

# Cation Polyelectrolyte Interactions in Aqueous Sodium Poly(vinyl sulfonate) as Seen by Ce<sup>3+</sup> to Tb<sup>3+</sup> Energy Transfer

María José Tapia\*<sup>†</sup> and Hugh D. Burrows<sup>‡</sup>

*Departamento de Química, Universidad de Burgos, Plaza Misael Bañuelos s/n, Burgos 09001, Spain, and Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal*

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The interaction between trivalent lanthanide ions and the polyelectrolyte poly(vinyl sulfonate) (PVS) has been studied in aqueous solutions by monitoring lanthanide luminescence. The existence of specific binding of cations by PVS is indicated by blue-shifts in the maximum of the emission of cerium(III), effects on the decay of terbium(III) luminescence, and a slight broadening of the gadolinium(III) electron paramagnetic resonance (EPR). From the isotope effect observed on the decay of luminescence of Tb(III) bound to PVS in H<sub>2</sub>O and D<sub>2</sub>O solutions, it is suggested that complexation leads to a decrease in the number of bound water molecules from nine to three. In mixed PVS systems containing Ce(III) and Tb(III), energy transfer is observed. The efficiency of this is found to fit a multiple equilibrium model. The slope of the corresponding plot is shown to provide an effective measure of the extent of lanthanide binding to the polyelectrolyte. This is found to increase with temperature but to decrease upon addition of alcohols. The effect of alcohols is found to depend on their chain length, suggesting the importance of hydrophobic interactions. Increasing ionic strength by adding NaCl increases ion binding, while complex behavior, due to competing effects and precipitation, is observed upon addition of tetraalkylammonium bromide surfactants. Finally, from the energy-transfer data, it is possible to estimate the distance between lanthanide ions on the polyelectrolyte chain. Lanthanide luminescence promises to be an excellent technique for studying the interaction between metal ions and polyelectrolytes in aqueous solutions.

## Introduction

Polyelectrolytes can be considered as charged polymers formed from the repetition of smaller units containing charged groups such as carboxylate, sulfonate, sulfate, and ammonium. They can be classified in two groups: biological macromolecules, including such molecules as proteins and polysaccharides, which have a vital role for life processes, and nonbiological macromolecules with many technical applications as thickeners, dispersants, flocculation aids, and so forth.<sup>1</sup>

It is well established that the polymer chain conformation is affected by a variety of factors. For example, on increasing polymer concentration or adding surfactants or other polymers, structures generally become more compact and entangled, while, with increasing temperature, polymers generally expand.<sup>2,3</sup> The nature of the solvent also affects polymer conformations.<sup>2</sup>

A wide range of techniques have been used in characterization of polymer structures in solutions. Light scattering, vapor pressure osmometry, and viscosimetry are probably the most common ones.<sup>4</sup> In addition, various spectroscopic techniques have been successfully used in polymer science. Vibrational (infrared and Raman), spin resonance (nuclear magnetic resonance and electron spin

resonance), electronic spectroscopy (ultraviolet–visible, fluorescence), and various other scattering methods (X-ray, electron, and neutron) have all made valuable contributions to this area.<sup>5–7</sup>

The high sensitivity of fluorescence spectroscopy has permitted the use of a number of different luminescence techniques to study central issues relating to solutions of surfactants, polymers, and polymer–surfactant association, providing information on molecular association, microstructure, and molecular dynamics. Both extrinsic and intrinsic probes have been used for these studies.<sup>8</sup> Lanthanides have been used extensively as luminescent probes in the investigation of metal-binding sites in biological materials because of their isomorphous substitution of ions, such as Ca(II) or Zn(II), that do not possess useful spectroscopic properties.<sup>9–12</sup> In addition, we have recently shown that lanthanide luminescence and energy transfer is a valuable method for studying ion binding in aqueous sodium dodecyl sulfate micelles.<sup>13</sup>

Lanthanide ions present well-defined luminescence resulting from f–f transitions. This can give information on both the coordination environment and the degree of

\* To whom correspondence should be addressed. E-mail: mjtapia@ubu.es.

<sup>†</sup> Universidad de Burgos.

