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Complete Initial Evaluation of Novel Complexants for Tc Holdback for Simplified Single Cycle Separations

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SUMMARY

Management of technetium at the back end of nuclear fuel cycle is complicated by its unique physico-chemical characteristics, but must be addressed due to the environmental, storage and reprocessing challenges presented by this fission product. In a single-cycle scenario, the recovery and purification of uranium is particularly challenging due to the tendency of a pertechnetate anion to follow the uranyl cation. This report summarizes initial studies of two options for controlling technetium's chemistry in solvent extraction. Molecular recognition of pertechnetate by aqueous complexants based on guanidinium moieties was compared to redox manipulation of technetium using dihydrazide reagents. Solvent extraction, potentiometric and nuclear magnetic resonance spectroscopy studies were performed. The influence of guanidinium reagents on the liquid-liquid partitioning of technetium is less pronounced, relative to dihydrazides. Strong impact exerted by dihydrazides originates from the technetium-catalyzed decomposition of such compounds which reduces technetium to a tetravalent, non-extractable state. Although this route of technetium management is very effective the destruction of dihydrazides is undesirable. Guanidinium complexants show a more tempered influence on technetium. The effect on the liquid-liquid partitioning of pertechnetate is evident and likely guided by anion recognition due to ion-pair and hydrogen bond formation. Guanidiniums are stable in presence of technetium as evidenced by nuclear magnetic resonance studies. The steady state chemistry of guanidiniums identifies this class of aqueous complexants as solid candidates for structure-function pertechnetate recognition studies.

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ACRONYMS

Adh	Adipic acid dihydrazide
AHA	Acetohydroxamic acid
Ch	Carbohydrazide
Dag	Diaminoguanidine
DEH*i*BA	*N*,*N*-di(2-ethylhexyl)*iso*butyramide
DNO_3	Deuterated nitric acid
DF	Decontamination Factor
DU	Depleted Uranium
Eddg	1,1′-(ethane-1,2-diyl)diguanidine
FEP	Fluoroethylene polymer
GANEX	Group Actinide Extraction process
Gn	Guanidinium nitrate
HAN	Hydroxylamine Nitrate
HNO_3	Nitric acid
$HTcO_4$	Pertechnetic acid
HZ	Hydrazine
INL	Idaho National Laboratory
LWR	Light Water Reactor
MRWFD	Materials Recovery and Waste Forms Development
NMR	Nuclear Magnetic Resonance
ORNL	Oak Ridge National Laboratory
Pu	Plutonium
PUREX	Plutonium Uranium Reduction Extraction process
PWR	Pressurized Water Reactor
Sdh	Succinic acid dihydrazide

TBq	Terabecquerel
TBP	Tributylphosphate
Tc	Technetium
TMS	Tetramethylsilane
U	Uranium
UNF	Used Nuclear Fuel
Zr	Zirconium

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Complete Initial Evaluation of Novel Complexants for Tc Holdback for Simplified Single Cycle Separations.

1. Introduction

Technetium, Tc, – the lightest element on the periodic table without any stable isotopes – was first isolated in 1937 by Emillio Segré and Carlo Perrier.[1] Its name underscores its lack of natural abundance, as derived from Greek word *tekhnetos* (τεχηνετοσ) meaning "artificial." Indeed, evidence of naturogenic Tc exists in Oklo natural fission reactors,[2] but anthropogenic reactors are a dominant source of technetium on Earth. For uranium-235, 6 out of 100 nuclear fission events yield an isotope with atomic mass of 99.[3,4] This fission yield results in an annual production of ~40 kg of Tc-99 in a typical light water reactor, LWR.[5] When discharged, a metric ton of irradiated commercial LWR fuel contains ~0.8 kg of Tc-99 (normalized to initial heavy metal), which accounts for about 2% of total fission product mass.[6] A high fission yield of Tc-99, coupled with its relatively long half-life (211,000 years), renders this isotope an important component of nuclear waste. The fission product radioactivity of spent LWR fuel is dominated by Tc-99 after 1000 years of cooling.[6] Historically, plutonium production legacy wastes accumulated large quantities of Tc residing in a variety of waste streams. At Hanford, WA, 177 underground tanks contain roughly 25,000 Ci or ~1500 kg of Tc-99 in 53 million gallons of radioactive waste.[7] In addition, during the most intense decades of nuclear weapons testing, between 100-140 TBq (160 – 220 kg) of Tc-99 was released into the atmosphere.[8]

Technetium is mobile in terrestrial, freshwater and marine environments. In aerobic conditions, its most stable form is the highly soluble pertechnetate ion, TcO_4^-.[9] This anion does not adhere to many environmental surfaces as oxygenated sediments near neutral pH conditions are negatively charged.[10] This electrostatic repulsion explains the high environmental mobility of pertechnetate ion.

