Short Communications

Polyol−Europium(III) Ion Interactions in Aqueous Solution

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Luminescence spectroscopy of the europium(III) ion has proved to be a useful tool in studying the primary solvation sphere of the cation. The reciprocal lifetimes of the delayed fluorescence in Eu(III) ion have shown to be environmentally sensitive. These decay constants have observed to be proportional to the number of water molecules in the first coordination sphere of the Eu(III) ion.[1] That is why the procedure has been successfully applied to elucidate the hydration numbers, the inner and outer sphere complexations and the binding sites in the metal to ligand interactions.[2–4] There do not exist, however, any ample data concerning neutral oxygen donor ligands, which exert only weak interactions on a spherical positive ion like europium ion. These types of ligands compete evenly with water molecules in the neighborhood of the cation in aqueous solution. If a ligand has got a favorable configuration, it will have possibilities to expel water molecules out from the primary solvation sphere. We have elsewhere applied luminescence spectroscopy to determine binding sites and stabilities of some Eu(III) ion methyl glucofuranoside complexes.[5] In the present paper we examine the interactions that a group of weak oxygen donor ligands, various diols and related compounds, exert on the Eu(III) ion in aqueous solutions. These ligands are liquids and wholly miscible with water, which makes it possible to carry out measurements in the whole range of mole fractions in binary mixtures. The present data enable us to discuss about the changes and trends in the value of the decay constant, when the two OH bonds of water molecule in the primary hydration sphere are replaced by hydroxyl groups or ether oxygens of the ligands.

The reciprocal lifetimes, *i.e.* the decay constants, of the delayed fluorescence were obtained by a Perkin Elmer Luminescence Spectrometer LS-5−Apple II Computer System in the way described elsewhere.[5] Commercial reagents of analytical grade were used in all experiments. The water content of the ligands was checked by Karl Fiscer titration using an equipment of Metrohm 652 KF-Coulometer. The mole fractions of the diols and other solvent ligands in the mixed solutions were corrected in relation to this water content. The measured decay constants are in H_2O, $k_{H_2O}=9.12$ ms^{-1}, and in D_2O, $k_{D_2O}=0.41$ ms^{-1}, both determined in 10^{-2} mol dm^{-3} EuCl$_3$ solution. These values agree well with those reported earlier.[1,3,4] Strictly speaking, it is the difference of $\Delta k=9.12-0.41=8.71$ ms^{-1} that correlates with the number of H_2O molecules in the inner solvation sphere of the Eu(III) ion in aqueous solution.[1] From the value of Δk we can calculate a contribution of one OH bond provided that the hydration number is known. Assuming that there occurs only slight changes in the solvent medium when polyols are added, we are able to use the above group contribution as a measure in the following examination. The assumption implies that the radiative contributions in the deexcitation processes have crudely similar magnitudes in water−polyol mixtures.

The results are summarized in Fig. 1, where the decay constant, k, has been plotted against $x(L)$, the mole fraction of the ligand or second solvent. At low values of $x(L)$, the figure tells us clearly the order followed by the ligands in scaling off water molecules from the primary hydration sphere of the ion. Accordingly, three categories of ligands can be separated. In other words, the solvation of the ion takes place in three typical ways in the
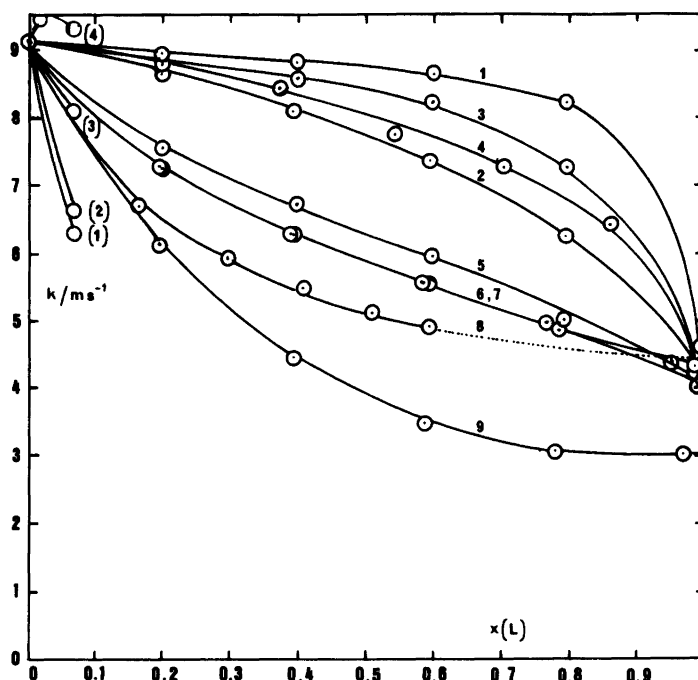
Fig. 1. The decay constants, *k*, of the delayed fluorescence in Eu(III) ion plotted against mole fraction of the ligands, *x*(L). The number refer to solvent ligands as follows: 1. Ethyl alcohol, 2. 1,3-Propanediol, 3. 1,4-Butanediol, 4. 1,5-Pentanediol, 5. Ethyleneglycol, 6. 1,2-Propanediol, 7. 2,3-Butanediol, 8. Glycerol, 9. Diethyleneglycol. Numbers in parentheses refer to the following glycoside compounds: (1) Methyl α-D-lyxofuranoside, (2) Methyl β-D-ribofuranoside, (3) Methyl β-D-ribofuranoside, (4) Methyl α-D-arabinofuranoside.