<sup>‡</sup> Universidade de Coimbra.

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hydration of these ions.<sup>14,15</sup> However, the f–f transitions in these complexes are generally forbidden by both spin and Laporte selection rules, and hence have very low molar absorption coefficients. In contrast, with cerium(III) the lowest energy electronic band corresponds to the allowed 4f → 5d transition and has a reasonable molar absorption coefficient. In addition, cerium(III) has been shown to be capable of transferring its electronic energy to other lanthanide ions, such as Eu(III) and Tb(III).<sup>16</sup> Energy transfer between lanthanide ions requires close contact and is favored by complexation or by binding the ions to appropriate species of opposite charge, such as micelles.<sup>13</sup> In this study, we report the use of energy transfer between hydrated cerium(III) and terbium(III) ions in aqueous solutions of sodium poly(vinyl sulfonate) to study the changes in the polymer structure on increasing temperature, or the addition of other species, such as NaCl, alcohols, cationic surfactants, or other polymers. Evidence for lanthanide ion binding is presented on the basis of Tb(III) luminescence lifetime data and ESR studies with Gd(III).

### Experimental Section

**Reagents.** Sodium poly(vinyl sulfonate) (25% water solution) was purchased from Aldrich. The polymer purity is greater than 98%, and as the polymer is prepared from vinyl sulfonate, it is expected to have a high degree of functionality. The weight average molecular weight is 1000 (number average,  $M_n = 800$ ), and its polydispersity is 1.25. Since the commercial polymer solution was not clear or suitable for spectroscopic studies, this was purified by diluting twice with Millipore-Q water, filtered with a PTFE (polytetrafluoroethylene) Whatman membrane with a 0.45 μm pore size, and freeze-dried (TELSTAR CRYODOS lyophilizer) to obtain the pure polymer as a solid for preparation of solutions. Poly(ethylene glycol) (monodisperse, molecular weight 200, and measured polydispersity 1.00), cerium(III), terbium(III), and gadolinium(III) perchlorates (40% water solution), dodecyltrimethylammonium bromide (99%), hexadecyltrimethylammonium chloride (25% water solution), and 1-butanol (99%) were purchased from Aldrich and used as received. Hexanol (99%), octanol (99.5%), and sodium chloride from Fluka, and ethanol (99.8%) from Merck were also used without further purification. Deuterium oxide (99.9%) from Aldrich was used in preparing solutions for determining the number of coordinated water molecules. All other solutions were prepared using Millipore-Q water.

**Apparatus and Methods.** For luminescence spectral measurements, a Shimadzu spectrofluorimeter RF-5301 PC with a 5 nm bandwidth in excitation and 1.5 nm bandwidth in emission was used in the right-angle configuration with excitation at 258 nm. For variable temperature measurements, the sample holder was thermostated using water circulating from a Grant LT D6G thermostatic bath. Tb(III) luminescence lifetimes were measured using a Spex 1934D phosphorimeter accessory with a Jobin Yvon-Spex Fluorolog 3-22 instrument, and decays were analyzed using the program Origin 5.0 (Microcal). Electron spin resonance (ESR) measurements were carried out in aqueous solutions using samples in the sealed capillary part of Pasteur pipets. Spectra were recorded on a Bruker EMX10/12 spectrometer, equipped with a Bruker N<sub>2</sub> temperature controller device BVT3000, operating at X band, and calibrated with DPPH (α,α'-diphenyl-β-picrylhydrazyl).

### Results and Discussion

**Preliminary Experiments.** The initial confirmation of adsorption of lanthanides by the polyelectrolyte in aqueous sodium poly(vinyl sulfonate) solutions at 1%

**Table 1. Tb(III) Lifetime in Water or D<sub>2</sub>O ([Tb] = 10<sup>-2</sup> M), on SDS (10<sup>-2</sup> M) with [Tb] = 2 × 10<sup>-4</sup> M and on PVS (1%) with [Tb] = 7.5 × 10<sup>-5</sup> M and 10<sup>-4</sup> M**

| sample                      | $\tau^a$ (ms) | $n^b$ |
|-----------------------------|---------------|-------|
| Tb (H <sub>2</sub> O)       | 0.4           | 9     |
| Tb (D <sub>2</sub> O)       | 4.0           |       |
| Tb (SDS + H <sub>2</sub> O) | 0.4           | 8     |
| Tb (SDS + D <sub>2</sub> O) | 2.3           |       |
| Tb (PVS + H <sub>2</sub> O) | 0.5           | 3     |
| Tb (PVS + D <sub>2</sub> O) | 0.7           |       |

<sup>a</sup>  $\tau$  = lifetime. <sup>b</sup>  $n$  = number of coordinated water molecules.