The chemistry of technetium has proven difficult to master in used nuclear fuel reprocessing. In PUREX process, a pertechnetate anion is coextracted when U^{6+} (Equation 1), or Zr^{4+} and Pu^{4+} (Equation 2) are coordinated by tributylphosphate, TBP.

$$UO_2^{2+} + 2TBP + NO_3^- + TcO_4^- \rightleftarrows UO_2(NO_3)(TcO_4) \bullet 2TBP \tag{1}$$

$$M^{4+} + 2TBP + 3NO_3^- + TcO_4^- \rightleftarrows M(NO_3)_3(TcO_4) \bullet 2TBP \tag{2}$$

Depending on the aqueous acidity, pertechnetic acid, $HTcO_4$, can also be extracted via hydrogen bonding with a neutral extractant such as TBP according to Equation 3.

$$H^+ + TcO_4^- + TBP \rightleftarrows HTcO_4 \bullet TBP \tag{3}$$

The presence of Tc in TBP solvent complicates the Pu partitioning step where hydrazine, HZ, is used to prevent autocatalytic re-oxidation of Pu^{3+}.[11] Hydrazine – an effective scavenger of radiolytically-produced nitrous acid – is degraded as part of a Tc-catalyzed redox process.[12] The complex redox chemistry of Tc is also responsible for the oxidation of uranous cation, U^{4+}, which is an industrially preferred reagent for the reduction of Pu^{4+} as part of Pu partitioning step.[13]

The environmental, storage and reprocessing challenges of technetium highlight the essential need for its suitable management at the back end of nuclear fuel cycle. Research efforts have developed some understanding of Tc chemistry and its behavior in liquid-liquid partitioning systems.[14-29] However, the "technetium problem" in hydrometallurgical options of U and U, Pu recovery was not recognized until efforts to simplify the chemistry of PUREX began. In PUREX, the additions of HZ (nitrite scavenger in feed) and hydroxylamine nitrate, HAN, (holding reductant in scrub stream), initiate a multi-step reduction of Tc^{7+} to non-extractable Tc^{4+}, transitioning TcO_4^- into TcO_2.[12,30,31] This redox chemistry enables an efficient Tc cleaning process, where the degradation of HZ and HAN rejects Tc from U stream in the Pu partitioning step, and from Pu stream in the second Pu purification cycle of PUREX. Accordingly, Tc was not considered a problematic fission product in the early renditions of the PUREX process.[32] This changed over the years as the development of modified or novel flowsheets for the recovery of major actinides from used nuclear fuel, UNF, progressed. Alterations of traditional PUREX chemistry were motivated by Pu proliferation concerns, yielding recipes to blend U into the Pu product, or manipulate the redox chemistry of Np to route it with Pu.[30,33] Also, a continuous drive to simplify process operations has motivated efforts to eliminate the need for the second purification cycle via use of aqueous Pu reductant/complexants such as acetohydroxamic acid, AHA (Advanced PUREX).[34] The complex redox chemistry of Pu and Np in PUREX-type separations also prompted researchers in France to explore a salt-free option for U isolation based on *N*,*N*-dialkylamide extractants (1-cycle GANEX).[35-37] All flowsheet modifications are uniformly challenged by Tc management, where the lowest decontamination factors are typically reported for the U/Tc pair. For instance, a 1-cycle GANEX flowsheet test on genuine spent fuel feed accomplished the acceptable U product purity only with the help of HZ scrub (DF U/Tc of 40).[36] This redox approach is limited by two drawbacks: (1) slow Tc^{7+} reduction kinetics for the mechanism fed by HZ renders the use of equipment with short residence times challenging, and (2) decomposition of HZ yields ammonium nitrate and nitrogen. Novel, viable and effective options for Tc control must be explored as the emphasis on a single-cycle recovery and purification of U continues to grow.[38,39]

