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Journal of Alloys and Compounds 323–324 (2001) 164–168

Journal of ALLOYS AND COMPOUNDS

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Luminescence study on preferential solvation of Europium(III) in water/non-aqueous solvent mixtures

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Abstract

The solvent composition in the first coordination sphere of Eu(III) in water/non-aqueous solvent mixtures was investigated by measuring the luminescence lifetime. The inner-sphere hydration numbers of Eu(III) calculated from the lifetimes gave reasonable values in *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, formamide, hexamethyl phosphoramide, or *N*-methylformamide with water system. Eu(III) was preferentially solvated by the non-aqueous solvent in those systems, over the whole range of the non-aqueous solvent mole fraction in the bulk mixtures, X_s. The degree of the preferential solvation K_{PS}, defined as the solvent/water mole ratio in the first coordination sphere to that in the bulk solution, varied considerably with the X_s in all the systems. The order of the K_{PS} for Eu(III) was hexamethyl phosphoramide>dimethyl sulfoxide>*N*-methylformamide>*N*,*N*-dimethylformamide>formamide>*N*,*N*-dimethylacetamide>water>pyridine>methanol>ethanol>acetone>tetrahydrofuran>acetonitrile at $X_s = 0.5$. The Gibbs free energy of transfer of Eu(III) from water to non-aqueous solvent was also estimated from the K_{PS}.

Keywords: Europium(III) ion; Luminescence lifetime; Water/non-aqueous solvent mixture; Preferential solvation; Gibbs free energy of transfer

1. Introduction

Mixtures of non-aqueous solvents with water are used in chemical applications such as synthesis and separation, as well as in order to bring solutes into solution for making physicochemical study of them, like spectroscopic measurements. Preferential solvation based on the difference of ion–solvent interactions is a widely observed and rather complicated phenomenon in electrolyte solutions composed of mixed solvents. Furthermore, solvent–solvent and solvated ion-bulk solvent interactions may also affect the structure and behavior of ions in mixed solvents. In spite of many investigations by various electrochemical and spectroscopic methods [1], the preferential solvation has not been understood well quantitatively at the molecular level, especially for multivalent ions like f-elements.

In order to determine the inner-sphere hydration number N_{H_2O} (i.e. the number of water molecules in the first coordination sphere) of f-elements by measuring the luminescence lifetime, we have studied the relationship between the luminescence decay constant k_{obs} (i.e. the reciprocal of the excited state lifetime) and the N_{H_2O} of trivalent f-elements by time-resolved laser-induced fluorescence spectroscopy [2–5]. The relationships of the k_{obs} vs. N_{H_2O} derived from the linear correlations obtained in D_2O–H_2O solutions and the N_{H_2O} in H_2O were applied successfully for studies on hydration states of the ions in various aqueous solutions [6–8]. This method could be applied to not only the hydration studies in aqueous solution but also the solvation studies in non-aqueous and/or mixed solvents, if the quenching behavior of the ions by various solvent molecules were known well. Tanaka et al. [8] have measured the luminescence lifetime of Eu(III) in binary water/non-aqueous solvent mixtures and studied the solvent composition in the first coordination sphere. However, further study should be necessary for a systematic understanding of the preferential solvation of f-elements in various mixed solvents.

In the present study, the hydration number and solvent composition in the first coordination sphere of Eu(III) in twelve systems of water/non-aqueous solvent mixtures were investigated quantitatively by measuring the lumines-

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PII: S0925-8388(01)01121-5

cence lifetime. The Gibbs free energy of transfer of Eu(III) was further estimated from the degree of the preferential solvation.

2. Experimental

Eu(III) stock solution in 0.01 M $HClO_4$ was prepared by dissolving an appropriate amount of 99.99% Eu_2O_3 (Rare Metallic Co., Ltd.) in perchloric acid. Dehydrated acetone (AC), acetonitrile (AN), *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol (EtOH), formamide (FA), hexamethyl phosphoramide (HMPA), methanol (MeOH), *N*-methylformamide (NMF), pyridine (Py), and tetrahydrofuran (THF) were used as water miscible non-aqueous solvents as received from Kanto Chem. Co. or Wako Pure Chem. Ind., Japan. After the Eu(III) stock solution was fumed to dryness, the residue of the perchlorates was dissolved in pure or mixed solvents. The concentration of Eu(III) in the samples was fixed in 1×10^{-2} M.

