



# The effect of SO<sub>3</sub>-Ph-BTBP on stainless steel corrosion in nitric acid

Richard J. Wilbraham,  
Colin Boxall

**Abstract.** SO<sub>3</sub>-Ph-BTBP is a hydrophilic tetra-N-dentate ligand proposed for An(III)/Ln(III) separation by solvent extraction, and a candidate for use in future advanced reprocessing schemes such as GANEX and SANEX. We present the first study of the effect of SO<sub>3</sub>-Ph-BTBP on the corrosion behavior of stainless steels. Specifically, studies have been performed using steels and conditions equivalent to those found in relevant nuclear reprocessing flow sheets. SO<sub>3</sub>-Ph-BTBP has been shown to have little effect on either steel passivation or reductive dissolution. However, if driven cathodically into a region of hydrogen evolution at the electrode surface or conversely anodically into a region of transpassive dissolution, observed currents are reduced in the presence of SO<sub>3</sub>-Ph-BTBP, suggesting corrosion inhibition of the steel potentially through weak absorption of a SO<sub>3</sub>-Ph-BTBP layer at the metal-solution interface. The lack of any observed corrosion acceleration via complexation of Fe<sup>3+</sup> is surprising and has been suggested to be due to the slow extraction kinetics of SO<sub>3</sub>-Ph-BTBP as a result of a requirement for a *trans*- to *cis*-conformational change before binding.

**Key words:** corrosion • stainless steel • electrochemistry • 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridine

## Introduction

One of the aqueous flow sheets under review by the Safety of Actinide Separation Processes (SACSESS) consortium is the European Grouped Actinide Extraction (EURO-GANEX) process [1, 2]. From head end to product finishing this flow sheet is broadly similar to the Plutonium Uranium Redox EXtraction (PUREX/advanced-PUREX) flow sheet [3–7], which is currently employed at the Thermal Oxide Reprocessing Plant (THORP) in the UK for the reprocessing of spent nuclear fuel. However, there are two key differences between the EURO-GANEX and PUREX process:

- 1) Di(2-ethyl hexyl) isobutyramide (DEHiBA) and odourless kerosene (OK) are deployed in the primary separation cycle and *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) and *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide (DMDOHEMA) in the 2nd cycle trans-uranium element extraction in the EURO-GANEX process to produce an impure, proliferation resistant, plutonium stream.
- 2) Acetohydroxamic acid (AHA), while common to both EURO-GANEX and advanced-PUREX processes, is supplemented by the hydrophilic, aqueous phase, An(III) selective stripping ligand 2,6-bis(5,6-di(sulfophenyl)-1,2,4-triazin-3-yl)-pyridine (SO<sub>3</sub>-Ph-BTP), in the 2nd cycle trans-uranium element back extraction of EURO-

R. J. Wilbraham, C. Boxall✉  
The LRF Centre for Nuclear Engineering,  
Engineering Department,  
Lancaster University,  
Bailrigg, Lancashire, LA1 4YR, United Kingdom,  
Tel.: +44(0)1524 593109,  
E-mail: c.boxall@lancaster.ac.uk

Received: 19 June 2015  
Accepted: 21 August 2015

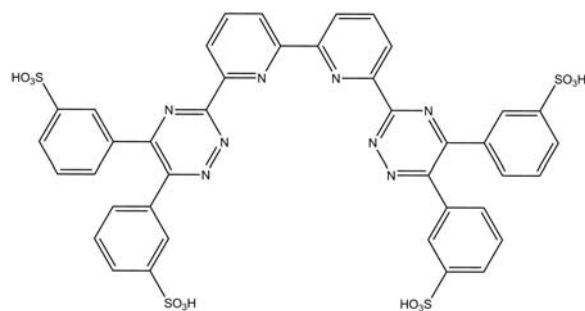


Fig. 1. General molecular structure of  $\text{SO}_3\text{-Ph-BTBP}$ .

-GANEX, in order to improve minor An separation through masking [8].

Furthermore, due to the degradation of BTP ligands under radiolysis [9], radiologically stable sulfonated bistriazinylbipyridine ( $\text{SO}_3\text{-Ph-BTBP}$ ) [10] and 1,10-phenanthroline ligands ( $\text{SO}_3\text{-Ph-BTPhen}$ ) [9, 11, 12] are currently under investigation as possible replacements for  $\text{SO}_3\text{-Ph-BTP}$  in the EURO-GANEX process.