(weight/volume, w/v) (PVS hereafter) was made using several experimental methods. Information on these systems was obtained at a molecular level by studying the emission spectrum of an aqueous solution of cerium(III) perchlorate. In the presence of PVS (1%), a small, but significant (4 nm) blue shift was observed in the emission maximum, as has previously been seen with Ce(III) on binding to sodium dodecyl sulfate (SDS) micelles.<sup>13</sup> While differences can be observed between emission spectra of solutions in pure water and in the presence of polymer due to light scattering, these will lead to red shifts.<sup>17</sup> The observed blue shift indicated that there is a specific interaction between the lanthanide and the polymer.

A second series of experiments to demonstrate the lanthanide–polymer interaction involved the study of its effect on the decay of Tb(III) luminescence. The decay of Tb(III) luminescence in aqueous and D<sub>2</sub>O solutions provides a valuable method for measuring the number of coordinated water molecules.<sup>15</sup> The lifetimes and decay constants of Tb(III) (10<sup>-2</sup> M) luminescence in water and D<sub>2</sub>O have been determined previously.<sup>13</sup> From these results, nine water molecules were calculated to be coordinated to Tb(III), in agreement with literature data.<sup>15</sup> On coordination by SDS micelles, one water molecule is lost.<sup>13</sup> Similar experiments carried out with Tb(III) and PVS for two different Tb(III) concentrations (7.5 × 10<sup>-5</sup> M and 10<sup>-4</sup> M) gave the lifetimes and decay constants shown in Table 1. As in pure water, a good monoexponential decay was obtained in all cases. However, the calculated number of water molecules coordinated to Tb(III) was reduced to three in both cases. From these data, it can be seen that when Tb(III) coordinates with PVS or SDS, it loses coordination water molecules. As the number of coordination molecules lost is higher for PVS than for SDS, it can be assumed that, in the polymer case, there is binding of Tb(III) by more than one sulfonate group and it is occluded by the polymer or separated from the bulk aqueous solvent, as has been proposed for enzyme–Gd(III)–substrate complexes in which the ESR spectra show a decrease in the number of metal-coordinated water protons.<sup>18</sup>

The third piece of experimental evidence showing lanthanide ions interacting with PVS comes from Gd(III) X band EPR spectra. Gd(III) is the only trivalent lanthanide whose ESR spectrum can be observed routinely at room temperature because of its relatively long electron relaxation times, 10<sup>-9</sup> to 10<sup>-10</sup> s. These are slower than those of other lanthanides (around 10<sup>-13</sup> s), where band broadening is observed.<sup>18,19</sup> The normalized Gd(III) ESR spectra for solutions with the gadolinium concentration 1.8 × 10<sup>-3</sup> M in pure water and in a solution of PVS (1%) are shown in Figure 1. A slight broadening of the lines is