The insertion of pertechnetate into the solvate complex, as shown by equations 1 and 2, is driven by the lower hydration energy of this anion (-251 kJ/mol), relative to nitrate (-306 kJ/mol).[40] It is easier to dehydrate TcO_4^- ion, relative to NO_3^-, and the phase transfer process for TcO_4^- is less energy intensive. Still, the solvation of a metal ion by a neutral extractant such as TBP is predominantly assisted by the partitioning of charge-balancing nitrate ions since, in typical reprocessing scenarios, nitrate ion exists in ~1000-fold excess, relative to TcO_4^-, after used nuclear fuel is dissolved.[6,41] This dominant abundance of nitrate in dissolved UNF effluents is the main thermodynamic barrier to selective coordination of TcO_4^-. Nitrate ions are also smaller, and more charge dense when compared with the bulky pertechnetate, which, according to the Hofmeister series, favors electrostatic interaction with organic complexants.[7,40] Multiple attempts to preferentially bind TcO_4^- ion exist in literature, utilizing a plethora of anion exchangers such as tetraphenylarsonium chloride,[42-46] phosphonium salts,[47,48] amines,[49-52] quaternary ammonium salts,[53-55] and neutral reagents such as ketones,[49,56] TBP,[15,57-62] glycols,[63-65] and crown ethers.[66] Attempts to engineer molecular templates sought to overcome the Hofmeister bias by matching the size and shape of the ligand cavity to recognize oxoanions such as pertechnetate to maximize the binding fit.[40] A recent example of such molecular recognition strategy utilized azacryptands. Amendola *et al.* studied recognition of ReO_4^- and TcO_4^- in several aqueous media using the hexaprotonated *p*-xylyl azacryptands.[67] The Lcage molecule (Figure 1, structure A) showed strong affinity for perrhenate and pertechnetate anions and formed a 1:1 inclusion complex stabilized with hydrogen bonding.[67] Isothermal titration results showed the Lcage molecule is selective for pertechnetate over nitrate. Later, Thevenet *et al.* used the Lcage azacryptand for the first time as a masking agent to prevent pertechnetate extraction from nitric acid.[68] The authors suppressed the distribution of Tc by a factor of 5 when using 0.04 mol L^{-1} Lcage, and later functionalized it with water-solubilizing groups to increase its applicability.[69] The azacryptands showing most promising results with the perrhenate studies are shown in Figure 1, structures B and C.[69] Extraction experiments with uranium present showed U/Tc separation factors of 8.0 and 8.5 for compounds B and C, respectively. In a Tc back-extraction scenario, the U/Tc separation factor was increased to 12 when 0.2 mol L^{-1} C was used in 1.0 mol L^{-1} nitric acid.[69] The molecular designs demonstrated by Amendola *et al.* and Thevenet *et al.* show great progress with the challenge of Tc management. Intricate synthesis and uncertainty with regards to hydrolytic and radiolytic stability of such constructs are the chief hurdles for such approaches.

Recently oxoanion molecular receptors based on guanidinium moieties have been garnering attention.[70,71] Guanidinium groups exhibit strong affinity to form ion-pairs with oxoanions as illustrated for carboxylates in Figure 1, structure D. The planar, Y-shaped geometry of the guanidinium group

