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The Influence of TBP on Americium Extraction by Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine Oxide*

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The most important characteristics of the TRUEX (*tr*ans*u*ranium *ex*traction) process, developed at the Chemistry Division of Argonne National Laboratory by Horwitz and coworkers, are reported in refs. 1–9. It is based on the use of the neutral organophosphorus extractant octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO).

The basic extraction chemistry of CMPO, whose structure is reported in Fig. 1, has been reported in a number of investigations [10–17]. The stoichiometry of Am(III) extraction reaction by CMPO in nitrate medium can be expressed by the following equilibrium [15]:

$$\mathrm{Am^{3+} + 3NO_3^- + \overline{3CMPO(HNO_3)_n} \longrightarrow \overline{Am(NO_3)_3(CMPO)_3(HNO_3)_m} + (3n - m)HNO_3} \quad (1)$$

where $n = 0$ to 2, $m = 0$ to 3, and the bar denotes organic species. The values of n and m depend on the nitric acid concentration in the aqueous phase. At low acidity, $[\mathrm{HNO_3}] < 1$ M, $n = m = 0$ and reaction (1) reduces to:

$$\mathrm{Am^{3+} + 3NO_3^- + 3CMPO \longrightarrow \overline{Am(NO_3)_3(CMPO)_3}} \quad (2)$$

The diluents used in the TRUEX process are typically a normal paraffinic hydrocarbon or a nonflammable chlorocarbon such as carbon tetrachloride or tetrachloroethylene (TCE), depending on the specific application. Unfortunately, extractants belonging to the CMPO class suffer from a lack of high loading capacity and, more seriously, from an incompatibility with aliphatic diluents which can cause third-phase formation [1, 12, 13]. Attempts to overcome this problem led to the addition of a second polar compound such as tributylphosphate (TBP) to the organic phase [2, 3, 15, 18, 19].

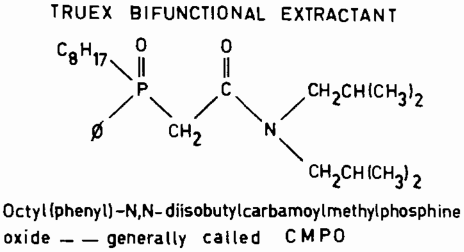

Fig. 1. The structure of CMPO.

A dramatic improvement in phase compatibility and loading capacity was brought about by the modification of the solvent properties upon TBP addition. Preliminary investigations revealed that, following TBP addition, the Am(III) extraction from nitric solutions by the CMPO–TBP mixture was also profoundly altered.

Because of the great practical importance of the extraction behavior of CMPO–TBP mixtures and in view of the application of the TRUEX process to the processing of actual nuclear wastes, further investigations have been performed. The aim of these investigations was to obtain as much information as possible on the effects of TBP addition on the Am(III) extraction chemistry by CMPO in the chlorocarbon diluents which are likely to be used in the first plant application of the TRUEX process [8].

In this paper the most important results and conclusions are reviewed with particular emphasis to the:

–extraction of Am(III) by CMPO–TBP mixtures in TCE as a function of nitric acid concentration;

–effect of extracting impurities produced by radiolytic degradation of CMPO.

Results and Discussion

Acid Dependency of D_{Am}

In Fig. 2 the acid dependency of D_{Am} (organic Am(III) concentration divided by aqueous Am(III) concentration) obtained in TCE for progressively increasing amounts of TBP added to 0.25 M CMPO is reported. Similar data obtained in decalin and in $\mathrm{CCl_4}$ have been reported previously [16–20].

The presence of TBP exerts a similar effect in all the diluents, this effect being much more pronounced in decalin than in chlorocarbon diluents. In the low acidity region, a reduction of D_{Am} values is always observed, while in the high acidity region an enhancement of distribution ratios is revealed. The acidity where the D_{Am} *versus* $\mathrm{HNO_3}$ concentration plots with or without TBP intersect is always in the region 1–2 M. In this region D_{Am} is practically insensitive to the presence of TBP and to its amount. Since about 1 M $\mathrm{HNO_3}$ is the acidity where the competition

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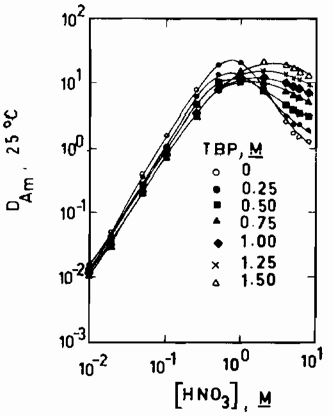

Fig. 2. Acid dependency of D_{Am} with 0.25 M CMPO in TCE in the presence of increasing TBP concentrations. T = 25 °C (from ref. 22).

of nitric acid with Am(III) for the P=O group starts to strongly affect the shape of the acid dependency curves, this is a strong indication that TBP itself interacts with nitric acid reducing its competition for the phosphoryl group of CMPO. In other words, the enhancement of D_{Am} at high acidity may be explained by the acid buffering effect caused by the large concentration of basic P=O groups introduced by the presence of TBP. It is well known, in fact, that the P=O of TBP, though less basic than that of CMPO, is still basic enough to react with nitric acid [21].

