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Ligand-sensitized fluorescence of Tb^{3+} in Tb^{3+}–dibutylphosphate complexes: Application for the estimation of DBP

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Abstract

The fluorescence of Tb^{3+} is sensitized by complexation with dibutylphosphate (DBP) and tri-*n*-butylphosphate (TBP). The excitation maximum for the Tb^{3+}–DBP complex occurs at 218.5 nm, while that for the Tb^{3+}–TBP complex is observed at 228.0 nm. Both complexes yield Tb^{3+} fluorescence at 548 nm. The difference in the excitation maxima for the two complexes has been used to advantage for the estimation of DBP in the presence of TBP. DBP is the main degradation product of TBP in the PUREX process and the method described in this work can thus serve as a useful analytical tool in monitoring the quality of the TBP in the process. This method has been shown to be applicable for the estimation of DBP when present to an extent of 0.1–10% of TBP, in TBP/dodecane solutions.

Keywords: Dibutylphosphate; Tri-*n*-butylphosphate; PUREX; Terbium; Fluorescence

1. Introduction

Terbium is often found to exhibit fluorescence enhancement when complexed with suitable organic ligands [1–6]. In earlier works from this laboratory, we have shown that the fluorescence of Tb^{3+} can be enhanced by over three orders of magnitude by complexing it with a number of aromatic carboxylic acids [7,8]. The fluorescence enhancement is due to efficient energy transfer from the ligand to the terbium. The fluorescence of this complex was further enhanced by a factor of 10 when treated with TOPO/Triton X 100. These methods lead to the use of terbium as probes and labels for direct determination of organic analytes, nucleic acids, etc. [9,10].

In this study, we have examined the use of ligand-sensitized fluorescence spectroscopy, not for the determination of the metal ion, but for the determination of the ligand. Specifically, we have examined the possibility of determining the concentration of dibutylphosphate (DBP) in tri-*n*-butylphosphate (TBP)/dodecane solutions, with Tb^{3+} as the fluorescence probe. As with aromatic carboxylic acids, DBP sensitizes the fluorescence of Tb^{3+}, through an efficient energy transfer to the metal ion. The fluorescence of Tb^{3+} is proportional to the DBP concentration, which can therefore be exploited for the determination of DBP concentrations to monitor the quality of the extractant in the PUREX process.

In the PUREX process, tri-*n*-butylphosphate diluted with a hydrocarbon is used as an extractant for uranium and plutonium. This extraction mixture operates in a strongly acid medium and in a radiation environment; the TBP, consequently, undergoes degradation to yield mainly dibutylphosphate along with monobutylphosphate and phosphoric acid as minor products. The presence of DBP deteriorates the process performance [11,12] by forming strong organic soluble actinide–dibutylphosphate complexes. TBP is, therefore, given an alkali wash to remove these degradation products, prior to recycling. To monitor the extent of degradation and the quality of the extraction reagent, it is necessary to determine DBP in the reprocessing solvent.

Various analytical methods have been used for the determination of the concentration of DBP. They are gas chromatography, several types of liquid chromatography, ion-pair chromatography, nuclear magnetic resonance (NMR) spectrometry, titrimetry, spectrophotometric and electrospray ionization mass spectrometry (ESI-MS) methods [13–19]. Chromatographic techniques are time-consuming methods, for example, in the gas chromatography method [13,14], DBP is first methylated, while pre-concentration is required in case of ion-pair chromatography [15]. DBP estimation using NMR spectrometry [16] is also

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time intensive, particularly for low DBP levels. In tritrimetry [17], DBP is estimated in the two-component TBP–nitric acid medium after extraction with benzene. Spectrophotometry [18] is used for the DBP estimation based on the ability of DBP to reduce the colour intensity of a thorium–thoron complex, which method involves elaborate sample preparation.

Fluorescence spectroscopy, described here, provides a simple method for the estimation of DBP. To the best of our knowledge, fluorimetric estimation of DBP using sensitized Tb^{3+} fluorescence has not been reported earlier.

