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Development of alternate extractants for separation of actinides

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Abstract

Selection of an extractant plays a key role in the development of a commercial solvent extraction process. Though tri-*n*-butyl phosphate (TBP) is currently used as the extractant for the processing of fast reactor fuel, there is a need to introduce an alternate extractant to ensure the success of closing the fast reactor fuel cycle in India. Recent studies undertaken in our laboratory for the identification of the most suitable extractant for fast reactor fuel reprocessing are addressed in this paper. Studies carried out on the influence of alkoxy groups of dialkylalkyl phosphonates on the extraction behaviour of uranium and thorium is also discussed.

Keywords: Trialkyl phosphate; Uranium; Plutonium; Ejector Mixer-settler; Dialkylalkyl phosphonate; Thorium

1. Introduction

Tri-*n*-butyl phosphate (TBP) is one of the well-studied and thoroughly understood extractants because of its pivotal role in various stages of nuclear fuel cycle. Fast reactor fuel reprocessing involving handling plutonium-rich spent fuel with high levels of radioactivity is considered to be more challenging than thermal reactor fuel reprocessing, even though both employ the same solvent extraction process (PUREX) with 1.1 M solution of TBP in *n*-dodecane (DD) as solvent. Extraction of U(VI) and Pu(IV) from nitric acid media with high fission product decontamination factors, excellent stripping behaviour, high capacity

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of the PUREX solvent to load U(VI) and easy commercial availability are the main reasons for the selection of TBP as an extractant in thermal reactor fuel reprocessing [1]. However, third phase formation in the extraction of Pu(IV) is a serious issue with TBP in fast reactor fuel reprocessing [2]. Hence there is a need to identify an alternate extractant for fast reactor fuel reprocessing to improve the process performance. The alternate extractant should have high capacity to load Pu(IV) without third phase formation and its extraction and stripping behavior should be similar to that of TBP. In this context, several trialkyl phosphates such as tri-n-amyl phosphate (TAP) and some of its isomers such as tri-*iso*-amyl Phosphate (TiAP), tri-2-methyl butyl phosphate (T2MBP), tri-*sec*-amyl phosphate (TsAP) etc. have been synthesized in our laboratory to identify a viable extractant for fast reactor fuel reprocessing.

The extraction ability of organophosphorus extractants depends on the basicity of the phosphoryl oxygen which in turn depends on the nature of the substituents attached to the "P" atom. The basicity of the phosphoryl group increases by replacing the C-O-P group in the extractant by a C-P group. Therefore, the extraction ability of neutral organophosphorus extractants for a given alkyl group increases in the order, phosphates < phosphonates < phosphinates < phosphine oxides. Earlier we have reported the extraction behavior of actinides by diamylamyl phosphonate (DAAP) [3] and dibutylbutyl phosphonate (DBBP) [4]. Earlier studies also revealed that the extraction ability of dibutylalkyl phosphonates is not significantly influenced by increasing the chain length of the alkyl group from butyl to octyl group [5]. In the present study, two phosphonates, viz., dibutylhexyl phosphonate (DBHeP) and diamylhexyl phosphonate (DAHeP) have been synthesized and used to understand the influence of alkoxy groups on the extraction of U(VI) and Th(IV) with hexyl as alkyl group in both the cases.

2. Identification of TiAP as an alternate extractant for fast reactor fuel reprocessing

Earlier we have investigated the batch extraction of nitric acid, U(VI) and Pu(IV) by various trialkyl phosphates as well as their third phase formation behavior [6, 7]. Some of their physicochemical properties such as density, aqueous solubility, solubility of water in phosphate etc. have also been measured. Studies indicated that TAP, TiAP and T2MBP have high capacity to load Th(IV) and Pu(IV) without third phase formation. U(VI) can also be loaded in 1.1 M solutions of these extractants in n-DD up to theoretical limit. Distribution ratios for the extraction of nitric acid, U(VI) and Pu(IV) by these phosphates are comparable to that of TBP. Their physicochemical properties are also favourable for a solvent extraction process. In addition to these advantages, their aqueous solubility is low as compared to TBP. However, preliminary studies indicate that TAP is more susceptible to alpha radiolysis compared to TBP, whereas the radiation stability of TiAP is on par with TBP. Therefore, TiAP has been proposed as an alternate extractant for fast reactor fuel reprocessing. Flow sheet development studies with TiAP

3. Flow sheet development studies with TiAP

As a preliminary step towards the evaluation of the feasibility of using TiAP on engineering scale, a mixer-settler facility was set-up for flow sheet development studies. Continuous counter-current solvent extraction runs have been performed under various conditions by using this facility. Flow sheet development studies with TiAP as a preliminary step towards the evaluation of the feasibility of using TiAP on engineering scale, a mixer-settler facility was set-up for flow sheet development studies. Continuous counter-current solvent extraction runs have been performed under various conditions by using this facility.