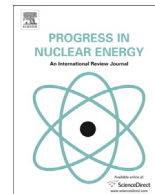




Contents lists available at ScienceDirect

## Progress in Nuclear Energy

journal homepage: [www.elsevier.com/locate/pnucene](http://www.elsevier.com/locate/pnucene)

# Radical degradation stability of ether linkage in *N,N,N',N'*-tetraoctyldiglycolamide and related organic extractants: A density functional study

Tomáš Koubský\*, Jaroslava Fojtíková, Ladislav Kalvoda

Department of Solid State Engineering, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Czech Republic

## ARTICLE INFO

## Article history:

Received 10 September 2015

Received in revised form

19 May 2016

Accepted 11 July 2016

Available online xxx

## Keywords:

Density functional theory

DMol<sup>3</sup>

Gaussian

TODGA

Diglycolamides

Solvent extraction

## ABSTRACT

*N,N,N',N'*-tetraoctyldiglycolamide (TODGA) has been recently subjected to extensive investigation as an organic extractant which can be used to separate trivalent actinides and lanthanides from spent nuclear fuel. In this paper, computer simulations based on Density Functional Theory (DFT) were performed in order to theoretically analyse molecular stability of TODGA and its two derivatives, methyl tetraoctyldiglycolamide (TWE-21) and dimethyl tetraoctyldiglycolamide (TWE-14). Gaussian 09 and DMol<sup>3</sup> computational codes were used to evaluate electronic structure- and orbital-based stability descriptors together with possible reaction pathways for a model degradation reaction. Calculated results were compared to those from prior published experimental observations with findings generally corresponding except in regards to kinetic behavior of TWE-21.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

During past several decades, much effort has been spent on the development of wet extraction and selective separation methods of actinide elements from highly active spent nuclear fuel. The latter constitute a key step in current waste reprocessing technologies (Poinssot et al., 2014). One of the most promising organic ligand families applicable for trivalent actinides and lanthanides co-extraction are diglycolamides (DGAs) represented by TODGA and its derivatives. The co-extraction procedure plays a crucial role in numerous partitioning processes for advanced fuel cycles including DIAMEX, 1cycle-SANEX, and GANEX (Magnusson et al., 2009; Wilden et al., 2011; Brown et al., 2012).

During reprocessing, agents present in the organic phase encounter rather harsh conditions and are exposed to high doses of ionising radiation and high concentrations of nitric acid. Thus, it is necessary to ensure sufficient hydrolytic and radiolytic stability for the extracting agents in use. It has already been demonstrated that the ether linkage in TODGA's diglycolamide functional group is especially susceptible to radiolytic attack (Galán et al., 2012, 2014,

2015). Aimed at enhanced stability, methylated TODGA derivatives such as TWE-21 and TWE-14 (Fig. 1) have been proposed with their chemical structures modified by the presence of methyl group(s) in close vicinity to the ether group (Iqbal et al., 2010; Wilden et al., 2014). The extraction efficiencies for TWE-21 and TWE-14 are lower than TODGA's, probably due to different conformations of the core chain. Nevertheless, TWE-21 can play an important role in the GANEX process because its extraction efficiency of An(III) and Ln(III) is still acceptable when compared to remarkably lower efficiency of fission products.

This article provides a theoretically substantiated estimations of TODGA, TWE-21, and TWE-14 resistance against selected radiolytic degradation processes. This work is based on the assumption that indirect radiolysis is dominant due to a low concentration of the ligand in solvent (Galán et al., 2012, 2015). In such cases, radiolysis of the solvent (usually TPH) takes place first and a subsequent chemical interaction with the ligand, mainly radical attack, is dominant.

Experimental chemical and radiation stability studies have already been performed on TODGA and TWE-21 (Galán et al., 2012; Galán et al., 2015) and suggest that TODGA is highly stable against hydrolytic attack in 3 M HNO<sub>3</sub>. Thus, radiation stability of TODGA and its derivatives is under examination in this paper. Radiation stability of TWE-21 has been reported to be comparable or,

\* Corresponding author.

E-mail address: [tomas.koubsky@jfifi.cvut.cz](mailto:tomas.koubsky@jfifi.cvut.cz) (T. Koubský).

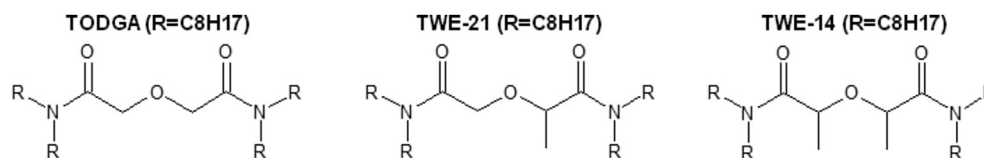


Fig. 1. Chemical structures of TODGA, TWE-21, and TWE-14.

surprisingly, even lower than that of TODGA (Galán et al., 2015). At the same time, a significant increase in radiolytic stability is observed for TWE-14 dissolved in *n*-dodecane without any contact with HNO<sub>3</sub>. However, it is not very clear what type of mechanism is responsible for such behaviour. Based on analysis of observed radiation degradation products, Galán et al. (2015) suggest that the “unprotected” C–O bond in the ether group in TWE-21 is more susceptible to rupture than the “protected” one (the C–O bond adjacent to the stabilizing methyl group is also referred to as the “protected” C–O bond, and vice versa). At a constant total dose, overall degradation of TWE-21 was found to be inversely proportional to the applied irradiation speed.