2. Experimental

2.1. Apparatus

All fluorescence spectra were recorded using a Shimadzu RF 5000 spectrofluorimeter, with a 150 W xenon lamp source. Solutions were taken in a 1 cm path length fused silica cell. The band pass for the excitation and emission monochromators was set at 5 nm each. A long-wavelength pass filter (UV-39, Shimadzu), with a maximum and uniform transmittance (>85%) above 400 nm, was placed in front of the emission monochromator, in order to reduce the scatter of the incident beam into the emission monochromator.

2.2. Purification and preparation of DBP and MBP solutions

Commercially, monobutylphosphate (MBP) and dibutylphosphate are available as mixtures (Fluka, AG) and were therefore separated using the following procedure. The DBP–MBP mixture was treated with CCl_4 and washed with water. As MBP is more soluble in water than in CCl_4, it is extracted into the aqueous phase. The aqueous layer was washed thoroughly with CCl_4 and dried to obtain pure MBP. Similarly, the organic layer containing DBP was washed repeatedly with water to remove any traces of MBP and then dried to obtain pure DBP. The purity of the MBP and DBP, thus obtained, was estimated tritimetrically and found to be 98.5%. Stock solutions of DBP and MBP were prepared by dissolving appropriate amounts of these phosphates in dodecane.

2.3. Preparation of solutions for fluorimetric studies

A 1.5 ml of commercial TBP (98%) (BDH, GPR) was taken in a 5 ml test-tube along with different amounts of DBP and the resulting mixture was diluted with AR grade dodecane. These solutions contained DBP over the concentration range from 1.1×10^{-3} M to 1.1×10^{-1} M, while the TBP concentration was 1.1 M. The concentration of DBP in these solutions was 0.1–10% of TBP and represented typical solutions encountered in degraded TBP solutions. Stock solutions of Tb^{3+} were prepared by dissolving nitrate and chloride salts of Tb^{3+}. $TbCl_3$ was obtained by treating Tb_4O_7 with concentrated hydrochloride acid and evaporating to dryness. The residue was then dissolved in distilled water. $Tb(NO_3)_3$ available commercially was used as such.

From the mixtures of TBP/DBP in dodecane prepared above, solutions for fluorimetric analysis were prepared as follows. The 25 μl of DBP–TBP mixtures in dodecane was placed in a 5 ml calibrated flask and the volume was made up with HPLC grade cyclohexane (the rationale behind the choice of cyclohexane will be presented later; in short, cyclohexane was the best solvent for observing Tb^{3+}–DBP fluorescence). To this solution, 30 μl of aqueous Tb^{3+} (6.5×10^{-2} M), prepared using either the nitrate or chloride salt, was added and was allowed to mix thoroughly by shaking it manually for 5 min. The fluorescence intensity of Tb^{3+} was measured with excitation and emission wavelengths of 218.5 nm and 548 nm, respectively.

3. Results and discussion

3.1. Spectrofluorimetric results

At the outset, we show in Fig. 1, the *excitation* spectra of Tb^{3+}, Tb^{3+}–TBP and Tb^{3+}–DBP in cyclohexane. The excitation spectra were recorded by monitoring the Tb^{3+} emission at 544/548 nm. For Tb^{3+}, the emission maximum is at 544 nm, while for the Tb^{3+}–TBP and Tb^{3+}–DBP complexes, the maxima occur at 548 nm.

It can be seen that no signal due to Tb^{3+} was seen (Fig. 1, trace 'a') when terbium was taken without the phosphates, as Tb^{3+} has poor solubility in cyclohexane. Similarly, no signal was observed with Tb^{3+}–MBP (Fig. 1, trace 'b'). Even though MBP is known to complex strongly with Tb^{3+}, the absence of any Tb^{3+} fluorescence may be either because of poor sensitization of the lanthanide fluorescence by MBP or possible quenching of the Tb^{3+} fluorescence by the O–H groups in MBP. With Tb^{3+}–TBP, a weak feature was observed near 228 nm (Fig. 1, trace 'c'). However, a strong signal due to Tb^{3+} fluorescence was observed

