

Development of an oil tracer labelled with ^{137m}Ba

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Abstract. The extraction of barium ions by isooctane solutions of di-nonyl naphthalene sulfonic acid (HDNNS) and di-cyclohexano-18-crown-6 (DC18C6) from aqueous solutions of hydrochloric acid and sodium chloride has been investigated. The extraction and the associated back extraction results suggest that this barium complex is a suitable oil tracer for petroleum related applications, such as measurement of Residence Time Distribution (RTD) and oil carry-over to the gas outlet in multiphase separators and scrubbers.

1. INTRODUCTION

Radioactive tracers are extensively used in industry as a problem solving tool, and they have been applied in the petroleum industry for several decades. Petroleum related applications include reservoir characterization, well operations, and process monitoring. Short-lived radiotracers may be employed in mass transport studies, in a non-intrusive manner, in production equipment like multiphase separators and scrubbers.

Some short-lived radionuclides may be conveniently produced using the radionuclide generator technique. The concept requires a chain of at least two radioactive nuclides in radioactive equilibrium, often referred to as mother and daughter nuclides. The mother nuclide is preferentially adhered to an inorganic backing material, which is most often an ion exchanger. The generator is based on selective separation of the daughter nuclide from the mother by an appropriate elution solution. The radioactive decay of ^{137}Cs ($T_{1/2} = 30\text{ y}$) to decay product ^{137m}Ba ($T_{1/2} = 2.55\text{ m}$), is an example of such a decay chain suitable for a radionuclide generator.

The use of ^{137m}Ba in process studies benefits from the short half-life. It provides the possibility of conducting consecutive measurements in close time intervals as residual activity will quickly have decayed. However, the short half-life poses challenges as well. Preparation of barium compounds is limited to systems of fast chemical complexations.

This work is concerned with the preparation of organically complexed radioactive barium, suitable for tracing organic fluids in industrial processes. A rapid barium complexing system coupled with a $^{137}\text{Cs}/^{137m}\text{Ba}$ radionuclide generator forms a radio-tracer generator.

Few organic barium complexes are known, which in addition to easy and rapid formation can withstand the presence of high salinity waters. McDowell et al. has reported on the extraction of barium in a system of naphthalene sulfonic acid and crown ether [1]. The naphthalene sulfonic acid is in practice a liquid ion exchanger, and the presence of crown ether seems to stabilize the complex.

We report on the extraction of barium with di-nonyl naphthalene sulfonic acid (HDNNS) and di-cyclohexano-18-crown-6 (DC18C6), and the stability of this complex against saline waters.

2. EXPERIMENTAL

2.1. Materials

Radioactive barium, ^{133}Ba ($T_{1/2} = 10.51\text{ y}$) in chloride form in 0.1 M HCl solution was supplied by Eckert & Ziegler. HDNNS was obtained from Sigma Aldrich as a 50% solution in heptane. The heptane was removed in a rotary evaporator and the resulting solution was purified using an anion exchange technique similar to the procedure described in reference [2]. All other chemicals were of p.a. quality and obtained from Sigma Aldrich, except 1-dodecanol which was from Fluka. Liquid scintillation cocktail, Ultima Gold XR was from Perkin Elmer.

2.2. Solvent extraction experiments

The barium chloride solutions were of 0.154 M NaCl and 0.1 M HCl. These concentrations of NaCl and HCl were chosen as they form a suitable elution solution for the $^{137}\text{Cs}/^{137m}\text{Ba}$ radionuclide generator. The organic phase consisted of 0.008 M HDNNS, 0.004 M DC18C6 and 0.04 M 1-dodecanol in isooctane. 1-dodecanol is added as a modifier, to ensure good phase separation in the extraction experiments. The extraction solutions were pre-equilibrated with a solution of 0.154 M NaCl and 0.1 M HCl.

The barium complex was tested against synthetic brine and production water from a reservoir in the North Sea. The composition of synthetic brine is: 0.65 M NaCl, 0.01 M MgCl_2 , 0.01 M CaCl_2 , 0.0085 M KCl, 0.001 M SrCl_2 , 0.001 M NaHCO_3 , 10^{-5} M BaCl_2 , and $10^{-5}\text{ M Na}_2\text{SO}_4$.