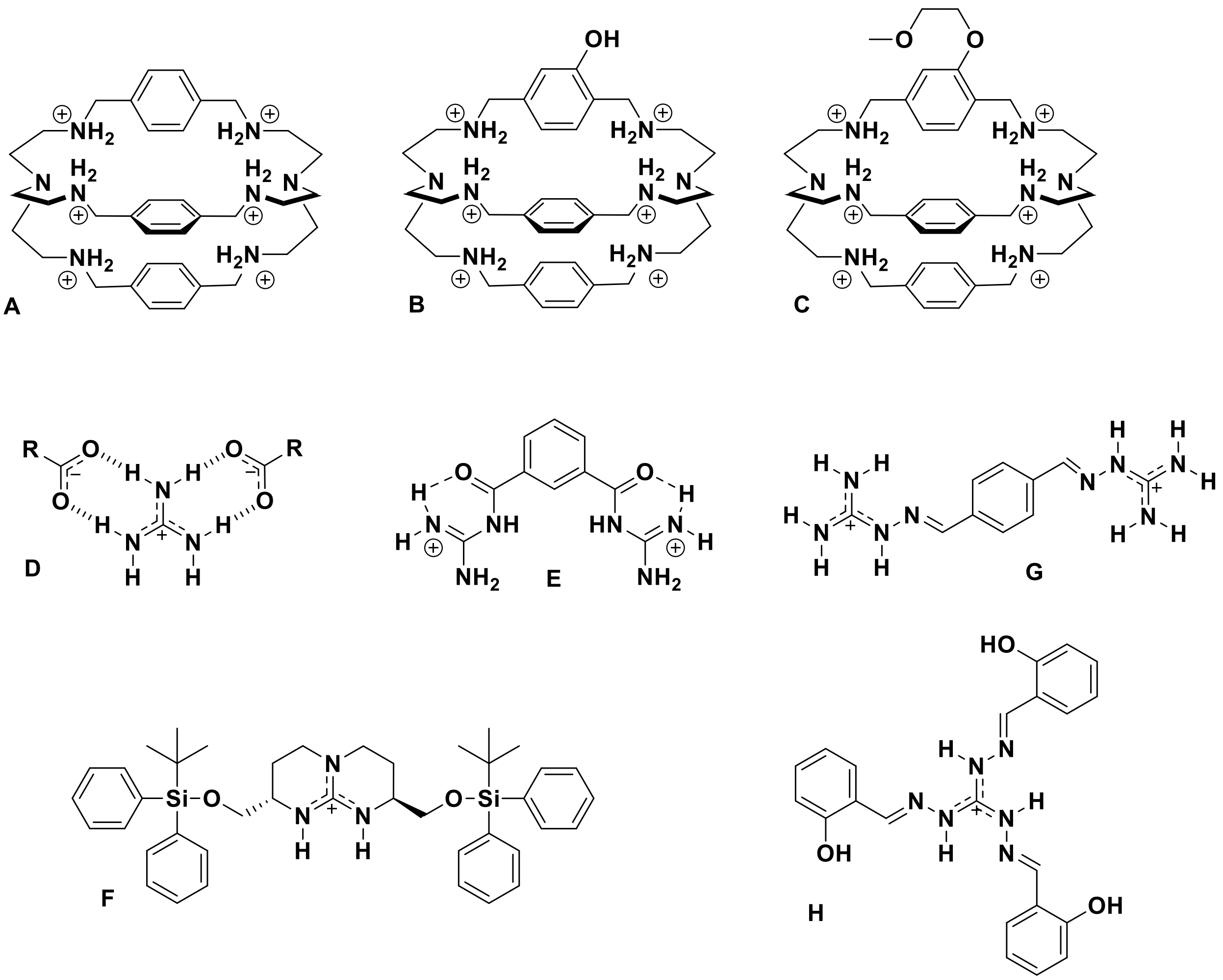

Figure 1. Selected technetium sequestering reagents reported in the literature and discussed here.

renders it naturally pre-organized to support hydrogen bonding with oxoanions. A single guanidinium ion, when fully protonated, consists of six hydrogen bond donors, and the positive charge is delocalized over three nitrogen atoms. Such structural configuration introduces a geometrical versatility when constructing a host for a specific oxoanion. Thermodynamically, the energy of binding benefits from ion-pair formation and hydrogen bonding when balancing the cost of oxoanion dehydration. Ease of synthetic manipulation of guanidiniums allows to build simple receptors such as one reported by Dixon *et al.*[72] Based on earlier success with phosphorodiamidate molecular recognition,[73] the authors developed a receptor containing two acyl-guanidinium groups (Figure 1, structure E) produced by reacting guanidinium hydrochloride and dimethyl isophthalate in a one-step synthesis. This linking strategy showed a 10-fold increase of the binding constant with anionic phosphodiesters, relative to the structure containing a single guanidine group.[72] The ease of synthetic manipulation, geometrical flexibility, and a collection of literature studies targeting oxoanion recognition render the guanidinium moiety an interesting option for pertechnetate binding. Studies utilizing guanidinium-based receptors for management of TcO_4^- are limited to a liquid-liquid partitioning approach by Stephan *et al.* and a selective crystallization strategy by Xie *et al.*[74,75] Stephan *et al.* characterized TcO_4^- binding properties of bicyclic guanidinium reagents functionalized to offer solubility in non-aqueous media.[74] Utilizing the reagents as extractants the authors found the efficiency of Tc partitioning increased for the more lipophilic compounds, with distribution ratios reaching >20000 for structure F shown in Figure 1. The authors attributed this excellent Tc extraction performance to stabilizing benefits of hydrogen bonding in addition to electrostatic attraction.[74] Xie *et al.* engineered a guanidinium-based self-assembly supported by the uptake of TcO_4^- anions, charge-assisted hydrogen bonding and stabilization by π–π stacking.[75] The benzene linked guanidiniums (Figure 1, structure G) showed promising removal efficiencies for ReO_4^- and TcO_4^-, although the performance was drastically reduced in mixtures where anion composition is dominated by nitrate. The study by Xie *et al.* hints at excellent radiolytic stability of guanidinium molecules. The authors did not observe changes in powder x-ray diffraction patterns of structure G material after a 600 kGy β dose was delivered via a 1.5 MeV electron beam from the electron accelerator.[75] The efficiency of ReO_4^- removal was also not affected. Da *et al.* constructed cationic covalent organic nanosheets utilizing guanidine units (Figure 1 structure H), allowing for selective capture of ReO_4^- in presence of nitrate, which did not vary after the exposure to 200 kGy of γ and β radiation.[76]