The Eu(III) in the samples was excited to the excited states of $^5L_6$ by a pulsed laser beam of 394 nm. Subsequently, the emission from the lowest luminescent level to the ground state manifold, i.e. $^5D_0\rightarrow{}^7F_1$ (592 nm) or $^5D_0\rightarrow{}^7F_2$ (615 nm), was measured to obtain the luminescence lifetime. The temperature of the samples was held at 25°C. The 394 nm laser beam was obtained from a pulsed (10 Hz) 308 nm output of a Lambda Physik COMPex201 XeCl excimer laser pumping PBBO (Lambda Physik) in dioxane solution in a Lambda Physik SCANmate2 dye laser head. The pulse power was typically 3 mJ per pulse and the pulse width was about 15 nanoseconds. The emission light was collected at 90° into a Oriel 77257 monochromator using a optical fiber and detected by a Hamamatsu R3896 photomultiplier tube. The whole emission wavelength range (12.8 nm width) was observed. The signal was fed into a Hewlett Packard 54510A digitizing oscilloscope which was connected to a NEC PC-9801RX computer through a GP-IB interface. The luminescence decay curves observed in this work were fitted to single-exponential curves with correlation coefficients 0.99–0.999.

3. Results and discussion

The luminescence lifetimes τ_{obs}(s) of Eu(III) were measured in twelve systems of binary water/non-aqueous solvent mixtures as a function of the non-aqueous solvent mole fraction in the bulk mixtures, X_s. As shown in Fig. 1, the inner-sphere hydration numbers N_{H_2O} of Eu(III) were calculated directly from the measured lifetimes by using the following relationship reported in our previous paper [5]:

$$N_{H_2O}=1.05\times10^{-3}\,(1/\tau_{obs}) - 0.44 \qquad (1)$$

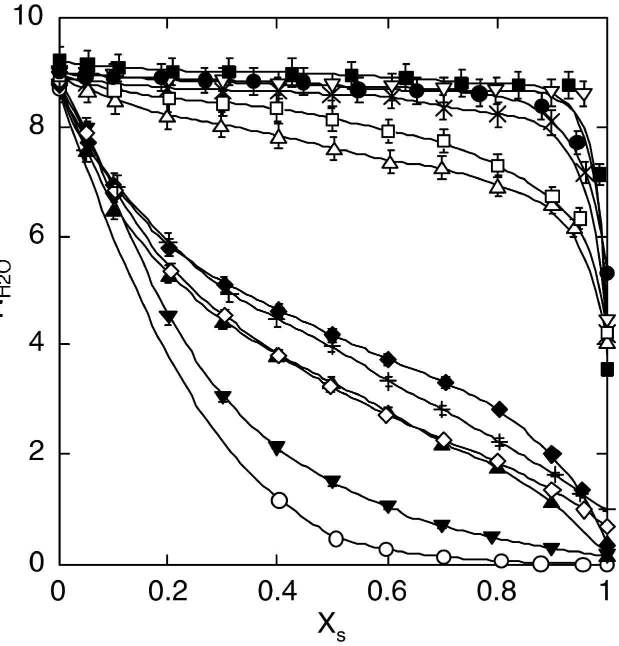

Fig. 1. Inner-sphere hydration numbers N_{H_2O} of Eu(III) as a function of the bulk mole fraction X_s in the binary mixed solvents: ●, AC-H_2O; ■, AN-H_2O; ♦, DMA-H_2O; ▲, DMF-H_2O; ▼, DMSO-H_2O; ×, EtOH-H_2O; +, FA-H_2O; ○, HMPA-H_2O; □, MeOH-H_2O; ◇, NMF-H_2O; △, Py-H_2O; ▽, THF-H_2O.

The principle of this method is based on the fact that electronic–vibrational energy transfer from the excited state of Eu(III) to the O–H vibrations of hydrated H_2O molecules is dominant in the de-excitation processes and the rate is proportional to the number of hydrated H_2O molecules [2,3,5]. If there is no contribution from the non-aqueous solvent to the de-excitation of the excited state, the N_{H_2O} of Eu(III) can be obtained directly from the τ_{obs} measured in mixed solvents, within the uncertainty of the luminescence method, ±0.5 H_2O molecules. In pure solvents at $X_s=1$, the N_{H_2O} of Eu(III) in HMPA, DMSO, DMF and DMA show the values of almost zero or less than 0.4, and those in NMF and FA give the values of 0.7 and 1.0, respectively. This means that O–H vibration in H_2O is much more effective quencher than C–H, O=P, O=S, and O=C vibrations in those solvent molecules. From comparison among DMF, NMF and FA having similar chemical formulae, it was found that N–H vibrations in the solvent molecules would also contribute slightly to the de-excitation processes of the excited Eu(III). In HMPA, DMSO, DMF, DMA, NMF or FA with H_2O system, the N_{H_2O} decreased remarkably with increasing X_s, indicating that H_2O molecules in the first coordination sphere of Eu(III) were exchanged considerably with each solvent molecule and the observed N_{H_2O} were reasonable values in the mixed solvents because of less quenching by the solvent molecules.