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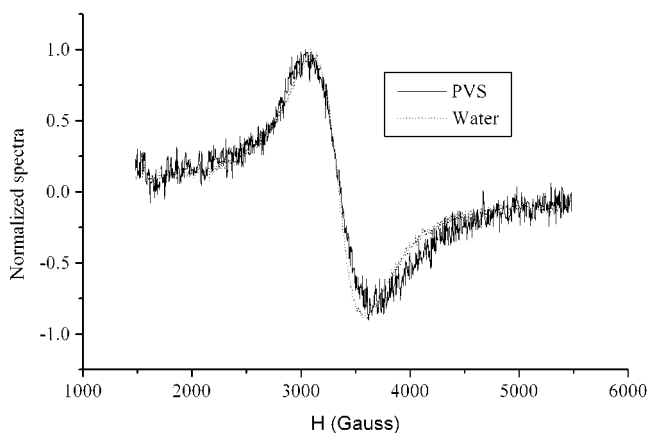
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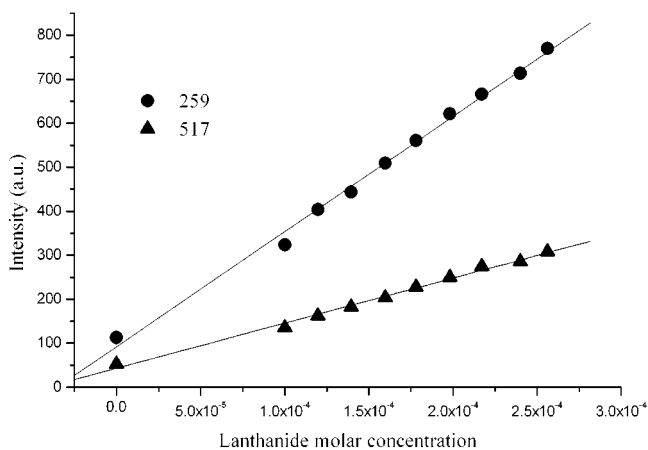
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**Figure 1.** Normalized ESR Gd(III) spectra in water and adsorbed in PVS (1%).

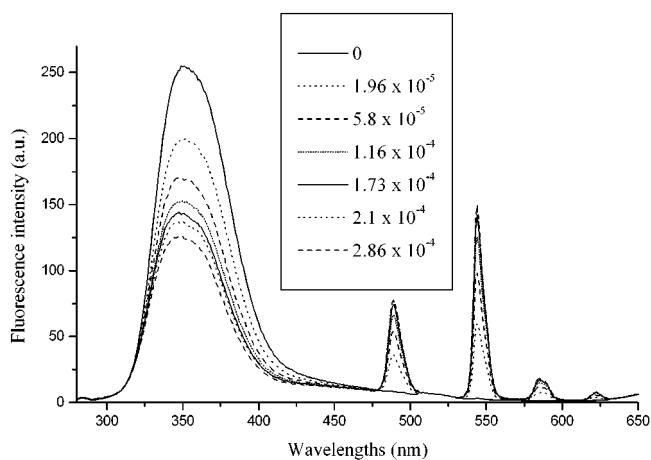


**Figure 2.** Rayleigh scattering and double resonance band intensity (at 259 and 517 nm, respectively) versus lanthanide concentration.

observed on addition of PVS. Assuming that dipole–dipole relaxation between Gd(III) spin states involves the protons of coordinated water molecules, this should be reduced on decreasing the number of coordinated water molecules. Also, if we assume that there will be a large decrease of Gd(III) rotation rate when it is bound within the polymer, the ESR line should be narrowed instead of broadened. Only a change in the coordination geometry of lanthanide–water complexes or a change in viscosity could justify the observed line broadening. Preliminary studies indicate an increase in viscosity of aqueous PVS solutions on adding lanthanide(III) ions.

The effect of adding lanthanide ions on the structure of an aqueous PVS (1%) solution was monitored over the whole concentration range studied by static light scattering. The Rayleigh scattering band intensity at 259 nm and double resonance band intensity at 517 nm increase linearly upon lanthanide addition, as shown in Figure 2. This suggests that PVS has a more expanded conformation when lanthanide is added and the average particle size in solution increases. This is also confirmed by visual observation. All the experiments have been carried out by adding the same lanthanide aliquot in such a way that the lanthanide concentration effects are the same.