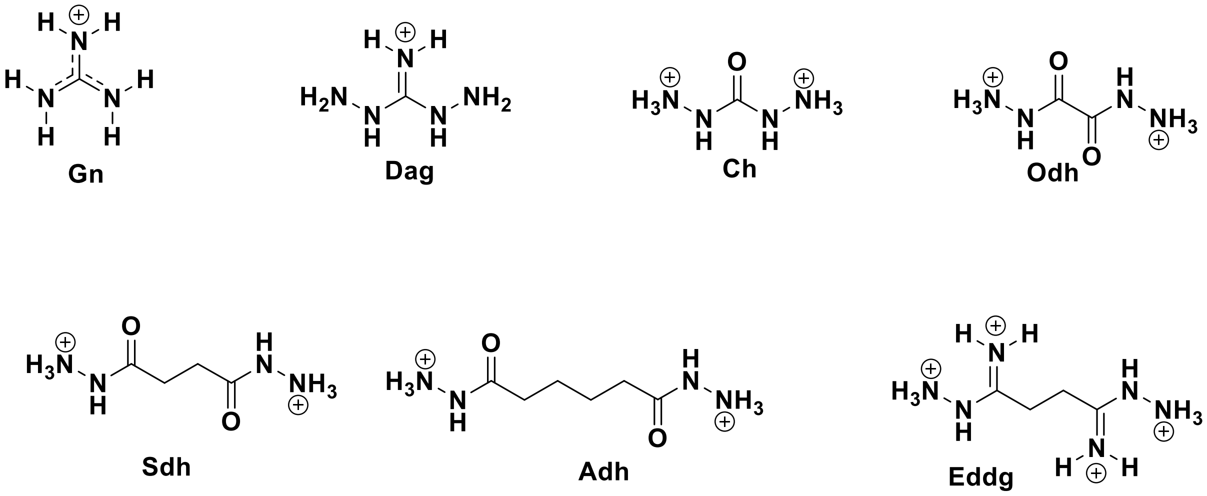

Figure 2. Structures of aqueous soluble reagents investigated in uranium / technetium partitioning studies. Gn: guanidinium nitrate, Dag: diaminoguanidine, Ch: carbohydrazide, Odh: oxalyldihydrazide, Sdh: succinic acid dihydrazide, Adh: adipic acid dihydrazide, Eddg: 1,1′-(ethane-1,2-diyl)diguanidine.

Considering the promising properties of guanidinium-based anion receptors it was hypothesized that this molecular moiety can be used as platform to design a solvent extraction methodology for Tc removal in single-cycle U purification process. To begin, liquid-liquid partitioning behavior of UO_2^{2+} and TcO_4^- as facilitated by DEH*i*BA monoamide extractant was monitored in the presence of guanidinium- and dihydrazide-based reagents. Initial studies were conducted with commercially available, simple guanidine reagents, seeking evidence of any perturbation of Tc liquid-liquid partitioning behavior. Dihydrazide reagents were included in the preliminary work as an alternative, redox-based option to manage Tc in a separation flowsheet designed to recover uranium. Dihydrazides are related to hydrazine in their high redox activity, which sustains a Tc-catalyzed oxidation of such compounds, yielding a non-extractable Tc^{4+}.[12,31,77] Figure 2 shows structures of all reagents investigated in FY22. This document was prepared to meet FCT level 2 milestone M2FT-22IN030101021 under the FY22 Single Cycle MRWFD work package.