On the other hand, the calculated N_{H_2O} in AC, AN, EtOH, MeOH, Py or THF with H_2O system decreased slightly or gradually with increasing X_s, but those remained ca. 4–5 even at $X_s = 1$. This suggests that the non-aqueous solvents or small content of water as an impurity would act as a quencher of the excited Eu(III) in their pure solvents. Further study is necessary for each solvent itself on the quenching behavior of the excited Eu(III), although it can be expected that EtOH and MeOH containing O–H vibration contribute to the de-excitation processes as a quencher with about half efficiency of H_2O molecule. There are two possibility of water contamination in the pure solvents at $X_s = 1$, i.e. water in their solvents or that brought via europium(III) perchlorate. To evaluate the effect of the latter water, the τ_{obs} of Eu(III) in MeOH or DMSO as a reference were measured by varying Eu(III) concentration. The calculated N_{H_2O} in MeOH increased from 3.8 to 5.0, whereas those in DMSO remained constant at 0.2 or less with increasing Eu(III) concentration from 1×10^{-3} to 1×10^{-1} M, indicating that water brought via europium(III) perchlorate rather than that as an impurity in the pure solvents (i.e. 50 ppm H_2O at maximum) might be more significant as a quencher in AC, AN, EtOH, MeOH, Py and THF. Therefore, the calculated N_{H_2O} of Eu(III) were overestimated and gave only apparent values in those systems, probably due to the quenching by the solvent itself or less solvation relative to the hydration.

In order to clarify the relative affinity (i.e. the preferential solvation) of water or non-aqueous solvent with Eu(III), the solvent composition in the first coordination sphere of Eu(III) in the binary mixed solvents was then studied using the measured luminescence lifetimes. The non-aqueous solvent mole fraction in the first coordination sphere L_s was calculated from the measured decay constants $k_{obs}(=1/\tau_{obs})$ by Eq. (2):

$$L_s = (k_w - k_{mix})/(k_w - k_s) \tag{2}$$

where the subscripts w, s and mix denote water, non-aqueous solvent and binary mixed solvent, respectively. Eq. (2) was derived from $k_{mix} = L_w k_w + L_s k_s$ and $L_w + L_s = 1$, under the assumptions that each molecule of water and non-aqueous solvent in the first coordination sphere contributes separately to the non-radiative decay of Eu(III) and that total solvation number of Eu(III) is constant over the whole range of X_s. The calculated L_s are shown in Fig. 2 as a function of X_s, indicating that Eu(III) is preferentially solvated by non-aqueous solvent in DMF, DMSO, FA, HMPA or NMF with H_2O system and by H_2O in AC, AN, EtOH, MeOH, Py or THF with H_2O system, over the whole range of X_s. In the case of DMA-H_2O system, Eu(III) is preferentially solvated by DMA at $0 < X_s < 0.6$ and by H_2O at $0.6 < X_s < 1$. The results of Eu(III) in DMSO, DMF or MeOH with H_2O system almost agreed with those in the literature [9], except for that Eu(III) in DMF-H_2O system was preferentially solvated by H_2O above $X_s = 0.7$. In the calculation of L_s, Tanaka et al. [9] have used $\Delta k = k^H - k^D$ as the non-radiative decay rate of Eu(III) due to each solvent, where the superscripts H and D denote protonated and deuterated solvents. The same results were nevertheless obtained by only use of k^H within 2% errors which was smaller than those of the lifetimes.