**Lanthanide–Lanthanide Energy Transfer.** Energy transfer between lanthanides is of considerable interest. New materials with interesting spectroscopic properties have been investigated as doping matrixes, such as sol–gel glasses,<sup>20</sup> ceramics,<sup>21</sup> or polymers<sup>22</sup> with rare earth ions, and the energy transfer processes between them have been detected. In particular, Ce<sup>3+</sup> has been extensively



**Figure 3.** Emission spectra of Ce(III),  $2 \times 10^{-4}$  M, adsorbed on sodium poly(vinyl sulfonate), 1%, aqueous solution, with addition of different Tb(III) concentrations. In all the spectra the double resonance band at 517 nm has been removed.

used as a sensitizer for Tb<sup>3+</sup>.<sup>23,24</sup> Energy transfer in this case is interpreted in terms of the dipole–dipole interaction and is favored in the matrix in which Ce emission is shifted to lower energy because of host ligands because the overlap of the Ce emission and Tb excitation line function is greatly improved, as in CaAlO<sub>7</sub>/Tb<sup>3+</sup>/Ce<sup>3+</sup>.<sup>24</sup> Energy transfer from Ce(III) to Tb(III) also takes place when these ions are adsorbed on sodium poly(vinyl sulfonate), as Figure 3 shows. No emission of Tb(III) is detected after excitation at 258 nm for samples with PVS (1%) and Tb(III), even for the highest Tb(III) concentrations used in this study ( $2.9 \times 10^{-4}$  M). However, when aliquots of Tb(III) are added to solutions containing Ce(III) ( $2 \times 10^{-4}$  M) and the solutions are excited at 258 nm, four bands characteristic of Tb(III) emission are observed at 489, 544, 585, and 623 nm (Figure 3). The band at 544 nm is the most intense and sensitive to Tb(III) concentration. By increasing this ion concentration, Ce(III) emission decreases (Figure 3).

The increase in Tb(III) emission intensity is not linear with Tb concentration, tending to plateau at high concentration (Figure 4). The terbium emission arises from energy transfer from cerium, as is seen by the reduction in the Ce(III) luminescence. For this, we need to have cerium and terbium on the same polymer chains. To attempt to model the observed energy transfer behavior, a number of assumptions are necessary. First, theoretical studies<sup>25</sup> strongly suggest that virtually all the trivalent lanthanide ions will be bound to the PVS over the whole concentration range studied. Second, it can be assumed that only the Tb(III) adsorbed on chains containing Ce(III) emits and that the emission at 544 nm is proportional to its concentration on these chains ( $[Tb]_{Ce}^{ads}$ ). A final assumption is that the observed concentration dependence of the Tb(III) emission intensity corresponds to competitive binding of Tb(III) by free PVS chains and by PVS chains containing Ce(III). Various attempts have been made to model the binding of high valent ions by polyelectrolytes. These are complicated by the fact that the Poisson–Boltzmann distribution fails completely for these sys-

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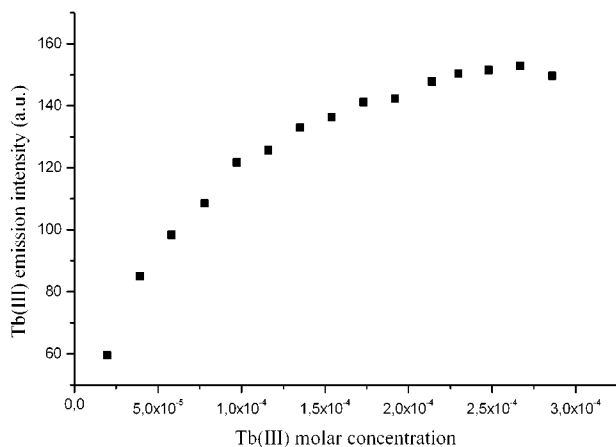
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**Figure 4.** Tb(III) emission intensity at 544 nm in samples with Ce(III) ( $2 \times 10^{-4}$  M), PVS (1%), and increasing Tb concentration.

tems.<sup>25</sup> An alternative approach is to treat competing equilibria for cerium and terbium binding to the same PVS chain. Such cases can be treated using a multiple equilibrium model.<sup>26</sup> Although this is a phenomenological approach, our main objectives are to establish the value of the lanthanide energy transfer method for studying cation–polyelectrolyte binding and to see how this is affected by parameters such as temperature and the presence of additives. The multiple equilibrium model has the same mathematical form as that of the Langmuir isotherm, the expression for which in the linear form is<sup>27</sup>

$$\frac{c}{w} = \frac{1}{w_{\max}K} + \frac{c}{w_{\max}} \quad (1)$$

where  $c$  is the total Tb(III) concentration,  $w$  is  $[\text{Tb}]_{\text{Ce}}^{\text{ads}}$ ,  $w_{\max}$  is the maximum of  $[\text{Tb}]_{\text{Ce}}^{\text{ads}}$ , and  $K$  is a constant. We note that  $K$  is not a simple binding constant but involves the competition for Tb binding by PVS and by PVS chains containing Ce ions.

