

Notes

Lanthanide Ion Binding in AOT/Water/Isooctane Microemulsions

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Introduction

Microemulsions are finding increasing use as reaction media in areas such as biological catalysis¹ and ultrafine powder formation,² and they have also found applications in various commercial formulations.³ With microemulsions formed from inverted or reversed micelles, a water core is surrounded by the surfactant polar headgroups, and the alkyl chains together with a nonpolar solvent make up the continuous medium.^{1,4} One common amphiphile that forms inverted micelles is sodium bis-2-ethylhexylsulfosuccinate (AOT). Although this has normally been used as its sodium salt, there is increasing interest in replacement of Na⁺ by higher valent ions such as Mg²⁺, Ca²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺.^{5–11} Water-in-oil (w/o) microemulsions formed from these have structures which are strongly dependent on the counterions, varying from spherical to cylindrical. It is suggested that the interaction between the counterion and the sulfonate headgroup plays a dominant role in determining structure.⁶

Spectroscopic techniques, including in particular fluorescence spectroscopy, have been found to be good techniques for studying cation–amphiphile interactions. Trivalent lanthanide ions have been widely used to carry out spectroscopic studies because they have well defined luminescence and can isomorphously substitute Ca(II) and Zn(II), which are not spectroscopically active.^{12,13} In

addition, Gd(III) can act as an electron paramagnetic resonance probe. Luminescence^{14–16} and small angle neutron scattering (SANS)¹⁶ have previously been applied to the study of Ln(AOT)₃ microemulsions where Ln = Tb, Eu, and Nd. From the SANS measurements it has been shown that spherical reversed micelles are present.¹⁶ In recent publications, we have focused on the study of interaction of cations with both surfactants (sodium dodecyl sulfate (SDS) micelles)¹⁷ and polymers (sodium poly(vinyl sulfonate), PVS)¹⁸ as seen by energy transfer from Ce(III) to Tb(III) or by Gd(III) EPR. We report the extension of these studies to the behavior of trivalent lanthanides in sodium AOT/water/isooctane w/o microemulsions. As with the previous studies, our objective is to use luminescence and EPR spectroscopy to look at the interactions of lanthanide cations with the negatively charged surfactant surface and to see how this affects their mobility.

Experimental Section

Reagents. Sodium bis-2-ethylhexylsulfosuccinate (AOT hereafter), 2,2,4-trimethylpentane (isooctane), cerium(III), terbium(III), and gadolinium(III) perchlorates (40% water solution), and deuterium oxide (99.9%) were purchased from Aldrich. Millipore-Q water was used to prepare solutions.

Apparatus and Methods. For steady-luminescence spectral measurements, a Spex Fluorolog 111 and a Shimadzu RF-5301 PC were used in right-angle configuration. Tb(III) luminescence lifetimes were measured using the Spex 1934D phosphorimeter accessory with a Jobin-Yvon-Spex Fluorolog 3-22 instrument; decays were analyzed by using the program Origin 5.0 to analyze decays. Electron paramagnetic resonance (EPR) measurements were carried out in aqueous solutions using samples in the sealed capillary part of Pasteur pipets; all spectra have been corrected for the background. Spectra were recorded on a Bruker EMX10/12 spectrometer, equipped with a Bruker N₂ temperature controller device BVT3000, operating at X band and calibrated with DPPH (α, α' -dipheyl- β -picrylhydrazyl).

Results and Discussion

Initial studies on this system used cerium(III), which has a spectroscopically allowed 4f → 5d transition.¹⁹ Absorption and emission spectra were measured for various concentrations of Ce(III) in AOT/water/isooctane microemulsions. Small (\approx 4 nm) blue shifts were observed in the emission maxima compared with that of cerium(III) in water. Similar blue shifts have been observed with

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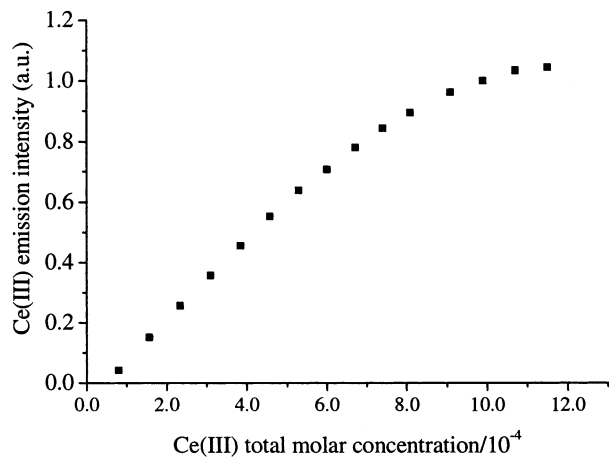


Figure 1. Ce(III) emission intensity versus Ce(III) total molar concentration in AOT (0.1 M)/water/isooctane solutions ($\lambda_{\text{excitation}} = 258 \text{ nm}$, $\lambda_{\text{emission}} = 358 \text{ nm}$).

