Molecular modelling of tantalum in an aqueous phase

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Synopsis

The transition metals tantalum (Ta) and niobium (Nb) are of significant importance, for example in the nuclear energy sector where they are used as cladding materials, as well as in capacitors and specialized materials. For these applications a high-purity metal is needed. The separation of Ta and Nb is always a challenge since they are found together in nature and have similar chemical and physical properties, resulting in costly and laborious separation processes. A technology that has been used successfully for the separation of these metals entails solvent extraction (SX)[1]. While separation was achieved in a previous SX study using a sulphuric acid (H_2SO_4) medium with the extractants diiso-octyl phosphinic acid (PA) and di-(2-ethylhexyl) phosphoric acid (D2EHPA), due to the absence of speciation data for Ta and Nb it is not clear how the separation occurred.

One method that might be suitable for determining the speciation of a reaction is molecular modelling. Calculations based on the density-functional theory (DFT) are now used not only for light elements and small molecules, but also metal complexes, heavy metals, and especially metal separation in SX[2]. In this study the aqueous phase used during SX was investigated by studying periodic systems of Ta, as a metal and in salt form, when it is in contact with H_2O and H_2SO_4. The results were used to predict the reaction mechanism occurring during SX. Results showed that (i) in a 1:1 acid-water ratio, the deprotonation of H_2SO_4 was endothermic, (ii) in a 1:5 ratio deprotonation was exothermic forming HSO_4^-, and (iii) in a 1:10 ratio double deprotonation occurred to form SO_4^{2-} exothermically.

Keywords

tantalum, niobium, solvent extraction, reaction mechanism, molecular modelling.

Introduction

Tantalum (Ta) and niobium (Nb) are two metals found in the same group (VB) of the periodic table of elements. Owing to their similar chemical and physical properties, they are difficult to separate. Ta and Nb are usually found together in various minerals, of which the most important are columbite ((Fe, Mn, Mg)(Nb, Ta)$_2O_6$) and tantalite ((Fe, Mn)(Nb, Ta)$_2O_6$) (Agulyanski, 2004). Ta is used in a variety of applications, including capacitors in electronic circuits, rectifiers, pins for bone fixtures, surgical and dental instruments, and in chemical heat exchangers (Krebs, 2006). For many applications, pure Ta is needed; however, increasing purity entails a proportional increase in production cost. One way of ensuring an economically viable process for the production of high-purity Ta is to find a cost-effective way to separate Ta and Nb.

Solvent extraction (SX) is used for the separation and purification of various metals, including copper (Bidari, Irannejad, and Gharabaghi, 2013), nickel (Noori *et al.*, 2014), iron (Li *et al.*, 2011), platinum group metals (PGMs) (Kumar *et al.*, 2008), zirconium (Biswas and Hayat, 2002), hafnium (Lee, Banda, and Min, 2015), and Ta, and Nb (Zhu and Cheng, 2011). Ungerer *et al.* (2014) studied the separation of Ta and Nb (in the form of MF$_5$) by SX using safer and more environmentally friendly chemicals and techniques. Although partial separation was achieved in a sulphuric acid (H_2SO_4) medium with the extractants diiso-octyl phosphinic acid (PA) and di-(2-ethylhexyl) phosphoric acid (D2EHPA), the main obstacle remained the lack of data on the speciation of Ta and Nb compounds, without which it was not possible to fully explain the separation data obtained.

One method that could be used for speciation of the compounds is computational methods for SX, which entails a step-by-step analysis of the extraction process on a molecular level and determination of the molecular reactions occurring during SX from a thermodynamic perspective, which could lead to the development of a new method for the analysis of Ta and Nb separation by SX.
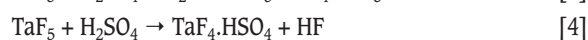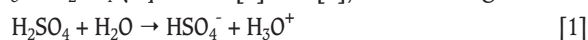
[1]Narbutt, J. and Czerwinski, M. 1992. Computational chemistry in modelling solvent extraction of metal ions. *Solvent Extraction Principles and Practice.* Rydberg, J., Cox, M., Musikas, C., and Choppin, G.R. (eds). Wiley, New York. Chapter 16.

[2]Ungerer, M.J., van der Westhuizen, D.J., Lachmann, G., and Krieg, H.M. 2014. Comparison of extractants for the separation of TaF5 and NbF5 in different acidic media. *Hydrometallurgy*, vol. 144–145. pp. 195–206.