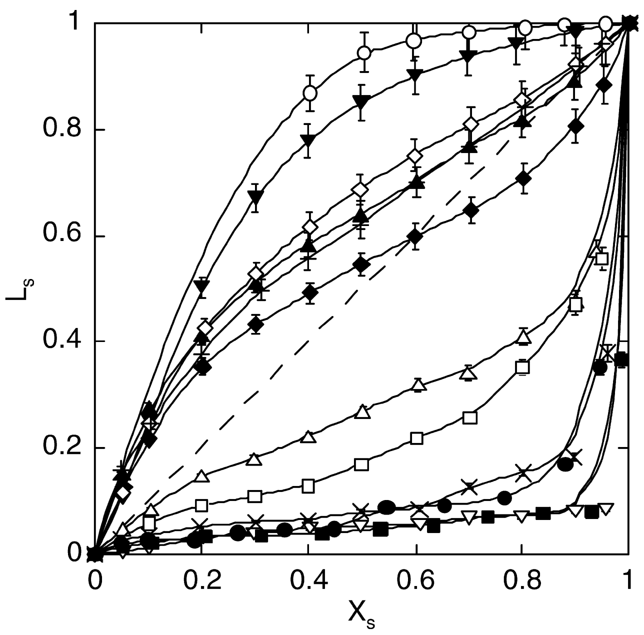

Fig. 2. Relationships between the mole fraction of non-aqueous solvent in the first coordination sphere L_s of Eu(III) and the bulk mole fraction X_s: ●, AC-H_2O; ■, AN-H_2O; ♦, DMA-H_2O; ▲, DMF-H_2O; ▼, DMSO-H_2O; ×, EtOH-H_2O; +, FA-H_2O; ○, HMPA-H_2O; □, MeOH-H_2O; ◇, NMF-H_2O; △, Py-H_2O; ▽, THF-H_2O.

For more quantitative consideration, the degree of preferential solvation was defined as the solvent/water mole ratio in the first coordination sphere to that in the bulk solution by Eq. (3):

$$K_{PS} = (L_s/L_w)/(X_s/X_w) \tag{3}$$

The K_{PS} were calculated as shown in Fig. 3. Since the K_{PS} values of Eu(III) in HMPA-H_2O system are very high (about 10–100), the results are not shown in Fig. 3. In the cases of $K_{PS} > 1$ or $K_{PS} < 1$, Eu(III) is preferentially solvated by non-aqueous solvent or water, respectively. The K_{PS} values varied considerably as a function of X_s in all the systems, i.e. the K_{PS} in HMPA or DMSO with H_2O system increased, while those in the other systems decreased with increasing X_s. The former case means that in spite of the large volume of HMPA or DMSO molecule, they have very strong ion–solvent interaction with Eu(III),

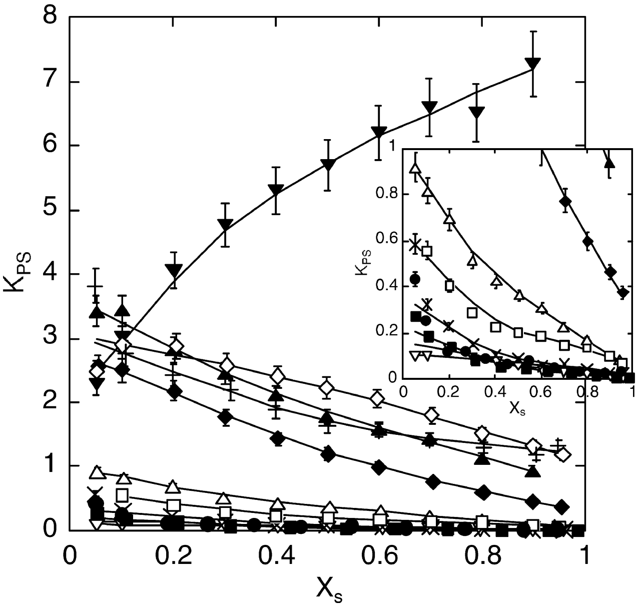

Fig. 3. The degree of preferential solvation K_{PS} for Eu(III) as a function of the bulk mole fraction X_s in the binary mixed solvents: ●, AC-H_2O; ■, AN-H_2O; ♦, DMA-H_2O; ▲, DMF-H_2O; ▼, DMSO-H_2O; ×, EtOH-H_2O; +, FA-H_2O; □, MeOH-H_2O; ◇, NMF-H_2O; △, Py-H_2O; ▽, THF-H_2O.

while the latter suggests that the other solvents undergo the steric effects on the solvation of Eu(III) because of the weak solvent–solvent interaction relative to that of water. The K_{PS} for Eu(III) have the following order at $X_s = 0.5$:

$$\begin{aligned}&\mathrm{HMPA} > \mathrm{DMSO} > \mathrm{NMF} > \mathrm{DMF} > \mathrm{FA} > \mathrm{DMA} > \\ &\mathrm{H_2O} > \mathrm{Py} > \mathrm{MeOH} > \mathrm{EtOH} > \mathrm{AC} > \mathrm{THF} > \mathrm{AN}\end{aligned} \tag{4}$$