Importantly, little is known about the influence of the above ligands on the corrosion behavior of the steels that typically make up tanks, pipework and centrifugal contactors in each extraction step/unit operation. Considering the ability of said ligands to complex with  $\text{An(III)}$  and  $\text{Ln(III)}$  species [13, 14], the potential stripping via complexation of either  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$  from the process steel and subsequent destabilization of the protective oxide film is a concern.

Herein we present preliminary electrochemical corrosion studies that have been performed on the nuclear process steels, 304L and 316L stainless (SS), in the presence of one of the radiolytically stable ligands under study for future GANEX processes,  $\text{SO}_3\text{-Ph-BTBP}$ .

Originally used in its hydrophobic form,  $\text{CyMe}_4\text{-BTBP}$ , in the SANEX process (an additional  $\text{Ln(III)}$  extraction step of PUREX raffinates) [9, 11], fundamental studies by Trumm *et al.* [15] suggested that BTBP (and BTP) retains the selectivity in the aqueous phase, resulting in the synthesis through sulfonation [16] of  $\text{Ph-BTBP}$  by Geist *et al.* [8, 10, 13], Fig. 1. Relatively few studies have been published on the complexation properties of  $\text{SO}_3\text{-Ph-BTBP}$  [8, 10, 13]. However, from what data is available on  $\text{Am(III)}$  and  $\text{Eu(III)}$  complexation in a TODGA system,  $\text{SO}_3\text{-Ph-BTBP}$  appears to have a similar selectivity to  $\text{SO}_3\text{-Ph-BTP}$ . Thus, as well as providing information on the corrosion behavior of  $\text{SO}_3\text{-Ph-BTBP}$ , the data presented here also provided much needed further information on the complexation behavior of this new hydrophilic separation ligand with the primary product of steel dissolution,  $\text{Fe}^{3+}$ .

## Experimental section

### Materials

$\text{SO}_3\text{-Ph-BTBP}$  was synthesized by the University of Reading (UK). All other chemicals were of AnalaR grade or better and supplied by Sigma-Aldrich (Gill-

ingham, Dorset, UK). All  $\text{H}_2\text{O}$  used was ultrapure from a Direct-Q 3 UV Millipore water purification system (Millipore, Watford, UK) to a resistivity of  $18.2 \text{ M}\Omega\cdot\text{cm}$ .

### Linear sweep voltammetry (LSV) studies of SS304L and SS316L in the presence of $\text{SO}_3\text{-Ph-BTBP}$

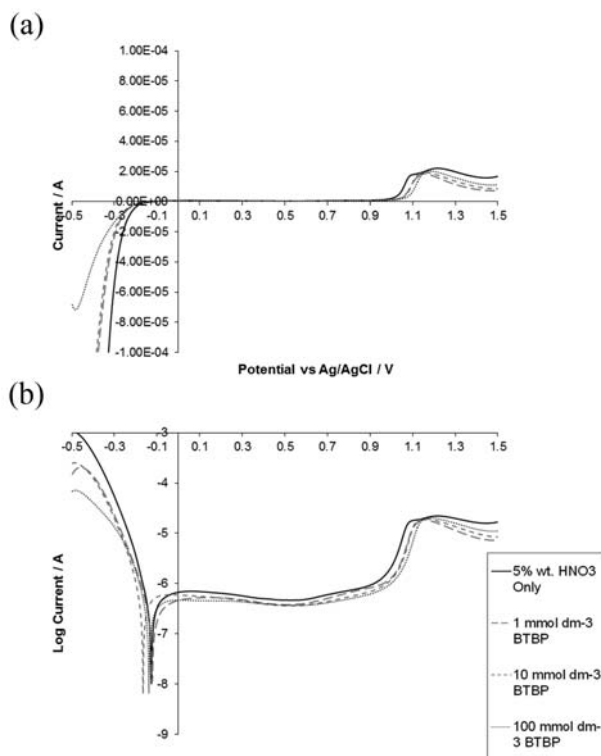
LSV measurements were performed using a PGSTAT120N potentiostat (Metrohm Autolab B.V., Utrecht, Netherlands). Working electrodes were constructed using 1 mm diameter SS316L and SS304L wire (Advent Research Materials, Oxford, UK) in glass Pasteur pipettes, backfilled with epoxy resin and polished using decreasing SiC paper grades and 6, 3 and  $1 \mu\text{m}$  diamond polishing pastes. To complete the three electrode cell, a  $\text{Ag/AgCl}$  reference electrode and coiled platinum wire counter electrode were inserted via a simple PTFE manifold. Due to the limited quantities of  $\text{SO}_3\text{-Ph-BTBP}$  available, experiments were conducted in a small volume ( $200 \mu\text{l}$ ) electrochemical cell in order to achieve ligand concentrations up to  $100 \text{ mmol}\cdot\text{dm}^{-3}$ . Current measurements were then recorded from 0.5 to 1.5 V at a scan rate of  $10 \text{ mV}\cdot\text{s}^{-1}$ . All experiments are performed in  $1.13 \text{ mol}\cdot\text{dm}^{-3}$  (5 wt%)  $\text{HNO}_3$ . This concentration is slightly higher than that employed in the 2nd cycle TRU back-extraction in EURO-GANEX ( $0.8 \text{ mol}\cdot\text{dm}^{-3}$ ) [2], but representative of that found in the AHA extraction step in an advanced-PUREX process [7].