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In this study we propose the use of molecular modelling to determine the behaviour of Ta in a sulphuric acid medium. Reactions of H_2SO_4 and water (Equations [1] and [2]) and TaF_5 in H_2SO_4 (Equations [3] and [4]) were investigated.
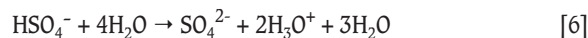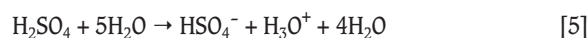
$$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+ \qquad [1]$$

$$HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+ \qquad [2]$$

$$TaF_5 + H_2SO_4 + H_2O \rightarrow TaF_5.HSO_4^- + H_3O^+ \qquad [3]$$

$$TaF_5 + H_2SO_4 \rightarrow TaF_4.HSO_4 + HF \qquad [4]$$

Computational methods

For the molecular modelling of H_2SO_4 with H_2O (Equations [1] and [2]) as well as TaF_5 with H_2SO_4 (Equations [3] and [4]), both in an aqueous phase, the DMol3 module – a density functional theory (DFT) (Hohenberg and Kohn, 1964; Levy, 1979) quantum mechanical modelling method of the Materials Studio 6.1 software from Accelrys (2012) was used. For all the calculations on the different molecules, a geometry optimization (Perdew and Wang, 1992; Delley, 1992) was first performed with the generalized gradient-corrected approximation (GGA) with Perdew-Wang (1992) correlation functional (PW91). The basis set used was DNP (double-numeric polarization functions) with basis file 4.4 and OBS dispersion correction. The core treatment parameter was set to 'All Electron' and therefore all the calculations were done for the electrons as if they are valence electrons. Under the electronic properties, smearing of 0.005 Hartree (Ha) was also chosen (Delley, 1995) and the solvation model COSMO (conductor-like screening model) (Delley, 2006) was used, with water as the solvent with a dielectric constant of 78.54. COSMO was used to account for the surrounding of implicit H_2O molecules. After the geometry optimization, various properties were calculated using single-point energy calculations with the same settings as stated previously. The calculations were done in the aqueous phase at 0 K and the energy correction term was added to give Gibbs free energy values at 298.15 K.

Results and discussion

The relative energies for Reactions [1] and [2] are presented in Figure 1, where the dotted line represents the reaction energies when using a 1:1 H_2SO_4:H_2O ratio and the solid line when using a 1:5 H_2SO_4:H_2O ratio, where five explicit water molecules were added. For each line three points are presented, the first being the energy of the starting materials, the second the energy of the intermediate products, and the third the energy of the final products. When using a 1:1 H_2SO_4:H_2O ratio (dotted line) it can be seen that when one H_2SO_4 molecule reacted consecutively with two H_2O molecules to firstly form HSO_4^- and H_3O^+, and then SO_4^{2-} and $2H_3O^+$, 33.5 kJ/mol and 153.4 kJ/mol were needed respectively, indicating an endothermic reaction for both steps.

However, according to laboratory results and values from the literature, Reaction [1] is highly exothermic and Reaction [2] moderately exothermic. Steyl (2009) used DFT modelling (DMol3 v.4.2) to show that when H_2SO_4 reacted with H_2O, five H_2O molecules were needed to form an outer sphere around the H_2SO_4 molecule to react to form HSO_4^-. Therefore a balanced reaction equation was modelled where five H_2O molecules reacted with H_2SO_4 as follows:

$$H_2SO_4 + 5H_2O \rightarrow HSO_4^- + H_3O^+ + 4H_2O \qquad [5]$$

$$HSO_4^- + 4H_2O \rightarrow SO_4^{2-} + 2H_3O^+ + 3H_2O \qquad [6]$$

According to Figure 1 (solid line) the reaction becomes exothermic, as expected, when sufficient water molecules are available. To determine the effect of adding further water molecules it was decided to model the H_2SO_4-H_2O system with 10 explicit waters surrounding the acid (Figure 1 – dashed line). After the geometry optimization of the 1:10 system, it was seen that double deprotonation of H_2SO_4 took place, without the formation of HSO_4^- as an intermediate step. The energy decrease to –816 kJ/mol indicates an exothermic reaction with a stabilized ion forming as the final product. As when using five H_2O molecules, the surrounding H_2O molecules stabilized the ion by hydrogen bonding. Ding and Laasonen (2004), using DFT modelling with PW91(DNP) as well as BLYP calculations, showed that when less than five H_2O molecules are present with H_2SO_4 the first deprotonation occurs exothermically, and when eight to ten H_2O molecules surround H_2SO_4, the second deprotonation also occurs, resulting in the formation of SO_4^{2-} with the other surrounding H_2O molecules forming hydrogen bonds and stabilizing the formed ions. Hammerich, Buch, and Mohamed (2008) used *ab initio* modelling methods and also showed that when ten H_2O molecules are present double deprotonation occurs, but also observed proton hopping between the different oxygen sites of HSO_4^- and the surrounding H_2O molecules. Although it is generally assumed that H_2SO_4:H_2O is a 1:1 reaction, it was shown that, energetically, from five to ten explicit H_2O molecules are needed for the reaction to occur. According to these results, the 1:10 reaction of H_2SO_4 in H_2O showed the best correlation to the real system.

In the second part of the investigation, the reaction of TaF_5 and H_2SO_4 in the presence of 1, 5 and 10 H_2O molecules was modelled at TaF_5:H_2SO_4:H_2O ratios of 1:1:1, 1:1:5, and 1:1:10. Since TaF_5 has a trigonal bipyramidal structure, the H_2SO_4 molecule will most likely approach from an equatorial position (where more space and best orbital overlap is available) to form $TaF_5.HSO_4^-$ (octahedral structure) before rearranging to $TaF_4.HSO_4$, where the HSO_4^- group can be either axial or equatorial (Figure 2).
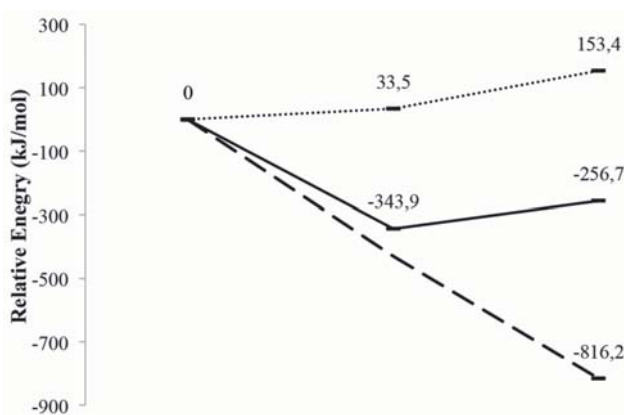

Figure 1—Relative reaction energy (kJ/mol) for H_2SO_4 and H_2O (dotted line is H_2SO_4:H_2O = 1:1; solid line is H_2SO_4:H_2O = 1:5; dashed line is H_2SO_4:H_2O = 1:10)

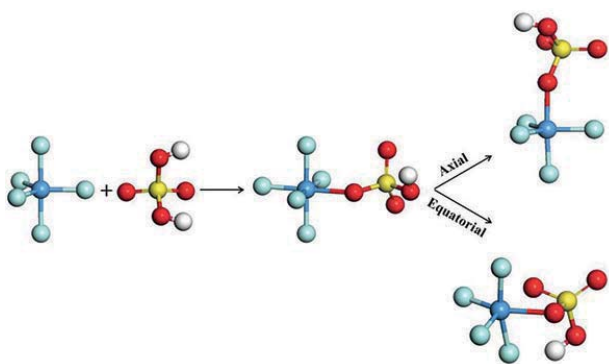# Molecular modelling of tantalum in an aqueous phase

Figure 2—Possible reaction pathway of TaF$_5$ and H$_2$SO$_4$

As with Equations [1] and [2], it was expected that the relative reaction energies would be lower when adding explicit water molecules to Equations [3] and [4]. To confirm this, the same calculations done for Equations [1] and [2] were performed for Equations [3] and [4]. The relative energies of the reactions of TaF$_5$ with H$_2$SO$_4$ and H$_2$O are shown in Figure 3. The dotted line shows the energies for a TaF$_5$:H$_2$SO$_4$:H$_2$O ratio of 1:1:1, the solid line the energies for a TaF$_5$:H$_2$SO$_4$:H$_2$O ratio of 1:1:5, and the dashed lines the energies when the TaF$_5$:H$_2$SO$_4$:H$_2$O ratio is 1:1:10. Again, the first data point is the energy of the reagents, the second the energy of the intermediates, and the third the energy of the products.