The D_{Am} behavior at low acidity can be explained in a different way. Although there is no evidence for the existence of mixed Am–TBP–CMPO complexes, we believe that TBP hydrogen bonds through water molecules and hydrogen ions to uncomplexed CMPO, or interacts through dipole-induced dipole bonds with the P=O and C=O of the CMPO molecule. This effectively lowers the basicity of the donor groups reducing their availability for Am(III) extraction.

An association phenomenon can also be utilized to further explain the D_{Am} enhancement at high acidity brought about by the presence of TBP. It is likely that the high concentration of TBP and the increased solvent polarity of the TBP–diluent mixture enhance the stability and solubility in non-aqueous media of the complex $Am(NO_3)_3(CMPO)_3(HNO_3)_m$ by solvation of HNO_3 present in the complex. In this case TBP molecules would be present in the outer coordination sphere and CMPO molecules in the inner coordination sphere of the above complex.

For the first application of the process [22], the TRUEX process solvent composition 0.25 M CMPO + 1 M TBP in TCE has been chosen, based on the data of Fig. 2.

Radiolytic Degradation of CMPO

The results of an extensive investigation on the hydrolytic and radiolytic degradation of CMPO in decalin and CCl_4 have been reported previously [20]. This study was performed in CCl_4 instead of TCE since at that time CCl_4 was the leading candidate for the TRUEX process solvent. TCE was then chosen as a diluent based on its higher boiling point. It was demonstrated in that work that CMPO degrades primarily to methyl(octyl)(phenyl)phosphine oxide and octyl(phenyl)phosphinic acid. This last compound has a detrimental effect on the stripping performance of the TRUEX process since it is a relatively strong extractant of Am(III) at low acidity. At the low nitric acid concentration used in the stripping section of the process (0.04 M), octyl(phenyl)phosphinic acid can effectively complex Am(III) in the organic phase, preventing its re-extraction into the aqueous phase.

To evaluate the effect that the addition of TBP has on the degradation of CMPO, two types of experiments were performed. In the first experiment a 0.25 M CMPO solution in CCl_4 was first exposed to an absorbed gamma dose of 97 watt hour/liter (Wh/l) (^{60}Co, dose rate = 2.5×10^5 rad/h) under vigorous stirring with 5 M nitric acid at 50 °C. The D_{Am} values of the irradiated solution were then measured at 2 M and 0.01 M HNO_3. As expected, a much higher value (almost six orders of magnitude) of D_{Am} at low acidity was obtained, due to the presence of substantial amounts of acidic degradation products produced by radiolysis. To the degraded organic solution enough pure TBP was added in order to have a TBP concentration of 0.73 M, and the D_{Am} values were measured again. The addition of TBP caused a pronounced decline of the Am(III) distribution ratios at low acidity. This indicates that TBP somewhat suppresses the influence of acidic degradation products preventing them from extracting Am(III). The mechanism by means of which this effect takes place is probably the bonding of TBP to the phosphinic acid, presumably via a hydrogen bond, which apparently increases the stability of CMPO.

In the second experiment a CCl_4 solution containing both CMPO (0.25 M) and TBP (0.75 M) was irradiated under the same conditions as the previous experiment. The D_{Am} values were then measured at the same HNO_3 concentrations as before. The D_{Am} values at low acidity obtained by degrading CMPO in the presence of excess TBP were much lower. This indicates that, in addition to the effect shown by the previous experiment, the presence of TBP is also beneficial for an additional reason. TBP, in fact, absorbs radiation degrading itself to dibutylphosphoric acid, which is easily removed by carbonate washes, thus reducing the amount of radiation available for CMPO degradation.

The overall effect of the presence of TBP is a remarkable increase in the CMPO stability toward radiolysis, as measured by Am(III) distribution ratio determinations at low acidity.

Conclusions

The addition of TBP to CMPO in the formulation of the composition of the TRUEX process solvent was a major breakthrough for the development of a solvent showing good 'solvent extraction' characteristics.

TBP was initially added to CMPO as a phase modifier in order to reduce third-phase formation (especially when a normal paraffinic hydrocarbon was used) and to increase the loading capacity of the solvent. Amazingly, a number of other effects, all beneficial, were brought about by TBP addition.

These effects and the role of TBP in the TRUEX process solvent can be summarized as follows:

– it enhances D_{Am} above 1 M HNO_3;

– it decreases D_{Am} below 1 M HNO_3;

– it reduces the sensitivity of D_{Am} to acidity above 1 M HNO_3;

– it improves phase compatibility (higher loading and less third-phase formation);

– it reduces the equilibrium aqueous concentration of CMPO;

– it reduces the radiolytic degradation of CMPO;

– it reduces the effect of acidic degradation products.

A more extended version of this investigation will be published elsewhere.

Acknowledgements

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