## Results and discussion

Linear sweep voltammograms and associated polarization curves for SS304L electrodes in  $\text{SO}_3\text{-Ph-BTBP}$  concentrations from 0.1 to  $100 \text{ mmol}\cdot\text{dm}^{-3}$  are shown in Fig. 2.

From the LSV and polarization curve of Fig. 2a and 2b, it can be seen that there is very little difference in the current across the steel passive range ( $\sim -0.1$  to 1 V) at all  $\text{SO}_3\text{-Ph-BTBP}$  concentrations tested, suggesting  $\text{SO}_3\text{-Ph-BTBP}$  has little effect on the  $\text{Cr}_2\text{O}_3/\text{Fe}_3\text{O}_4$  protective passive oxide film. This is further supported by the lack of movement of the corrosion potential,  $E_{\text{corr}}$ , in the polarization curve of Fig. 2b, suggesting no change to the region of steel passivity compared to  $1.13 \text{ mol}\cdot\text{dm}^{-3}$   $\text{HNO}_3$  only.

In the region of active reductive dissolution,  $< -0.1$  V, the current decreases as  $\text{SO}_3\text{-Ph-BTBP}$  increases, suggesting that hydrogen evolution at the electrode surface is inhibited by the presence of  $\text{SO}_3\text{-Ph-BTBP}$ . Similarly in the region of transpassivity,  $> 1$  V, where the  $\text{Cr(III)}$  passive film is oxidized to soluble  $\text{Cr(VI)}$  allowing free dissolution of iron as  $\text{Fe}^{3+}$  [17], currents are slightly lower in the presence of  $\text{SO}_3\text{-Ph-BTBP}$  than in  $1.13 \text{ mol}\cdot\text{dm}^{-3}$   $\text{HNO}_3$  only. This would suggest that  $\text{SO}_3\text{-Ph-BTBP}$  has a small corrosion inhibition effect under such oxidizing conditions. Both these effects may be explained by the formation of an adsorbed layer of  $\text{SO}_3\text{-Ph-BTBP}$  at the metal-solution interface that forms a barrier

