions as well.

The relatively stronger interactions in the octaaquaions than in the nonaaquaions explain another question of Mikheev *et al.*:[32] Why, in oposition to Sr^{2+}, do the ions of Eu^{2+}, Yb^{2+} and Es^{2+} form inner sphere 1 : 2 (and 1 : 1) complexes with tetraphenylborate, $(H_2O)_n$ (Ln or An) $(TPB)_2$?[32] in aqueous-ethanolic solutions? Such complexes increase kinetic stability of +2 state, e.g., for Sm^{2+}_{aq} from $t_{1/2} = 3$ h to 170 h, similarly as those of exactly fitting by size Sm(II) with cis-cis DC9 18-crown-6. As mentioned above, Gibbs energies of complex formation and those of solution in Fig. 1 are proportional to the difference $(A_{aq}/R_{aq} - A_c/R_c)$ where substrict c denotes complex or crystal phase (and where the repulsive terms for simplicity are included in the Madelung constant and in the corresponding constant, A_{aq}, for the aqueous phase). This difference, as the radius of a central cation varies, increases, decreases or reaches an extremum. For the An^{2+}_{aq} and Ln^{2+}_{aq} ions and their radii at CN = 9, ${}^{IX}r$, the stability of the complexes with TPB^- [32] is expected to be as follows: Mg < Ca > Ln(II), An(II) >> Sr > Ba > Ra. The latter three ions are more strongly complexed by water molecules in the aquo ions than by TPB^-, viz. aquation prevails over anation, and no inner sphere complexes are formed. So, in this case the f-block ions are thought to be shifted towards

Ca as in case of EDTA, DCTA and 2-picolinate complexes of stability increasing with $1/r$, i.e., from Ba to Ca. (A maximum stability at Ca was observed for over 50 systems of polynitrilopolyacetic acids and their derivatives.[12]) Lowered stability of the Mg complexes results from the great stability of the $[Mg(OH_2)_6]^{2+}_{aq}$ aquo ion of low CN. A similar situation takes place for hydroxycarboxylic, polycarboxylic and polyaminocarboxylic acids[12] where the stability order, opposite to that for the sulfate type systems, is expected to be usually as follows: Mg < Ca > Ln(II), An(II) > Sr > Ba > Ra. For the sulfate ligand, HSO_4^-, and presumably also for very weak complexes of the large nitrate, perchlorate, iodide, bromide and chloride anions, if they exist in concentrated solutions, the respective series is expected to be: Mg < Ca < Sr < Ln(II), An(II) < Ba <Ra. For complexation with the small F^- ion, the reverse series is expected with the f-block ions shifted again from Ba towards Ca: Mg > Ca > Ln(II), An(II) > Sr > Ba > Ra. In the more labile $[M(OH_2)_9]^{2+}_{aq}$ species, where M = Ra, Ba, Ln(II) and An(II), water is more readily replaced than in the $[Ca(OH_2)_8]^{2+}_{aq}$ or $[Mg(OH_2)_6]^{2+}_{aq}$ species even by such week complexing agents as halides. Therefore, the respective salts crystallize as anhydrous, contrary to those of Mg and Ca.

The stronger hydration in the $[Sr(OH_2)_8]^{2+}_{aq}$ aquo ion, compared to the nonaaquaions(II), also answers the next question of Mikheev *et al.*:[30,33] Why, contrary to the Ln^{2+}_{aq} and An^{2+}_{aq} species, does Sr^{2+}_{aq} not form complexes with o-phenantroline and dipyridyl? It is the EDTA, DCTA and TPB type of ligand with the complex stability increasing from Sr to Ca, where the Ln(II) and An(II) species are usually shifted towards Ca, and starting from Sr(II) through Ba and Ra where aquation prevails over complexation.

As far as the EDTA complexes are concerned, the CN values of Sr(II) and Ca(II) probably remain the same as in the aquo ion and equal to 8 as in $Ca[CaEDTA].7H_2O$,[29] while the CN of the Ln(II) and An(II) decreases by 1 from 9 in the aquo ions to 8 in the $M(EDTA)^{2-}_{aq}$ complexes. This fall of the inner sphere cation water coordination by 1 is accompanied by an apparent decrease in ionic radii,[1] and consequently this leads to a displacement of the Ln^{2+} and An^{2+} ions from the Sr–Ba range to the Sr–Ca range. Similarly, an increase in CN of the Sc(III) by 2 makes its behavior analogous to that of Ho(III) and Y(III) in some systems.[1]

In other words, for a reaction where differences in the structure of all the reagents, and in particular those in the aquo ion coordination number, are removed,[31]

$$\mathrm{MSO_{4,\,c}} + \mathrm{EDTA^{4-}_{aq}} \Leftrightarrow \mathrm{M(EDTA)^{2-}_{aq}} + \mathrm{SO^{2-}_{4,aq}}, \qquad (6)$$

e.g., for M = Sr and Eu, the shift of Eu towards Ba in the sulfate system and that towards Ca in the EDTA system become compensated, and Eu(II) falls on the ΔG°_{c} curve close to Sr, according to the respective ionic radii given in Table I. Only for equations of the type (6), where reaction substrates, MSO_4, and reaction products, $M(EDTA)^{2-}_{aq}$, are isostructural, can the covalent shortening be discussed. Unfortunately, in the present case the data originating in different laboratories are of insufficient accuracy. Minute differences in mutual cation positions on the roughly parallel $\Delta G^{\circ}_{\mathrm{hydr}}$ and $\Delta G^{\circ}_{\mathrm{latt}}$ curves produce substantial shifts of the f-block divalent cations on the $\Delta G^{\circ}_{\mathrm{soln}}$ or $\Delta G^{\circ}_{\mathrm{compl}}$ plot which cannot be calculated.