The production water that was tested has relatively low ionic strength, typically between 0.4 – 0.85 M. It also contains unspecified water soluble organic components because it has been equilibrated with the corresponding oil through the reservoir and production process.

A 1:1 volume ratio was used between the organic and the aqueous solutions in the solvent extraction

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experiments (4.0 ml of each phase) and in the subsequent back extractions into the saline waters (1.5 ml of each phase). Equilibration was for two minutes and mixed by hand, except when otherwise is noted. The samples were then centrifuged for one minute, to ensure good phase separation. The experiments were carried out at ambient temperatures.

2.3. Measurements

Gamma-ray spectroscopy and liquid scintillation counting were used to measure the activity of barium in the samples. Extraction yields were determined by the distribution value, given by

$$D = \frac{A_{\text{org}}(^{133}\text{Ba})}{A_{\text{aq}}(^{133}\text{Ba})}$$

Back-extraction yields are given by $1/D$.

Aliquots of $500\ \mu\text{l}$ of each phase were measured employing a HPGe detector. Liquid scintillation samples were prepared from $400\text{-}\mu\text{l}$ aliquots. The values were determined by the average of three parallels, and both measuring methods were included for each parallel. The given uncertainties are three standard deviation of the six measurements.

3. RESULTS

3.1. Formation of barium complex

A barium complex based on short-lived $^{137\text{m}}\text{Ba}$ requires relatively fast formation. Solutions of $40\ \mu\text{M}$ barium chloride and organic phase were mixed for 15, 30 and 120 seconds to obtain information about the extraction kinetics and the time needed for the extraction system to reach equilibrium. Table 1 lists the D-values for each mixing time. The D-values show a rapid formation of the barium-DC18C6-HDNNS complex, and it is fast enough to complex generator-eluted $^{137\text{m}}\text{Ba}$.

Table 1. Extraction of Ba-DC18C6-HDNNS complex: D-values for various mixing times.

Time	15 s	30 s	120 s
D	200 ± 30	210 ± 40	220 ± 50

Extraction with different barium chloride concentrations were performed to investigate the possible influence of barium ion-to-complexing agents ratio. Solutions of $40\ \mu\text{M}$, $4\ \mu\text{M}$, and $0.4\ \mu\text{M}$ barium chloride were tested, and the measured D-values are shown in Table 2. These concentrations correspond to a ratio of 10^2 to 10^5 between

Table 2. Extraction of Ba-DC18C6-HDNNS complex: D-values for various aqueous phase barium concentrations.

[BaCl ₂]	$40\ \mu\text{M}$	$4\ \mu\text{M}$	$0.4\ \mu\text{M}$
D	220 ± 50	220 ± 20	220 ± 20

complexing agents and barium ion, and presumably in a tracer generator design the ratio will be $\gg 10^2$.

3.2. Distribution into saline waters

The distribution of the barium complex into saline waters was evaluated by back-extraction experiments immediately following the extraction experiments. The results from back-extraction of the barium complex into synthetic brine and the North Sea production water are given in Table 3.

Table 3. D-values for back extraction of Ba-DC18C6-HDNNS complex into synthetic brine and production water from a North Sea reservoir.

[BaCl ₂]	1/D	
	Production water	Synthetic Brine
$40\ \mu\text{M}$	0.027 ± 0.007	0.0030 ± 0.0007
$4\ \mu\text{M}$	0.026 ± 0.003	0.0029 ± 0.0004
$0.4\ \mu\text{M}$	0.026 ± 0.003	0.003 ± 0.001

4. CONCLUSION

The extraction of barium ions by HDNNS and DC18C6 in isoctane from aqueous solutions of hydrochloric acid and sodium chloride has been presented. The complex formation rate is relatively fast. The distribution of the barium-DC18C6-HDNNS complex into typical saline solutions is small. Thus, a short-lived barium oil tracer is possible in the coupling of this chemical extraction system with a $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ radionuclide generator.

The thermal stability of the complex itself at elevated temperatures up to 100°C has not been tested. If the D-values do not change significantly from the reported ones, the $^{137\text{m}}\text{Ba}$ -DC18C6-HDNNS complex may be a useful tracer for the organic phase in multiphase transport monitoring operations, for example in production and fluid handling equipment like separators and scrubbers.

References

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