As recently suggested by Zarzana et al. (2015), the degradation reactions of DGAs induced by a charge transfer from the ligand to the radical cations on solvent molecules can also play an important role. However, simulation of such reactions requires application of more sophisticated theoretical methods, such as the Green’s function method or the Symmetry-Adapted Perturbation Theory combined with time-dependent DFT, and cannot be performed using the standard DFT approach used in this study, which is therefore restricted to radical degradation reactions only.

## 2. Methods and computational settings

The model system considered here is based on the laboratory experimental conditions used by Galán et al. (2015). The conditions were less complex than those encountered during real separation procedures. The selected organic ligand was dissolved in pure *n*-dodecane and the resulting solution irradiated by a <sup>60</sup>Co gamma source. The irradiation was performed in several steps resulting in a growing total accumulated dose. No organometallic complex formation occurred (i. e. no metal ions were added to the experimental solutions; the influence of possible traces of metallic impurities was neglected) and consequently, no influence of metallic ions was considered in the model system. The resulting chemical composition of the irradiated samples was analysed at room temperature several days after the irradiation, when steady state was achieved. It can be therefore assumed that the samples already had reached a state of thermodynamic equilibrium. Within the limits of the necessary approximations described below, the theoretical model proposed here follows all conditions of the aforementioned experiments. Furthermore, only the cases where no nitric acid was experimentally employed were considered, so the role of nitric acid was not included in the model. The role of acid in degradation mechanisms is still unclear and its use in the model would not

Table 1  
The HOMO-LUMO gap values calculated for TODGA, TWE-21, and TWE-14 by the indicated software and method.

Ligand	HOMO-LUMO gap (kJ mol <sup>-1</sup> )		
	(Gaussian, B3LYP)	(DMol <sup>3</sup> , B3LYP)	(DMol <sup>3</sup> , BLYP)
TODGA	649.01	621.44	414.76
TWE-21	648.93	654.32	446.26
TWE-14	629.24	637.74	422.34

provide reliable results. Simulation of radical degradation of the ligands is thus restricted to the analysis of only one probable mechanism selected from many other reaction pathways.

The calculations were performed with Gaussian 09 code (Frisch et al., 2009) involving the hybrid exchange-correlation functional B3LYP (Becke, 1993; Lee et al., 1988; Vosko et al., 1980; Stephens et al., 1994) and the 6-311++G(2d,d,p) basis set. For comparison, the generalized gradient functional BLYP (Becke, 1988; Lee et al., 1988) was used. Optimization of the geometry and electronic structure of the molecular systems was performed using DFT-based computational methods and followed by orbital analysis (NBO6 code; Glendening et al., 2013). Bond orders determination was calculated using the Mulliken Population Analysis (MPA; Mulliken, 1955) and the Natural Bond Theory (NBO – Wiberg bond indices), both implemented also in the NBO6 code.

The solvent effect was represented with a polarizable continuum model (PCM) cavity approximation used in conjunction with *n*-dodecane (Tomasi et al., 2005). Cavity approximation is a standard computational method for taking into account electrostatic interaction between the solvent and the optimized molecule. The solvent is represented by its dielectric constant only; molecular structure or any impurities of the solvent are neglected. This method bypasses the necessity of optimizing a high number of solvent molecules, which is unfeasible due to the high computational demands of DFT methods.

To eliminate the risk of finding an incorrect local energetic minimum, the starting geometries were taken from a statistical average of conformations pre-optimized with molecular dynamics (MD). Geometrical optimizations were performed with ensembles including TODGA, TWE21, and TWE14 molecules mixed with *n*-dodecane. The Amorphous Cell module (Flory, 1969) of the Material Studio 6.1 computational package was used to generate 20 cell configurations of the mixtures. The ratio of the selected ligand molecules to the surrounding molecules of the solvent was chosen so that it would resemble the concentration of the experimental solutions. Using methods based on MD, the canonical ensembles were subsequently equilibrated; 500 ps time evolution was used. The MS Forcite Plus module (Ermer, 1976) with the forcefield COMPASS (Sun, 1998) and the combined ABNR and Quasi-Newton algorithms were used in the MD calculations. Such MD geometrical optimization is very coarse, when compared to performance of DFT-based methods but offers the possibility for incorporating, on

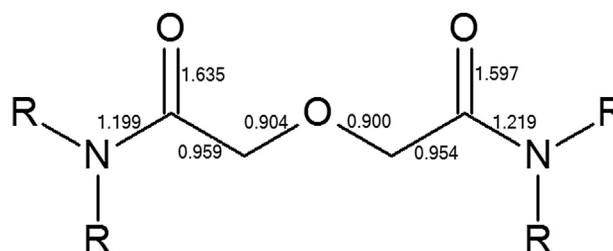


Fig. 2. Selected calculated bond orders in TODGA (Gaussian, B3LYP, NPA level of theory).

Download English Version:

<https://daneshyari.com/en/article/5478237>

Download Persian Version:

<https://daneshyari.com/article/5478237>

[Daneshyari.com](https://daneshyari.com)