Table 1. Lifetime of Tb(III) in AOT (10^{-1} M)/Isooctane with $w_0 = 33.6$ in Water and D_2O

Tb conc, M	$\tau_{\text{D}_2\text{O}}$ (ms)	$\tau_{\text{H}_2\text{O}}$ (ms)
6.2×10^{-5}	3.01	0.49
10^{-4}	3.05	0.48
1.4×10^{-4}	3.08	0.49
4×10^{-4}	3.16	0.47

the emission of cerium(III) in SDS and PVS solutions.^{16,17} This blue shift cannot be due to scattering, as a red shift would be expected in this case.²⁰ Instead, we believe this is due to selective binding of the lanthanide to the sulfonate headgroup of the surfactant. Similar binding of lanthanide ions to the sulfonate group of AOT has been invoked to explain the energy transfer behavior of 2-naphthylacetic acid to Tb and Eu in $\text{Ln}(\text{AOT})_3/\text{water}/\text{cyclohexane}$ microemulsions.¹⁴ When various volumes of an aqueous solution of cerium(III) (10 mM) are added to AOT (0.1 M) in isooctane, the cerium luminescence is found to increase with concentration (Figure 1). However, although the behavior was completely reproducible, luminescence intensity did not increase linearly with Ce^{3+} concentration. First, the curve does not pass through the origin. However, the concentration of cerium(III) was calculated from the quantity of added solution and did not take into account the residual amount of water present in commercial AOT.⁶ If a reasonable estimate of this is made and the concentrations are corrected, then the graph does go through the origin. The graph is then linear up to about $7 \times 10^{-4} \text{ M}$ (total added concentration) but levels out at higher concentrations. This corresponds to the onset of turbidity of the system and is probably due to the onset of phase separation.

Further information on the interaction between trivalent lanthanides and AOT comes from the study of Tb(III) luminescence decay in w/o microemulsions in isooctane in the presence of H_2O and D_2O . This is based on the effect of O–H and O–D oscillators on the deactivation of excited lanthanide ions and has been shown to be a valuable method for measuring the number of coordinated water molecules.^{16,21,22} Tb(III) fluorescence decays were measured for four different metal ion concentrations (6.2×10^{-5} , 10^{-4} , 1.4×10^{-4} , and $4 \times 10^{-4} \text{ M}$) in an AOT

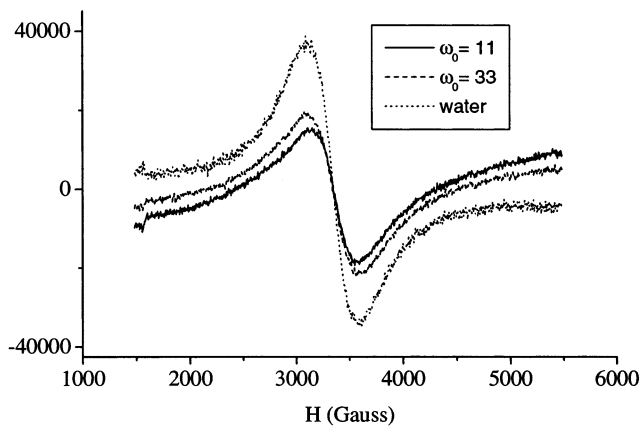


Figure 2. EPR spectra of Gd(III) ($1 \times 10^{-3} \text{ M}$) in AOT (0.1 M)/water/isooctane solutions at two different w_0 values and the normalized Gd(III) spectrum in aqueous solution.

microemulsion (10^{-1} M) in isooctane and a constant molar concentration ratio between water (or D_2O) and AOT (w_0) equal to 33.6. A reasonable monoexponential fitting was obtained for all the cases from which lifetimes were determined (Table 1).

From these data, the number of water molecules coordinated to Tb(III) can be calculated, and a value of 7.3 ± 0.3 was found for the four Tb(III) concentrations used. Previous studies on $\text{Ln}(\text{AOT})_3/\text{water}/\text{cyclohexane}$ microemulsions using the same technique with Tb^{3+} , Eu^{3+} , and Nd^{3+} show¹⁶ that, above $w_0 = 6$, the lanthanide hydration number has a constant value of about 8. These results can be compared with those of a pure aqueous solution, where Tb(III) coordinates nine water molecules.²³ The loss of coordinated water molecules as a consequence of the interaction between Tb(III) ions and other amphiphile systems has also been observed in micelles (sodium dodecyl sulfate, SDS)¹⁷ and polyelectrolytes (sodium poly(vinyl sulfonate), PVS).¹⁸ In SDS, one water molecule was lost, while for PVS¹⁸ the loss of six water molecules was observed. In agreement with what is expected for the behavior of a trivalent cation in the reverse micellar environment, our data strongly suggest that Tb(III) is associating with more than one sulfonate group of the surfactant. This is similar to what has previously been reported for the binding of copper(II) to AOT in microemulsions.⁹