We assume that the experimental emission intensity is proportional to the concentration of terbium bound to PVS containing cerium ( $[\text{Tb}]_{\text{Ce}}^{\text{ads}}$ ).

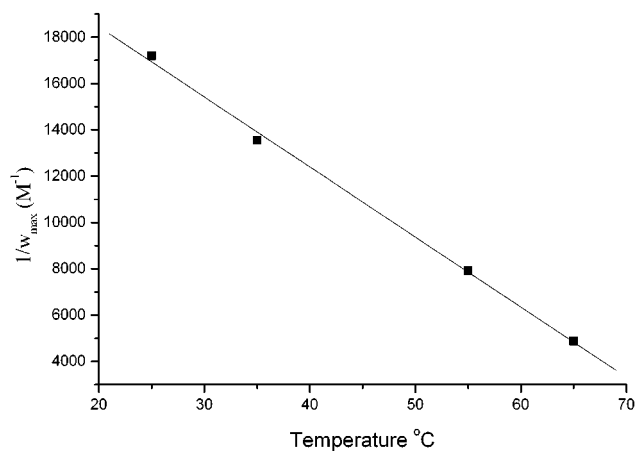
$$I^{\text{exp}} = \alpha[\text{Tb}]_{\text{Ce}}^{\text{ads}} \quad (2)$$

To normalize the data, we calculate  $\alpha$  in all cases from the emission intensity for the most dilute Tb(III) solution ( $1.96 \times 10^{-5}$  M). With this constant value,  $\alpha$ , and the solution Tb(III) concentrations, the sample emission intensity can be calculated,  $I^{\text{norm}}$ .

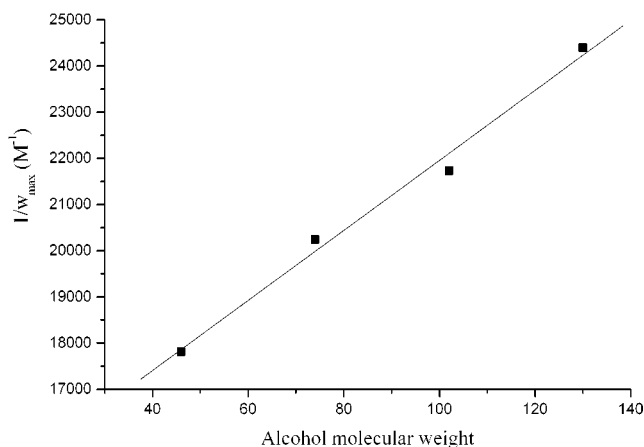
$$I^{\text{norm}} = \alpha[\text{Tb(III)}] \quad (3)$$

With these assumptions, the ratio  $d/w$  (total Tb(III) concentration/ $[\text{Tb}]_{\text{Ce}}^{\text{ads}}$ ) can be assumed to be proportional to the ratio  $I^{\text{norm}}/I^{\text{exp}}$ .

A plot of  $I^{\text{norm}}/I^{\text{exp}}$  versus Tb(III) concentration for a 1% PVS solution at 25 °C with Ce(III) concentration  $2 \times 10^{-4}$  M and Tb(III) concentrations changing from  $1.96 \times 10^{-5}$  M to  $2.86 \times 10^{-4}$  M was linear (correlation coefficient 0.999), with slope  $17\,200 \text{ M}^{-1}$ . The slope ( $1/w_{\max}$ ) gives a measure of the maximum binding of Tb to PVS chains containing Ce. We should note that with the relatively



**Figure 5.** Linear dependence of  $1/w_{\max}$  with temperature.



**Figure 6.** Linear dependence of  $1/w_{\max}$  on alcohol molecular weight.

small polyelectrolyte chains used it is possible that more than one PVS molecule will be bound to each lanthanide ion. Some support for this comes from viscosity measurements, which show an increase for solutions of PVS in the presence of Ce(III). Further studies are planned to investigate this.