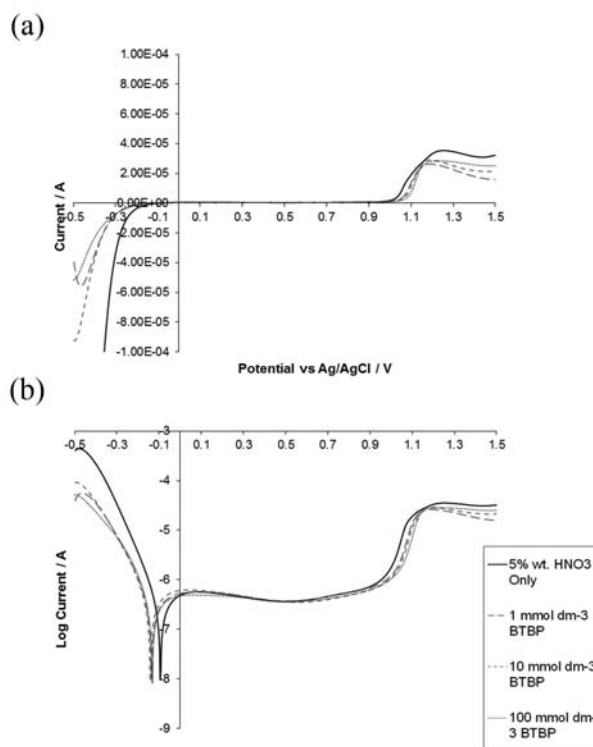


**Fig. 2.** Linear sweep voltammogram (a) and polarization curve (b) for SS304L in  $1.13 \text{ mol}\cdot\text{dm}^{-3} \text{ HNO}_3$  and  $\text{SO}_3\text{-Ph-BTBP}$  concentrations from  $0.1$  to  $100 \text{ mmol}\cdot\text{dm}^{-3}$ .

against  $\text{HNO}_2$ , the active corrosive species in this environment [18, 19], inhibiting both Fe dissolution under conditions of transpassive dissolution and reducing hydrogen evolution under conditions of reductive dissolution by hydrophobically restricting electrolyte access to the electrode surface. Indeed, such corrosion inhibition of mild carbon steels through weak surface adsorption of pyridine derivatives in stagnant solution condition acidic environments (similar to those used here) has already been previously reported [20–22]. However, under the hydrodynamic flow conditions encountered in reprocessing environments, the shear stress is likely to desorb  $\text{SO}_3\text{-Ph-BTBP}$  molecules from the steel surface and therefore reduce this corrosion inhibition effect [23].

Linear sweep voltammograms and associated polarization curves for SS316L electrodes in  $\text{SO}_3\text{-Ph-BTBP}$  concentrations from  $0.1$  to  $100 \text{ mmol}\cdot\text{dm}^{-3}$  are shown in Fig. 3.

From the LSV and polarization curve of Fig. 3a and 3b, it can be seen that again there is very little difference in the current across the steel passive range at all  $\text{SO}_3\text{-Ph-BTBP}$  concentrations tested. As shown in Fig. 2 for SS304L electrodes (and discussed above), in the region of active dissolution and transpassive dissolution currents are significantly lower than those recorded in the presence of  $1.13 \text{ mol}\cdot\text{dm}^{-3} \text{ HNO}_3$  only. Again this suggests the formation of an adsorbed layer of  $\text{SO}_3\text{-Ph-BTBP}$  at the metal-solution interface, providing a barrier that restricts electrolyte access to the electrode surface. However, while measured currents for SS316L in the presence/absence of  $\text{SO}_3\text{-Ph-BTBP}$  are almost



**Fig. 3.** Linear sweep voltammogram (a) and polarization curve (b) for SS316L in  $1.13 \text{ mol}\cdot\text{dm}^{-3} \text{ HNO}_3$  and  $\text{SO}_3\text{-Ph-BTBP}$  concentrations from  $0.1$  to  $100 \text{ mmol}\cdot\text{dm}^{-3}$ .

the same in the region of hydrogen evolution as those recorded for SS304L electrodes, Fig. 3b and Fig. 2b respectively; in the region of transpassive dissolution currents recorded on SS316L electrodes are almost double those of SS304L electrodes. Such an observation may be explained by differences in silica content between SS304L and SS316L (1.000% vs. 0.480% by mass [24, 25]). Low Si content stainless steels have been shown to have increased susceptibility to transpassive intergranular corrosion in nitric acid environments [18, 26].

The lack of any corrosion enhancement in the presence of  $\text{SO}_3\text{-Ph-BTBP}$  for both SS304L and SS316L is surprising considering the ligands known affinity for actinide/lanthanide 3+ oxidation state species [8, 10, 13] and the previously reported ability of similar BTP derivatives to complex strongly with Fe(II) species [27]. This may in part be due to the requirement for a conformational change in  $\text{SO}_3\text{-Ph-BTBP}$  from its preferred *trans*-conformation to the less favoured *cis*-conformation prior to metal binding [9, 11, 12], Fig. 4.