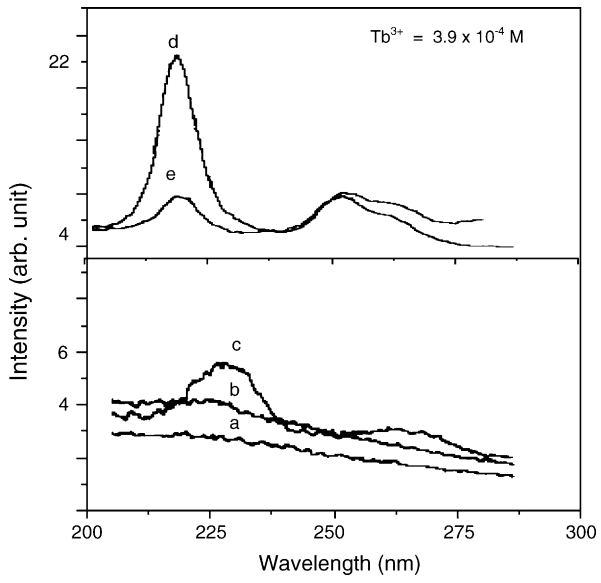

Fig. 1. Excitation spectrum of: (a) Tb^{3+}; (b) Tb^{3+}–MBP (1×10^{-4} M); (c) Tb^{3+}–TBP (5.5×10^{-2} M); (d) Tb^{3+}–DBP (5.5×10^{-5} M); (e) Tb^{3+}–DBP (6.6×10^{-4} M). All experiments were done using cyclohexane as solvent except (e) where the solvent was dodecane.

at 218.5 nm, with Tb^{3+}–DBP complex (Fig. 1, trace 'd'). As this fluorescence is obtained only in the presence of DBP, it clearly indicates the sensitization of terbium fluorescence by DBP.

Both Tb^{3+}–DBP and Tb^{3+}–TBP complexes, when excited at 218.5 nm and 228 nm, respectively, yield the emission spectra characteristic of Tb^{3+}.

3.2. Choice of solvent

Various solvents, such as cyclohexane, dodecane, hexane, acetone, carbon tetrachloride, chloroform were tried out in these experiments; among them, cyclohexane was found to be the best. As an example, we show in Fig. 1 (trace 'e') the excitation spectrum of Tb^{3+}–DBP in dodecane. It can be seen that fluorescence intensity of Tb^{3+} in the Tb^{3+}–DBP complex is clearly stronger in cyclohexane than in dodecane.

3.3. Effect of Tb^{3+} concentration

The effect of terbium concentration on the fluorescence intensity of Tb^{3+}–DBP complex was studied at DBP concentrations of 0.25%, 6% and 10%. Tb^{3+} concentration was varied from 1×10^{-4} M to 6×10^{-4} M. In the complex with 0.25% DBP, the fluorescence intensity does not increase with Tb^{3+} concentration, whereas at 6% and 10% DBP concentration, the fluorescence intensity increases with Tb^{3+} concentration. The maximum intensity was observed for Tb^{3+} concentration of $\sim 4 \times 10^{-4}$ M. In the following experiments, 3.9×10^{-4} M of Tb^{3+} was chosen as the optimum concentration.

3.4. Analytical calibration

Fig. 2 plots the excitation intensity of Tb^{3+} as a function of the DBP concentration in a solution containing Tb^{3+}, DBP and TBP. Both DBP and TBP were used in these experiments, as in real life samples, DBP would be required to be estimated in the presence of large amounts of TBP. The concentration of Tb^{3+} was maintained at 3.9×10^{-4} M and that of TBP at 5.5×10^{-3} M. The range of the DBP concentration was from 5.5×10^{-6} M to 5.5×10^{-4} M, which amounts to DBP being at levels of 0.1–10% of TBP.

Experiments were carried out to obtain calibration graphs, using both $TbCl_3$ and $Tb(NO_3)_3$. It can be seen that the slopes of the analytical curves are comparable for both the salts. The detection limit is around 2.5×10^{-6} M with a S/N of ~3 at this concentration.