More experimental evidence for the interaction between lanthanides and the AOT system comes from Gd(III) EPR spectra. Gd(III) is the only lanthanide that gives EPR spectra at room temperature because its electron relaxation times are higher than those of other lanthanides.³ The EPR spectra in microemulsions consist of a broad line, quite similar to that of Gd(III) in aqueous solution (Figure 2). The width of the Gd(III) EPR spectrum signal depends slightly on w_0 and is slightly broader at high w_0 values; that is, the higher the water fraction, the lower the relaxation time, probably because of a less hindered rotating movement. In addition to this, the fact that the EPR line is not narrowed suggests that the loss of water molecules and the reduction in the dipole–dipole relaxation between Gd(III) spin states and protons of coordinated water molecules should be compensated with changes in water coordination or viscosity.¹² However, in general, the EPR signal is fairly close to that in aqueous solutions, indicating that although the lanthanide ions

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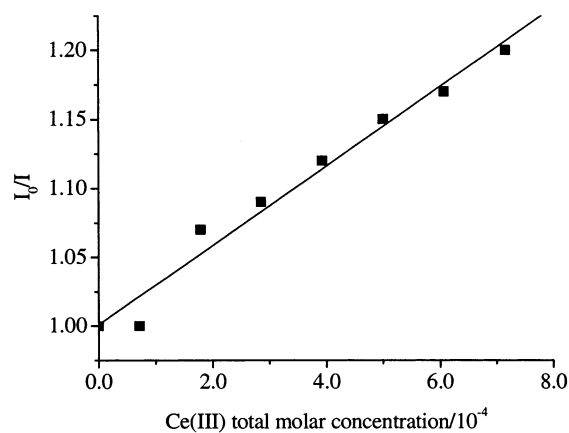


Figure 3. Stern–Volmer plot (I_0/I) of Tb(III) emission at 545 nm, where I_0 and I are the Tb(III) emission intensities without Ce(III) and with Ce(III), respectively, versus Ce(III) total molar concentration.

may be weakly bound to the surfactant, they still possess considerable lateral mobility.

To obtain further information on lanthanide mobility, the quenching of Tb(III) emission by Ce(III) in AOT/water/isooctane microemulsions was studied. Quenching has previously been observed with these ions in aqueous solution and is thought to involve energy transfer to a low lying state of Ce(III).¹⁷ From literature studies,²⁴ little intercluster quenching is expected during the lifetime of excited terbium(III), such that we are only looking at quenching within the water pool of microemulsion droplets. Various concentrations of cerium(III) were added to Tb(III) (3.4×10^{-4} M) in AOT/water/isooctane microemulsions ($w_0 = 33.6$). Quenching of the luminescence was observed, and this follows good Stern–Volmer kinetics (Figure 3). To obtain the intradroplet quenching constant, a number of assumptions have to be made. First, it is assumed that the droplets are monodisperse. Although this is not strictly true, the degree of polydispersity is

expected to be quite low.²⁵ Second, we assume that the aggregation number ($N = 562$) and water pool radius ($r_w = 52$ Å) are similar to those of AOT reversed micelles under similar conditions in the absence of lanthanides.¹⁶ Finally, we assume a simple cerium(III) distribution without any repulsive interactions. On this basis, we calculate an intradroplet quenching constant, $k_q = 1.1 \times 10^5$ M⁻¹ s⁻¹, which can be compared with the value for pure water,¹⁷ $k = 1.4 \times 10^5$ M⁻¹ s⁻¹. Although the excellent agreement between the numerical values may be fortuitous, the results strongly suggest that the lanthanide dynamics in the water pool under our experimental conditions are not too different from those of bulk water. This is in agreement with the Gd(III) EPR data, which show that trivalent lanthanide ions maintain a relatively high mobility within the water domain of AOT/water/isooctane microemulsions. We note that, in previous work on Cu(II) EPR in AOT/water/cyclohexane microemulsions, the mobility of cations in the water is about half that of bulk water.⁹

Conclusions

The interaction of trivalent lanthanide ions with the w/o microemulsion system AOT/water/isooctane has been probed with several spectroscopic techniques, which show that they bind weakly to the surfactant, with a loss of 1–2 water molecules coordinated to the metal. From both Gd(III) ESR line widths and rates of quenching of Tb(III) luminescence by Ce(III), very similar behavior is observed in AOT reversed micelles and bulk water. These results indicate that the trivalent lanthanide ions maintain a relatively high mobility within the water domain of the microemulsion droplets.

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