Such a requirement for a conformational change has been proposed, at least in part, to be responsible for slow kinetics of extraction of both An(III) and Ln(III) species by hydrophobic  $\text{CyMe}_4$  based versions of BTBP compared to  $\text{CyMe}_4$  based equivalents of BTP and BTPPhen [9, 11, 12]. Thus, we would expect such extraction kinetics to also be slow for  $\text{Fe}^{3+}$  extraction, resulting in the lack of an observed increase in the rate of reductive or transpassive dissolution for both SS304L and SS316L (Figs. 2 and 3). As such further studies are ongoing in our laboratories to determine the effect the kinetically

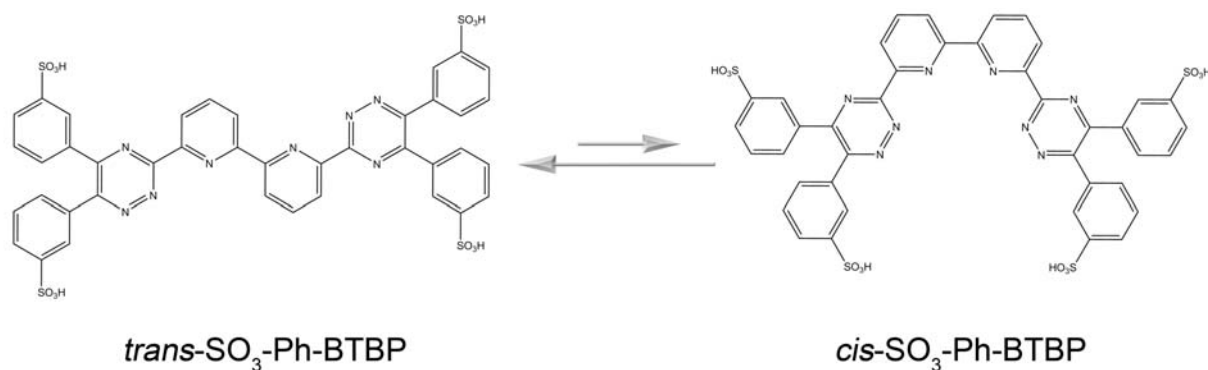


Fig. 4. *Cis*- and *trans*-conformations of  $\text{SO}_3\text{-Ph-BTBP}$ .

faster hydrophilic sulfonated derivatives of BTPen and BTP have on nuclear process steel corrosion.

### Conclusion

The effect of  $\text{SO}_3\text{-Ph-BTBP}$ , a hydrophilic tetra-N-dentate ligand proposed for  $\text{An(III)/Ln(III)}$  separation by solvent extraction, on the electrochemical corrosion behavior of typically encountered nuclear process steels has been explored.

SS304L steels show no change in either their range of passivation or corrosion potential ( $E_{\text{corr}}$ ) with  $\text{SO}_3\text{-Ph-BTBP}$  concentrations up to  $100 \text{ mmol}\cdot\text{dm}^{-3}$ . When electrochemically driven cathodically into a region of active dissolution, hydrogen evolution is found to reduce in the presence of  $\text{SO}_3\text{-Ph-BTBP}$ . Conversely, if SS304L is driven anodically into the region of transpassive dissolution  $\text{SO}_3\text{-Ph-BTBP}$  has been shown to reduce the rate of transpassive dissolution. This corrosion inhibition effect has been suggested to be due to the formation of a weakly adsorbed layer of  $\text{SO}_3\text{-Ph-BTBP}$  at the metal-solution interface.

SS316L electrodes show identical corrosion behavior to SS304L electrodes in the presence of  $\text{SO}_3\text{-Ph-BTBP}$ , albeit with increased currents in the region of transpassive dissolution due to the difference in Si content between the two steels. The lack of any obvious corrosion acceleration due to  $\text{Fe}^{3+}$  complexation may be attributed to the complexation kinetics of  $\text{SO}_3\text{-Ph-BTBP}$  as a result of a required *trans*- or *cis*-conformational change. As such further studies are ongoing in our laboratories to determine the effect the kinetically faster hydrophilic versions of BTPen and BTP have on nuclear process steel corrosion.

**Acknowledgment.** RJW and CB are supported by The Lloyd's Register Foundation (LRF). The Lloyd's Register Foundation helps to protect life and property by supporting engineering-related education, public engagement and the application of research. Many thanks to Professor Laurence Harwood, University of Reading, for providing  $\text{SO}_3\text{-Ph-BTBP}$  for this study.