3.5. Application of the method

In order to check the performance of the method, a set of six solutions containing known amounts of DBP in TBP/dodecane were prepared to mimic solutions that would be encountered in PUREX reprocessing applications. These six synthetic samples contained DBP ranging in concentration from 0.45% to 3.45% of TBP in TBP/dodecane solutions. The concentrations of DBP in these synthetic samples were estimated according to the experimental procedure outlined in this work. The results are shown in Table 1. The estimated values were within 5% of the actual values.

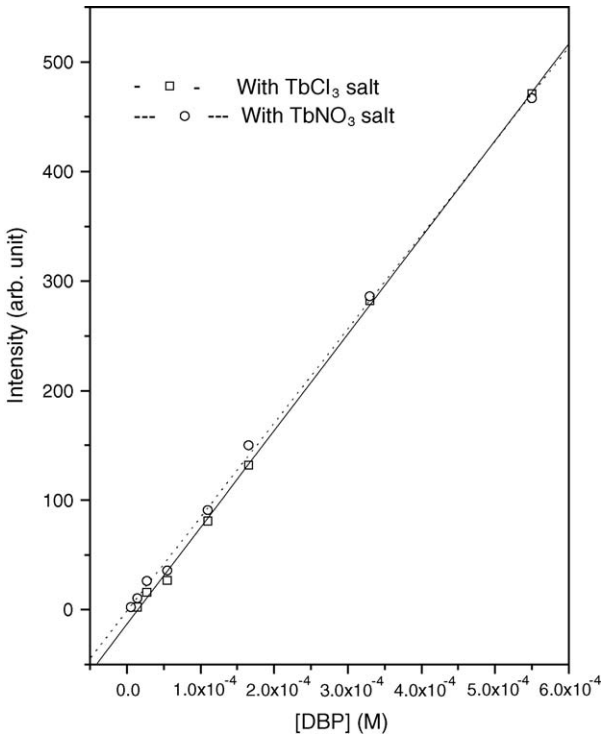

Fig. 2. A plot of excitation intensity of Tb^{3+} in the Tb^{3+}–DBP complex as a function of DBP concentration. Excitation wavelength was 218.5 nm and the emission wavelength monitored was 548 nm. Plots obtained using both $TbCl_3$ and $Tb(NO_3)_3$ have been shown.

3.6. Effect of MBP

Very often, DBP may have to be estimated in the presence of MBP, as both MBP and DBP are degradation products of TBP. It has already been shown earlier that MBP does not sensitize Tb^{3+} fluorescence as does DBP. However, it is still important to determine the influence that MBP exerts on the fluorescence of the Tb^{3+}–DBP complex. The effect of MBP on the fluorescence of Tb^{3+}–DBP was examined and shown in Fig. 3. As long as the MBP concentration is less than 10% of the DBP concentration, no perceptible change in the intensity of Tb^{3+}–DBP

Table 1
Estimates of DBP in TBP/dodecane solutions

Sample	[DBP] as prepared (M)	[DBP] estimated (M)	Deviation (%)
1	4.95×10^{-3} (0.45)[a]	5.21×10^{-3} (0.47)	5.2
2	1.00×10^{-2} (0.91)	9.85×10^{-3} (0.89)	1.5
3	1.50×10^{-2} (1.36)	1.52×10^{-2} (1.38)	1.3
4	1.80×10^{-2} (1.64)	1.75×10^{-2} (1.59)	2.8
5	1.90×10^{-2} (1.73)	1.83×10^{-2} (1.66)	3.7
6	3.80×10^{-2} (3.45)	3.94×10^{-2} (3.57)	3.7

Concentration of TBP in all the synthetic solutions was maintained at 1.1 M. Values in parentheses are in percent.

[a] Numbers in parenthesis give the percentage composition of DBP with respect to TBP in the different solutions.