solvents or ligands descibed. For the first, there are the ligands that exert practically no interaction or interact weakly *via* one oxygen. To these belong ethyl alcohol and the diols, in which the OH groups are located far from each other, *viz.* 1,3-propane-, 1,4-butane-, and 1,5-pentanediols. The second group is formed by the vicinal diols, ethylene glycol, 1,2-propanediol, and 2,3-butanediol, that are able to interact *via* two oxygens. This is seen as a greater decrease in the *k* value compared with the behavior of the former group. At last become the two ligands, glycerol and diethylene glycol, both of which can interact *via* three oxygens. This is observed as an effective discharge of water from the hydration sphere of the cation.

It is interesting to compare the results with those obtained for some methyl glycofuranosides.[5] Methyl α-D-ribofurano- and methyl α-D-lyxofuranosides exhibit interactions *via* three oxygens.[6,7] As seen from Fig. 1. the interactions are even stronger with these compounds than with diethylene glycol. Methyl β-D-ribofuranoside falls clearly into the second category as could be expected from the previous information.[6] Having a *cis* diol configuration it is able to interact bidentally with the cation. Methyl α-D-arabinofuranoside which has earlier been shown to be almost inert towards spherical cations belongs clearly to the first category in our classification.[6] The peculiar behavior of the arabinoside curve at moderate concentrations needs further examination. It could mean the increase of water molecules in the inner hydration sphere or the existence of radiationsless pathways other than those derived from OH groups.

The coordination number of Eu(III)ion in water and aqueous solutions seems to be a matter of some discrepancy.[2] On the basis of the present data it seems quite reasonable that

the coordination number, whatever it will be, remains unchanged in the solvent or ligand systems studied. If the Δk value in water, approximately 9 ms^{-1}, represents 9 water molecules or 18 OH bonds, which is an acceptable assumption, we can apply our measure discussed above. Relevant also is in the following that the primary hydration sheath includes nine oxygens. In the nonaqueous side of the diagram, we notice that the intercepts of the extrapolated curves lie at the k value of 4−4.5 ms^{-1}, for the diols, ethanol and glycerol. This value represents 9 OH bonds, which means that there still exist nine oxygens in the first solvation sphere of the cation. The k value of 3 ms^{-1} for ethylene glycol at $x(L)=1$ fits well in the picture. It represents approximately 6 OH bonds, $i.e.$ three ligand molecules and further nine oxygens (6 OH and 3 ether oxygens) in the first solvation sphere. It has to be remembered that the above discussion is based on many assumptions and is a simplification. Besides the possible changes in the coordination number, the possible anion (Cl$^-$) coordination in the nonaqueous conditions, for instance, is overlooked. This effect, however, may not necessarily be prominent in these moderately low concentrations. In water, stability constant of magnitude of 0.1 dm^3 mol^{-1} have been reported for the inner sphere complixation of chloride ion.[3] Despite of the generalizations made the procedure seems applicable in the study of solvation and complexation of a spherical ion in pure and aqueous polyols.

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