### References

1. Bell, K., Carpentier, C., Carrott, M. J., Geist, A., Gregson, C., Hères, X., Magnusson, D., Malmbeck, R., McLachlan, F., Modolo, G., Mullich, U., Sypula, M., Taylor, R. J., & Wilden, A. (2012). Progress towards the development of a new GANEX process. *Procedia Chem.*, 7, 392–397.
2. Carrott, M. J., Bell, K., Brown, J., Geist, A., Gregson, C., Hères, X., Maher, C., Malmbeck, R., Mason, C., Modolo, G., Mullich, U., Sarsfield, M., Wilden, A., & Taylor, R. J. (2014). Development of a new flow-sheet for co-separating the transuranic actinides: The “EURO-GANEX” process. *Solvent Extr. Ion Exch.*, 32(5), 447–467.
3. McKibben, J. M. (1984). Chemistry of the PUREX process. *Radiochim. Acta*, 36, 3–15.
4. Tkac, P., Precek, M., & Paulenova, A. (2009). Redox reactions of  $\text{Pu(IV)}$  and  $\text{Pu(III)}$  in the presence of acetohydroxamic acid in  $\text{HNO}_3$  solutions. *Inorg. Chem.*, 48, 11935–11944.
5. Taylor, R. J., May, I., Wallwork, A. L., Denniss, I. S., Hill, N. J., Galkin, B. Ya., Zilberman, B. Y., & Fedorov, Yu. S. (1998). The applications of formo- and aceto-hydroxamic acids in nuclear fuel reprocessing. *J. Alloys Compd.*, 271/273, 534–537.
6. Carrott, M. J., Fox, O. D., Le Gurun, G., Jones, C. J., Mason, C., Taylor, R. J., Andrieux, F. P. L., & Boxall, C. (2008). Oxidation-reduction reactions of simple hydroxamic acids and plutonium(IV) ions in nitric acid. *Radiochim. Acta*, 96, 333–343.
7. Bathke, C. G., Ebbinghaus, B. B., Collins, B. A., Sleaford, B. W., Hase, K. R., Robel, M., Wallace, R. K., Bradley, K. S., Ireland, J. R., Jarvinen, G. D., Johnson, M. W., Prichard, A. W., & Smith, B. W. (2012). The attractiveness of materials in advanced nuclear fuel cycles for various proliferation and theft scenarios. *Nucl. Technol.*, 179(1), 5–30.
8. Panak, P. J., & Geist, A. (2013). Complexation and extraction of trivalent actinides and lanthanides by triazinylpyridine N-donor ligands. *Chem. Rev.*, 113, 1199–1236.
9. Benay, G., Schurhammer, R., & Wipff, G. (2011). Basicity, complexation ability and interfacial behavior of BTBPs: a simulation study. *Phys. Chem. Chem. Phys.*, 13, 2922–2934.
10. Geist, A., Mullich, U., Modolo, G., & Wilden, A. (2012). Selective aqueous complexation of actinides with hydrophilic BTP and BTBP: Towards improved i-SANEX processes. In 11th Information Exchange Meeting Actinide and Fission Product Partitioning and Transmutation (pp. 1–9). Organisation for