This order agrees approximately with those reported for terbium(III) perchlorates by Batyaev et al. [10]; $H_2O >$ Py $\simeq$ MeOH $>$ DMF $>$ *n*-propanol $>$ AN, and by Bünzli and Vuckovic [11]; DMSO $>$ DMF $\simeq$ H_2O $>$ AC $>$ AN, which correlates qualitatively with that of the dipole moment (μ) or the donor number (DN) of these solvents. As some exceptions, the K_{PS} of Py or AN of which has the higher value of DN or μ are lower than that of H_2O, probably due to the lower value of μ or DN of them, respectively. Therefore, Eu(III) in mixed solvents can be preferentially solvated by the solvent of which both the μ and DN are high enough, indicating that the solvation of the ion by the solvents is mainly due to electrostatic ion–dipole interaction and also donor–acceptor interaction, respectively. Furthermore, as mentioned above the steric hindrance of the solvents on the solvation of Eu(III) also affects the order of K_{PS}, e.g. DMA has the highest DN in DMA, DMF, NMF and FA but the lowest K_{PS} in these solvent systems, because acetamide is more bulky than formamides.

The definition of the K_{PS} corresponds to the equilibrium constant for the solvation equilibrium (5) in the two solvents [12].

$$\mathrm{Eu}A_n^{3+} + mB \rightleftarrows \mathrm{Eu}B_m^{3+} + nA \tag{5}$$

where A and B denote water and non-aqueous solvent, respectively. The Gibbs free energy of transfer of Eu(III) from water to non-aqueous solvent can be estimated from the K_{PS} in Fig. 3 by using the following equation:

$$\Delta G_{tr} = -RT \ln K_{PS} \tag{6}$$

Fig. 4 shows the ΔG_{tr} calculated from the K_{PS} of Eu(III) in mixed solvents. Eq. (6) estimates entirely the ΔG_{tr} as the difference between the Gibbs free energy of solvation of the ion in the two solvents under some assumptions, although the ΔG_{tr} is originally the difference between the chemical potentials of the solute. In addition to the assumption for Eq. (2), it was assumed that the interactions of the ion with solvent molecules outside its first coordination sphere are independent of the medium. It is difficult to compare the results of Fig. 4 with the other data, since there are few data for the ΔG_{tr} of lanthanide(III) ions in the literature. However, the ΔG_{tr} of Eu(III) showed the similar orders with those of monovalent and divalent ions from water to non-aqueous solvents [13]. The variation of the ΔG_{tr} as a function of X_s suggests that there are some interactions neglected in the above assumptions, i.e. specific ion–solvent or solvent–solvent interaction in the first coordination sphere or in the bulk solvent, the effect of the second coordination sphere, and so on.

In conclusion, we have demonstrated that the luminescence lifetime measurements of Eu(III) provide the signifi-

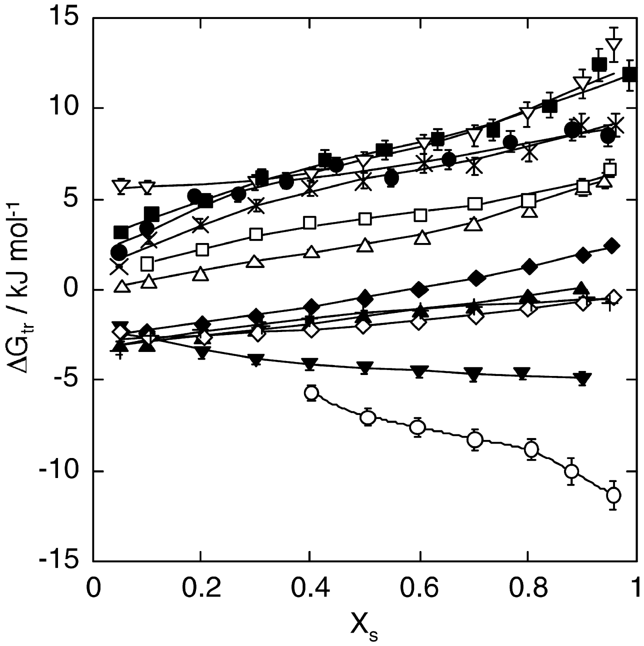

Fig. 4. Gibbs free energy of transfer of Eu(III) from water to non-aqueous solvent ΔG_{tr} as a function of the bulk mole fraction X_s in the binary mixed solvents: ●, AC-H_2O; ■, AN-H_2O; ♦, DMA-H_2O; ▲, DMF-H_2O; ▼, DMSO-H_2O; ×, EtOH-H_2O; +, FA-H_2O; ○, HMPA-H_2O; □, MeOH-H_2O; ◇, NMF-H_2O; △, Py-H_2O; ▽, THF-H_2O.

cant information on the preferential solvation in mixed solvents such as the hydration number and solvent composition in the first coordination sphere, the Gibbs free energy of transfer, etc. This method can be applied to the other luminescent lanthanide(III) and actinide(III) ions.

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