2. Experimental Methods

2.1 Reagents

Guanidinium nitrate (98%), diaminoguanidine hydrochloride (98%), carbohydrazide (98%), oxalyldihydrazide (98%), succinic acid dihydrazide (96%) and adipic acid dihydrazide (98%) were purchased from Sigma-Aldrich. The 1,1′-(ethane-1,2-diyl)diguanidine reagent was isolated as dihydrochloride salt at Oak Ridge National Laboratory. All aqueous solutions containing the above reagents were prepared gravimetrically, compensating for their corresponding purities. Monoamide extractant DEH*i*BA was purchased from Marshallton, Inc. (99 %) and used as received to prepare 1.5 mol L^{-1} solutions in *n*-dodecane (≥ 99%). Aqueous nitric acid solutions were prepared using 70 % HNO_3 (Trace Metals grade) and 18 MΩ deionized water. Depleted uranium nitrate (DU) hexahydrate was purchased from Manufacturing Sciences Corporation. A solution of 46 mg L^{-1} U-233 in 1 mol L^{-1} HNO_3 was obtained from INL stocks. Tc-99 radiotracer solution (1.85E7 Bq/mL) was purchased from Eckert&Ziegler.

2.2 Preparation of solutions

All HNO_3 solutions were standardized using sodium hydroxide to the phenolphthalein endpoint. Densities of all acid stocks were determined gravimetrically using Class A volumetric flasks. Each mixture containing aqueous holdback reagent was prepared gravimetrically prior to distribution experiments. A 1 mol L^{-1} DU stock in 1 mol L^{-1} HNO_3 was prepared and further diluted in appropriate acid concentration to yield working extraction samples containing 0.5 mol L^{-1} DU. U-233 tracer solution was prepared from 46 mg L^{-1} INL stock, diluting 30.6 µL with 5 mL of 1 mol L^{-1} HNO_3. Tc-99 tracer solution was prepared by blending 27 µL of Eckert&Ziegler stock and 5 mL of 1 mol L^{-1} HNO_3. The non-aqueous mixtures of all tested extractants in *n*-dodecane were prepared gravimetrically.

2.3 Solvent extraction

Guanidinium- and dihydrazide-based reagents were evaluated for their ability to back-extract technetium, which was initially co-extracted with uranium into the organic phase. Appropriate quantities of 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane were pre-equilibrated two times with 2 mol L^{-1} nitric acid solutions and contacted with aqueous phases containing 0.5 mol L^{-1} depleted uranyl nitrate in 2 mol L^{-1} nitric acid. In-parallel liquid-liquid distribution studies were performed where U-233 radiotracer was added ONLY, and U-233 AND Tc-99 radiotracer solutions were added together. This procedure enabled accurate alpha / beta discrimination using the liquid scintillation counter. The U, Tc forward extraction conditions yield a loaded organic phase containing approximately 70 g/L uranium and ~65% of introduced Tc-99. This loaded organic environment was equilibrated with aqueous mixtures containing 0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol L^{-1} concentrations of Gn, Dag and Ch. Aqueous solubility limits did not allow to study reagent Odh at 0.5 mol L^{-1}. Reagents Odh, Sdh and Adh were also compared using a 0.05 mol L^{-1} aqueous concentration. Reagents Dag and Ch were also evaluated when total aqueous acidity was reduced from 2.0 to 0.5 mol L^{-1} to evaluate the influence of proton concentration on the ability to strip Tc. Since Gn is a nitrate salt and Dag is isolated as a hydrochloride salt separate control dependencies were performed with 0 – 0.5 mol L^{-1} sodium nitrate and hydrochloric acid to verify that the presence of these additives does not influence the partitioning of technetium. All stripping dependencies were performed at organic-to-aqueous phase ratio of 1. The samples were equilibrated for 30 minutes using the Glas-Col multitube vortexer. After equilibration, liquid phases were separated and 100 µL of each phase was added to 10 mL of UltimaGOLD liquid scintillation cocktail. Samples were monitored radiometrically using a PerkinElmer 3180 liquid scintillation counter with an enabled alpha/beta discrimination protocol. Liquid-liquid distribution ratios for uranium were measured as the ratio of radioisotope alpha activity in the organic and aqueous phases. Liquid-liquid distribution ratios for technetium were measured as the ratio of radioisotope beta activity in the organic and aqueous phases, corrected for the beta activity present in samples containing depleted uranium spiked with U-233 only.