- Economic Co-operation and Development – Nuclear Energy Agency: San Francisco, USA.
11. Lewis, F. W., Harwood, L. M., Hudson, M. J., Drew, M. G. B., Wilden, A., Sypula, M., Modolo, G., Vu, T., Simonin, J., Vidick, G., Bouslimani, N., & Desreux, J. F. (2012). From BTBPs to BTPPhs: The effect of ligand pre-organisation on the extraction properties of quadridentate bis-triazine ligands. *Procedia Chem.*, 7, 231–238.
  12. Lewis, F. W., Harwood, L. M., Hudson, M. J., Drew, M. G. B., Hubscher-Bruder, V., Videva, V., Arnaud-Neu, F., Stamberg, K., & Vyas, S. (2013). BTBPs versus BTPPhs: Some reasons for their differences in properties concerning the partitioning of minor actinides and the advantages of BTPPhs. *Inorg. Chem.*, 52, 4993–5005.
  13. Geist, A., Mullich, U., Magnusson, D., Kaden, P., Modolo, G., Wilden, A., & Zevaco, T. (2012). Actinide(III)/lanthanide(III) separation via selective aqueous complexation of actinides(III) using a hydrophilic 2,6-bis(1,2,4-triazin-3-yl)-pyridine in nitric acid. *Solvent Extr. Ion Exch.*, 30, 433–444.
  14. Andrieux, F. P. L., Boxall, C., & Taylor, R. J. (2008). The hydrolysis of hydroxamic acid complexants in the presence of non-oxidising metal ions 2: Neptunium (IV) ions. *J. Solution Chem.*, 37, 215–232.
  15. Trumm, S., Lieser, G., Foreman, M. R. S. J., Panak, P. J., Geist, A., & Fanghanel, T. (2010). A TRLFS study on the complexation of Cm(III) and Eu(III) with 4-t-butyl-6,6'-bis-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2'-bipyridine in a water/2-propanol mixture. *Dalton Trans.*, 39, 923–929.
  16. Traister, G. L., & Schilt, A. A. (1976). Water-soluble sulfonated chromogenic reagents of the ferroin type and determination of iron and copper in water, blood serum, and beer with the tetraammonium salt of 2,4-bis(5,6-diphenyl-1,2,4-triazin-3-yl)pyridinetetra-sulfonic acid. *Anal. Chem.*, 48, 1216–1220.
  17. Padhy, N., Paul, R., Mudali, U. K., & Raj, B. (2011). Morphological and compositional analysis of passive film on austenitic stainless steel in nitric acid medium. *Appl. Surf. Sci.*, 257, 5088–5097.
  18. Fauvet, P., Balbaud, F., Robin, R., Tran, Q. T., Mugnier, A., & Espinoux, D. (2008). Corrosion mechanisms of austenitic stainless steels in nitric media used in reprocessing plants. *J. Nucl. Mater.*, 375, 52–64.
  19. Sicsic, D., Balbaud-Celerier, F., & Tribollet, B. (2014). Mechanism of nitric acid reduction and kinetic modelling. *Eur. J. Inorg. Chem.*, 2014(36), 6174–6184.
  20. Abd El-Maksoud, S. A., & Fouda, A. S. (2005). Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium. *Mater. Chem. Phys.*, 93, 84–90.
  21. Ergun, U., Yuzer, D., & Emregul, K. C. (2008). The inhibitory effect of bis-2,6-(3,5-dimethylpyrazolyl) pyridine on the corrosion behaviour of mild steel in HCl solution. *Mater. Chem. Phys.*, 109, 492–499.
  22. Tebbji, K., Oudda, H., Hammouti, B., Benkaddour, M., El Kodadi, M., & Ramdani, A. (2005). Inhibition effect of two organic compounds pyridine-pyrazole type in acidic corrosion of steel. *Colloids Surf. A*, 259, 143–149.
  23. Kosari, A., Moayed, M. H., Davoodi, A., Parvizi, R., Momeni, M., Eshghi, H., & Moradi, H. (2014). Electrochemical and quantum chemical assessment of two organic compounds from pyridine derivatives as corrosion inhibitors for mild steel in HCl solution under stagnant condition and hydrodynamic flow. *Corros. Sci.*, 78, 138–150.
  24. Hayward, T. M., Svishchev, I. M., & Makhija, R. C. (2003). Stainless steel flow reactor for supercritical water oxidation: corrosion tests. *J. Supercrit. Fluids*, 27(3), 275–281.
  25. Caire, J. P., Laurent, F., Cullie, S., Dalard, F., Fulconis, J. M., & Delagrangé, H. (2003). AISI 304 L stainless steel decontamination by a corrosion process using cerium IV regenerated by ozone – Part I: Study of the accelerated corrosion process. *J. Appl. Electrochem.*, 33, 703–708.
  26. Armijo, J. S. (1968). Intergranular corrosion of nonsensitized austenitic stainless steels. *Corrosion*, 24, 24–30.
  27. Byrne, J. P., Kitchen, J. A., & Gunnlaugsson, T. (2014). The BTP [2,6-bis(1,2,3-triazol-4-yl)pyridine] binding motif: a new versatile terdentate ligand for supramolecular and coordination chemistry. *Chem. Soc. Rev.*, 43, 5302–5325.