

The S shaped change in the overall hydration of the cation across the considered series is correlated to the change in the primary hydration number  $N$ . Using the variation of  $N$  versus the crystallographic radius of the lanthanide and diffusion coefficient data for the actinides, we estimated  $N$  for each trivalent ion of the actinide series. A change of  $N$  from 9 to 8 should occur between Bk and Cf. Moreover, since entropy of trivalent lanthanide ions depends on their structure we obtained a new determination of the entropy of the  $An^{3+}$  aqueous ions.

Finally we calculated hydration enthalpy of trivalent actinide ions with the same analytical expression we established for 37 monovalent, divalent, trivalent and tetravalent ions.

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#### A41

### The Investigation of Mixed Actinide, Lanthanide and Pycrolic Acid Complexes with Neutral Donor-Active Ligands

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The present paper reports the investigations on the complex formation of the actinide ions ( $UO_2^{2+}$ ,  $Tn^{4+}$ ,  $Am^{3+}$ ) and lanthanide ions ( $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Tb^{3+}$ ,  $Er^{3+}$ ,  $Yb^{3+}$ ,  $Lu^{3+}$ ) together with the pycrolic acid (1-nitrophenil-3-methyl-4-nitri-pyrazolone-5) and neutral donor-active ligands, *i.e.* tributylphosphate and the sulphoxides of oil origin or individual ones with different structures. The mixed complexes  $UO_2A_2 \cdot S$ ,  $UO_2A_2 \cdot 2S$ ,  $AmA_3 \cdot 2S$ ,  $ThA_4 \cdot S$ ,  $LnA_3 \cdot S$ ,  $LnA_3 \cdot 2S$ , where  $A$  is a ligand anion and  $Ln$  a lanthanide ligand, have been found to form in the process of complexing. IR, PMR and electronic spectra have evidenced the formation of the above mentioned complexes. The constant values for the formation of the actinide and lanthanide complexes with pycrolic acid have been determined. The stabilities of the complexes obtained of the following sequence  $UO_2^{2+} < Ln^{3+} < Th^{4+}$  are of regular increasing character. IR investigations suggest the formation of a chelate structure of the central ion which acts as a complexing agent with the pycrolic acid anion.

The constants of forming the mixed complexes  $Ma_n \cdot mS$  of the sequence  $UO_2^{2+} < Ln^{3+} < Th^{4+}$  increase as well. The organic diluent nature has been revealed to influence the mixed complex stabilities, the higher are the polarity and dielectric permeability of the hydrocarbon solvent the lower are the complex stabilities. The obtained data have been

confirmed by the limited coefficients  $\gamma^\circ$  of the hydrocarbons in the investigated complexes, those coefficients determined by GLC. The GLC analyses have revealed the parafin hydrocarbons to develop the positive non-ideal character in relation to the mixed actinides and lanthanides complexes. The dependence of the stabilities of the mixed complexes formed on the central ion effective charge which acts as a complex forming agent has been studied in the series  $Ce^{3+} - Eu^{3+}$ . The growth of the effective charge within this series should have led to increasing the acceptor properties of the chelate  $MA_3$ . In its turn it should have resulted in growing stability constants of the mixed complexes. Nevertheless, the things go quite the opposite way and it is probably due to the steric factors as well as to the mutual influence of the chelate and donor-active ligands in the coordination sphere of the metallic ion.

The influence of the basicity factor of the donor-active ligand upon the stabilities of the formed mixed complexes has been considered. Increasing basicities in the series diphenylsulfoxide < tributylphosphate < dihexylsulfoxide < oil sulfoxide < dicyclohexylsulfoxide < 2-amylthiophancyclohexylsulfoxide result in the stability regular growths of the complexes formed.

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#### A42

### The Synthesis and Properties of Lanthanide Complexes with Different Neutral Ligands

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The present paper reports the synthesis of new coordination complexes of lanthanide nitrates and chlorides with mono- and bidentate ligands. Dihexylsulfoxides (DHSO), tributylphosphate (TBP), amino-sulfides, aminosulfoxides of various structures, and the sulfoxides of oil origin have been used as ligands.

The structures and some physical chemistry properties of chloride and nitrate lanthanide complexes with the sulfoxides of oil origin are presented. The complex compound structures have been shown to depend upon the process of producing and to correspond to the formula  $LnA_3 \cdot mHCO \cdot NH_2O$ , where  $Ln - Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, m = 3-5, n = 0-3$ .

All the IR spectra of the isolated compounds have shown a 10-60  $cm^{-1}$  band shift of sulfoxide group stretching vibrations towards the low frequency region as compared with that band position of a free sulfoxide. These data evidence the formation of electron donor-acceptor bonding