Generally, the covalence effects, as increasing with the oxidation state and decreasing with CN, and larger in the 5f than in the 4f series,[1] are expected to be smaller for the larger Ln^{2+} and An^{2+} ions, compared with the Ln(III) and An(III) species of a closer M–L distance, higher ionic potential, and, in consequence, a more pronounced overlap of ligand orbitals with f-orbitals.

On the basis of early solubility vs. $1/T$ data of J. Wolfmann and F. Kohlrausch, compiled in the Pascal's and Mellor's encyclopedias, the solution enthalpies of $SrSO_4$ and $BaSO_4$ can be estimated. Such an evaluation[21] gives about 8 ± 5 kJ/mol for $SrSO_4$ (the plot of $\ln c^2$ vs. $1/T$ approaches the zero slope) and 43 ± 5 kJ/mol for $BaSO_4$ with counterbalancing, as always, $T\Delta S^{\circ}_{\mathrm{soln}}$ values of −29 kJ/mol and −14 kJ/mol, respectively. So, bearing in mind the solution enthalpy of $EuSO_4$ equal to +37 ± 5 kJ/mol evaluated above in the same manner (Table I), and the resulting entropy $T\Delta S^{\circ}_{\mathrm{soln}}$ equal to −10.5 kJ/mol, it can be seen that the solution enthalpy and the entropy of $EuSO_4$ values are different from the respective values for $SrSO_4$ and close to the respective parameters for $BaSO_4$. This reflects the differences in hydration of Sr^{2+}_{aq} (and Ca^{2+}_{aq}) vs. Eu^{2+}_{aq} (and Ba^{2+}_{aq}, Ra^{2+}_{aq}, Ln^{2+}_{aq}, An^{2+}_{aq}) shown in Fig. 1.

Writing the dissolution Eq. (1) in the opposite direction, i.e., as the reaction of crystallization,

$$\mathrm{Eu(OH_2)_{n+1}]^{2+}_{x,aq}} + \mathrm{SO^{2-}_{4,\,z,\,aq}} \Leftrightarrow \mathrm{EuSO_{4,\,c}} + (n+1+x+z)\mathrm{H_2O}, \qquad (7)$$

and similarly,

$$[\mathrm{Sr(OH_2)_n}]^{2+}_{y,\mathrm{aq}} + \mathrm{SO^{2-}_{4,\,z,\,aq}} \Leftrightarrow \mathrm{SrSO_{4,\,c}} + (n+y+z)\mathrm{H_2O} \qquad (8)$$

(where presumably n is 8 while 7 appears to be less probable), it can be seen that a more exothermic effect of substituting water molecules in the aquo ions by the sulfate anions occurs for Eq. (7), viz. –37 kJ/mol, than in Eq. (8), viz. –8 kJ/mol. This results from the less tightly bound and more distant water molecules in the Eu(II) aquo ion of higher CN than those in the Sr(II) aquo ion. For the latter aquo ion of the presumed square antiprism structure, D_{4d}, there is almost no net heat evolved, and the reaction (8) proceeds to the right-hand side mostly due to an entropic gain ($T\Delta S^{\circ} = +29$ kJ/mol) in the degrees of freedom and increasing disorder produced by released ($n + y + z$) water molecules, removed by the sulfate anions as a result of crystallization. Crystallization, dissolution and inner sphere complexation involve breaking and reforming cation–ligand bonds. The crystallization entropy increases to a greater extent for Eq. (8) than for Eq. (7) since, as far as the total hydration numbers are concerned, $n + y > n + 1 + x$. This is so because ions of a lower primary hydration number have a larger overall hydration number. The total hydrated cation radius concerns the overall hydration number, i.e., the total number of water molecules associated with the cation. It decreases from Be^{2+}_{aq} to Ra^{2+}_{aq} and plays a dominant role when interpreting reaction entropy variation, while the inner sphere cationic radius and changes in the primary hydration and in the cation–ligand bonds are correlated with the entalpy variation.

In summary, the evidence, given by the thermodynamic effects for the Eqs. (7) and (8), supports the change in the primary hydration number from 8 for Sr(II) to 9 for Eu(II).

In the case of the Ln^{3+}_{aq} aquo ions and the ethylsulfate crystallization, a similar thermodynamic effect was observed.[31] The entropy of crystallization was larger for the $[Ln(OH_2)_8]^{3+}_{aq}$ aquo ions of the Tb–Lu range than for the $[Ln(OH_2)_9]^{3+}_{aq}$ aquo ions in the La–Pm range. So, the discussed entropic effect is not merely coincidental. The stoichiometries of the aquo ions in question can be discussed in terms of the rules of 16- (CN = 8) and 18-electrons (CN = 9).

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