As shown in Figure 2, the position of the HSO$_4^-$ group can be either axial or equatorial. In Figure 3, for the 1:1:1 reaction (dotted line) 105 kJ/mol is needed for the HSO$_4^-$ group to bond to TaF$_5$, before HF is evolved and TaF$_4$.HSO$_4$ is formed at 97.2 kJ/mol and 54.4 kJ/mol for the axial and equatorial positions respectively, indicating an endothermic reaction. However when using more H$_2$O (five molecules – solid line) –304.8 kJ/mol is needed to form TaF$_5$.HSO$_4^-$, indicating that a stable ion forms. The formation of TaF$_4$.HSO$_4$ in the axial position requires –158.6 kJ/mol, and in the equatorial position -203.5 kJ/mol, indicating an exothermic reaction. The same trend was observed as for the 1:1:1 reaction, where the molecule with the HSO$_4^-$ group in the equatorial position was at a lower energy than when the group is axial. This is due to the orbital overlap that occurs between the HSO$_4^-$ group and TaF$_5$ when the reaction takes place. Steyl (2009) obtained similar results.

The 1:1:10 reaction of TaF$_5$:H$_2$SO$_4$:H$_2$O was also modelled. Again, the HSO$_4^-$ ion bonded axially and equatorially, and as with the 1 H$_2$SO$_4$:10 H$_2$O system, double deprotonation occurred. The intermediate molecule TaF$_4$.HSO$_4$ did not form, but the TaF$_4$SO$_4^-$ molecule formed and was stabilized by the surrounding H$_3$O$^+$ ions and H$_2$O molecules. This would imply that the 1:1:10 reaction scheme had the lowest energy and would therefore be energetically the most likely.

Furthermore, it was seen from the modelling results that when the HSO$_4^-$ group was in the equatorial position it formed a bidentate bond to Ta, lowering the overall energy of the molecule and changing the oxidation state of Ta from 5+ to 4+ in both the 1:5 and the 1:10 system.

Conclusion

The reactions of H$_2$SO$_4$ with H$_2$O and TaF$_5$ with H$_2$SO$_4$ and H$_2$O were investigated. When modelling a 1:1 reaction of acid and water an endothermic reaction was observed. The modelling software COSMO was used to account for the surrounding implicit H$_2$O molecules. By adding five explicit H$_2$O molecules to the reaction, an exothermic reaction was observed for the reactions of H$_2$SO$_4$ with H$_2$O. This indicated that COSMO adds a correction term for the long-range interactions that could occur if these reactions occurred in water as a medium, but does not show or calculate the explicit reactions and hydrogen bonding that occur with H$_2$O in the short range. This hydrogen bonding stabilizes the molecules, resulting in lower energy values. With the addition of 10 explicit H$_2$O molecules a double deprotonation was observed with the formation of SO$_4^{2-}$ stabilized by the surrounding hydrogen bonds. The same tendencies were observed for the reactions of TaF$_5$ with H$_2$SO$_4$ and H$_2$O, where the explicit H$_2$O molecules lowered the overall reaction energies, showing an exothermic reaction. The resulting ions were stabilized with the surrounding H$_3$O$^+$ ions and H$_2$O molecules.

Further investigations are needed to determine the side reactions and other geometries that may occur during these reactions, as well as the possible influence if a change in oxidation state occurs.

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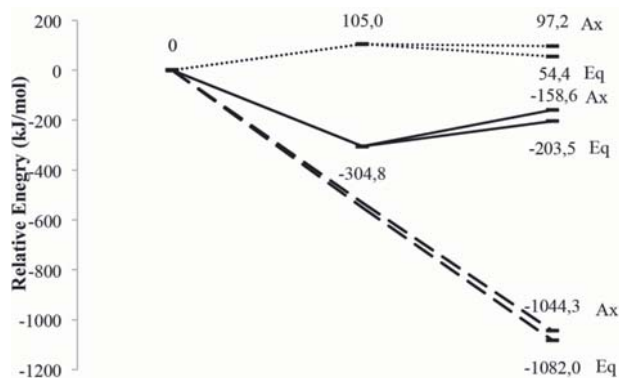
Figure 3—Relative reaction energy (kJ/mol) for TaF$_5$, H$_2$SO$_4$, and H$_2$O (dotted line is 1:1:1 reaction, solid line is 1:1:5 reaction, dashed line is H$_2$SO$_4$:H$_2$O = 1:1:10)

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