The slope,  $(1/w_{\max})$  as given in eq 1, is shown to be dependent on the experimental conditions, as can be seen by the effects of variation of temperature or addition of alcohols of different molecular weights. These aspects will be treated in the next paragraphs.

**Temperature Effect.** When energy transfer experiments are carried out at different temperatures in PVS (1%) with Ce(III) concentration  $2 \times 10^{-4}$  M and various Tb(III) concentrations, the slope of the plot of  $I^{\text{norm}}/I^{\text{exp}}$  terbium emission intensities versus Tb(III) concentration ( $1/w_{\max}$ ) was found to decrease linearly with increasing temperature (Figure 5). These changes cannot be explained in terms of the effect of temperature on the luminescence efficiency of Ce(III) or Tb(III), since experiments carried out on the emission of Tb(III) or Ce(III) ( $10^{-2}$  M) in aqueous solutions over the same temperature range showed that the luminescence intensity is more or less constant or decreases slightly with temperature. Instead, the decrease in slope represents an increase in the maximum value of  $[\text{Tb}]_{\text{Ce}}^{\text{ads}}$ . For this reason, the changes observed in our experiments can only be explained in terms of changes in the PVS conformation in solution. It is well established that polyelectrolytes tend to adopt a more expanded conformation with an increase in temperature,<sup>2,3</sup> and in a more expanded conformation, the probability of Tb(III) to bind to a Ce(III)-containing

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chain is higher because there is also more polymer surface available to adsorption.

**Effect of Alcohol Addition.** The same types of energy transfer experiments have been carried out for aqueous PVS solutions (1%) in the presence of various alcohols ( $10^{-3}$  M), with  $2 \times 10^{-4}$  M Ce(III) and Tb(III) concentration varying from  $1.96 \times 10^{-5}$  M to  $2.85 \times 10^{-4}$  M. Experiments were performed in the presence of ethanol, 1-butanol, hexanol, and octanol. The slope of the plot of  $I^{\text{norm}}/I^{\text{exp}}$  terbium emission intensities versus Tb(III) concentration ( $1/w_{\text{max}}$ ) is found to be very sensitive to the alcohol molecular weight, and increases linearly with this parameter; that is,  $[Tb]_{\text{Ce}}^{\text{ads}}$  decreases linearly. This strongly suggests the involvement of some hydrophobic interactions between the alcohol and the polyelectrolyte. In terms of polymer conformation, it can be suggested that alcohol addition provokes a less expanded conformation in the polymer and this grows linearly with the alcohol molecular weight. In agreement with this, the effect is accompanied by an increase in light scattering with increasing alcohol concentration and molecular weight and with a less efficient Ce(III) to Tb(III) energy transfer.

**Effects of Addition of Other Species.** The same kinds of energy transfer experiments have been carried out adding to the PVS solutions poly(ethylene glycol) (molecular weight 200), 1%, sodium chloride  $10^{-1}$  M, or cationic surfactants: hexadecyltrimethylammonium chloride or dodecyltrimethylammonium bromide,  $5 \times 10^{-4}$  M. On adding poly(ethylene glycol) (PEG), 1%, the slope  $1/w_{\text{max}}$  increased ( $20\ 100\ \text{M}^{-1}$ ) with respect to that obtained for pure PVS solutions ( $17\ 200\ \text{M}^{-1}$ ). PEG is an uncharged polymer with a high dipole moment and is strongly solvated in water,<sup>1</sup> and it is believed to compact PVS when it is in solution, diminishing the surface and free anionic groups available for lanthanide adsorption.

In contrast, on adding  $10^{-1}$  M sodium chloride, a decrease in the slope ( $1/w_{\text{max}}$ ) ( $13\ 300\ \text{M}^{-1}$ ) and an increase in  $[Tb]_{\text{Ce}}^{\text{ads}}$  were obtained. The presence of added salt will allow the polymer chain to contract, which would be expected to decrease  $[Tb]_{\text{Ce}}^{\text{ads}}$ . However, an increase in light scattering is observed in these solutions in the presence of salt, and it is possible that aggregation is occurring.