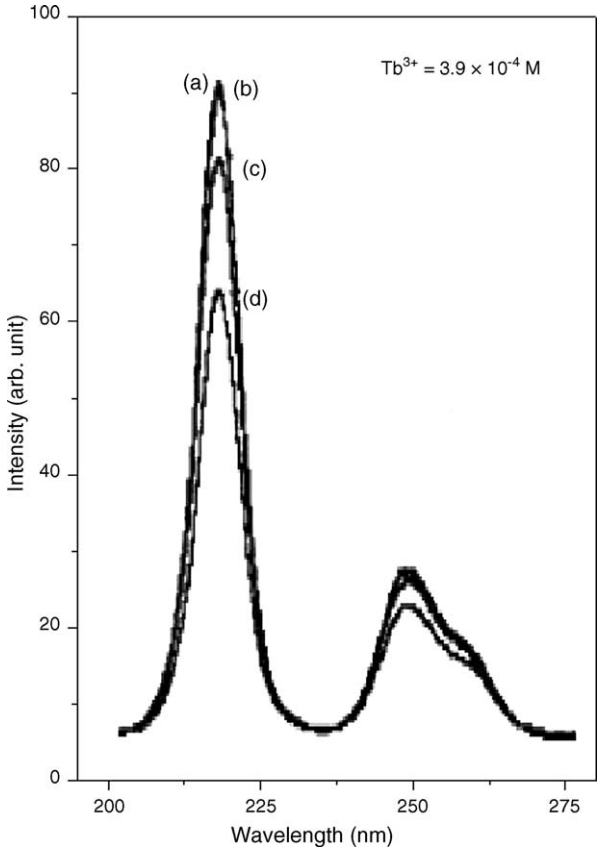

Fig. 3. Excitation spectra of Tb^{3+} in Tb^{3+}/DBP (1.2×10^{-4} M)/TBP (1.1×10^{-2} M)/MBP as a function of MBP concentration in the mixture. The concentrations of MBP were: (a) 0 M; (b) 1.0×10^{-5} M; (c) 1×10^{-4} M; (d) 5×10^{-4} M.

was observed. When the concentration of MBP was ~80% that of the DBP concentration, the fluorescence of the Tb^{3+}–DBP decreased by only 10%. When the MBP concentration was increased to about 400% that of the DBP concentration, the decrease in the fluorescence of the complex was about 30%. In typical TBP degraded solutions, the concentration of MBP is likely to be far less than that of DBP and hence the present method would not involve significant errors due to the presence of MBP in real life samples.

3.7. Validity of the method

In order to check the validity of the method, two samples are prepared in the following manner. The 10 ml portions of 30% TBP in dodecane were placed in duplicate into 25 ml volumetric flasks. Flasks were closed and kept in an irradiation chamber with ^{60}Co γ-source for different intervals of time, to simulate the irradiation dose received by extractant in the process cycle. Sample No. 1 was irradiated for 23 h and Sample No. 2 for 41 h with a dose 7.3 kGy/h. The concentrations of DBP produced by irradiation in these samples were quantified by the present fluorimetric method and the conventional gas chromatography (GC) method. It can be seen that the concentrations of DBP estimated using both these methods agree well (Table 2).

Table 2
Estimated values of DBP by the present method and GC method

Sample No.	Concentration of DBP (M) estimated by	
	Fluorimetric method[a] (described in this work)	GC method
1	1.35×10^{-2}	1.17×10^{-2}
2	2.32×10^{-2}	2.00×10^{-2}

[a] Errors in the estimates by fluorimetric method is about 7%.

4. Conclusion

Fluorescence of Tb^{3+} has been studied in the presence of MBP, DBP and TBP. DBP showed the strongest fluorescence sensitization of the Tb^{3+} fluorescence in cyclohexane solutions. The results of this study were used to establish a method for the determination of DBP in degraded TBP solutions in the PUREX process. The reproducibility and linearity of the analytical curve suggests that the method is suitable for the determination of DBP over a concentration range of 0.1–10% DBP in TBP. This concentration range is well suited for applications in real life for the estimation of DBP in recycled reprocessing solvents. This method is simple, accurate and quick compared with the currently used chromatographic methods. The method is also applicable in the presence of MBP, another common degradation product, as it has been shown that at the concentrations of MBP typically found in the degraded reprocessing solutions, the fluorescence of the Tb^{3+}–DBP complex is only hardly affected.

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