The effect of adding the cationic surfactants hexadecyltrimethylammonium chloride (CTAB) or dodecyltrimethylammonium bromide (DTAB) is rather more complex. For CTAB, the slope of the plot of  $I^{\text{norm}}/I^{\text{exp}}$  terbium emission intensities versus Tb(III) concentration ( $1/w_{\text{max}}$ ) ( $17\ 100\ \text{M}^{-1}$ ) is close to that obtained for PVS alone, while for DTAB the slope ( $12\ 900\ \text{M}^{-1}$ ) decreases considerably. Light scattering was particularly intense when hexadecyltrimethylammonium chloride was added and flocculation was observed in the solution. In addition, when dodecyltrimethylammonium bromide was added, precipitation was observed. In these two systems, there are probably competing effects involved. On one hand, an increase in polymer surface charge<sup>1</sup> favors attraction for the opposite charged surfactants, as confirmed visually by the observed flocculation and/or precipitation in the system, reducing the surface available for adsorption. On the other hand, an increase in the ionic strength would cause a polymer contraction. Both effects could compensate for hexadecyltrimethylammonium chloride, and the first effect seems to be predominant for dodecyltrimethylammonium bromide. The alkyl chain length could play an important role in the dominant effect observed, with the longer alkyl chain surfactant being the one which better favors a cross-linked polymer conformation.

**Estimation of Lanthanide–Lanthanide Distance.** The average distance between neighboring lanthanides<sup>3+</sup> has been calculated according to a method proposed elsewhere for energy transfer between lanthanides in well-defined solid matrixes.<sup>28</sup> The relative intensity of the Ce(III) emission decreases with Tb(III) concentration due to energy transfer to Tb(III). This decrease is suggested to be described by eq 4.

$$\frac{I(\text{Ce})}{I(\text{Ce})^0} = (1 - x)^n \quad (4)$$

where  $I(\text{Ce})$  and  $I(\text{Ce})^0$  are the Ce(III) emission intensities (spectral areas) with and without Tb(III),  $n$  is the number of sites around Ce(III) to which Ce is able to transfer its excitation energy if occupied by Tb(III), and  $x$  equals the relative Tb(III) concentration. Hence,  $(1 - x)$  gives the probability that such a site is not occupied by Tb.

The mean distance between neighboring lanthanides,  $l$ , can be calculated with eq 5.<sup>28</sup>

$$l = \left( \frac{\pi R_c^2}{n + 1} \right)^{1/2} \quad (5)$$

where  $R_c$  is the critical radius for energy transfer between Ce and Tb, which is  $8\ \text{\AA}$ .<sup>28</sup> At  $25\ ^\circ\text{C}$  the calculated average distance between lanthanides is  $10\ \text{\AA}$  for PVS alone or after addition of PEG, NaCl, or the cationic surfactants. This could mean that the distance between lanthanides is effectively determined by the position of adsorption on the polymer chain.

## Conclusions

In conclusion, it can be stated that Ce(III) and Tb(III) are adsorbed on PVS in aqueous solutions with a significant loss of coordination water molecules. Energy transfer between Ce(III) and Tb(III) takes place efficiently on PVS and can be theoretically analyzed with a multiple equilibrium model. A very good linear fitting is obtained when plotting the ratio between the normalized terbium emission intensity and the experimental terbium emission intensity versus terbium concentration. The slope of this plot is a very sensitive indicator of the polymer conformation and can be used to probe how this changes under application of external perturbations. It grows when polymer has a less expanded conformation, as when PEG or alcohols are added, and is dependent on the alcohol molecular weight. It also decreases when the conformation is more expanded (by increasing temperature). From energy transfer experiments the average distance between lanthanides can also be calculated and is about  $10\ \text{\AA}$ , not depending on polymer conformation. Lanthanide energy transfer could offer a valuable technique for studying interactions between anionic polyelectrolytes and cations and analyzing the effect on polymer conformation.

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