2.4 Potentiometric titrations

Acid dissociation constants in perchlorate electrolyte medium were determined by titrating ~0.005 mol L^{-1} solutions of Ch, Odh, Sdh and Adh using NaOH. Potentiometric titrations were performed using a Mettler Toledo T-90 autotitrator. Temperature of titrand solution was maintained at 20.0 ± 0.1 °C using a jacketed beaker and a circulating water bath. All titrations were blanketed with hydrated nitrogen gas (bubbled through 1.0 M NaOH) to prevent CO_2 absorption. All titrations utilized a Ross Orion semi-micro glass electrode filled with 5.0 M NaCl to stabilize the electrode junction potential. Gran analysis (strong acid / strong base titration) at ionic strength of 2.0 mol L^{-1} was utilized to standardize electrode response and to check for carbonate contamination in NaOH titrant. Potentiometric data was modeled using the Hyperquad2013 fitting software to determine acid dissociation constants.

2.5 Nuclear magnetic resonance studies

All nuclear magnetic resonance (NMR) spectroscopic experiments were performed using an Anasazi EFT-90 instrument (ν1H = 90.25 MHz). Experiments were conducted using 5 mm tubes with inner fluoroethylene polymer (FEP) inserts to contain the analyte solution, and a 2% v/v tetramethylsilane (TMS) in deuterated chloroform solution was placed interstitially to provide an internal reference for chemical shift and integration intensity. Samples were pneumatically spun in the probe between 41 and 45 Hz. A calibrated 90° pulse width of 12.4 μsec was used with a relaxation delay of 5 sec between scans, and data was collected using a sweep width of 1578 Hz (17.5 ppm) with a time domain of 8192 points. To avoid signal blurring due to both magnet drift and, in the case of the 2.0 mol L^{-1} DNO_3 solution with Tc-99, vigorous reactivity, experiments typically consisted of single scans. Spectra were analyzed using MestReNova 12.

3. Results

3.1 U and Tc Distribution Studies

The influence of guanidinium nitrate, Gn, diaminoguanidine, Dag, and carbohydrazide, Ch, on the partitioning of UO_2^{2+} and TcO_4^- was initially studied. Structures of these reagents are shown in Figure 2. Figure 3A shows the dependency of U-233 and Tc-99 partitioning in a liquid-liquid system where the organic phase contains 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane and the aqueous phase contains varying concentrations of Gn dissolved in 2 mol L^{-1} HNO_3. The raw experimental distribution ratios for the distribution of U and Tc are listed in Table 1. The collected trends were acquired in a stripping mode, after the initial extraction step loaded the organic environment with depleted uranium, U-233 and Tc-99. The equilibration with aqueous phase containing 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3 was chosen for the extraction stage, which assures presence of ~70 g/L uranium in the organic phase. At this condition nearly 65 % of Tc accompanies the transfer of uranium into the non-aqueous environment via the formation of $UO_2(NO_3)(TcO_4)$•2DEH*i*BA complex. Distribution trends shown in Figure 3A indicate the partitioning of uranium is enhanced, as expected, due to the increasing presence of nitrate introduced via the addition of aqueous complexant (guanidinium nitrate). The distribution of technetium shows a consistent downward trend, which may be either explained by nitrate outcompeting pertechnetate from the

$UO_2(NO_3)(TcO_4)\cdot 2DEHiBA$ complex or preferential electrostatic interaction between the guanidinium cation and pertechnetate anion. A control experiment as shown in Figure 3B was performed to monitor whether the observed U, Tc trends are predominantly due to growing nitrate concentration. The salting effect on the partitioning of uranyl cation was reproduced in the control study. The distribution trend for Tc-99 was nearly constant, which supports the conclusion that the observed Tc downward trend is due to a growing content of guanidinium cation. The overall influence of Gn on Tc distribution was minor, which prompted the studies of Dag and Ch, where the presence of multiple protonation sites is feasible.

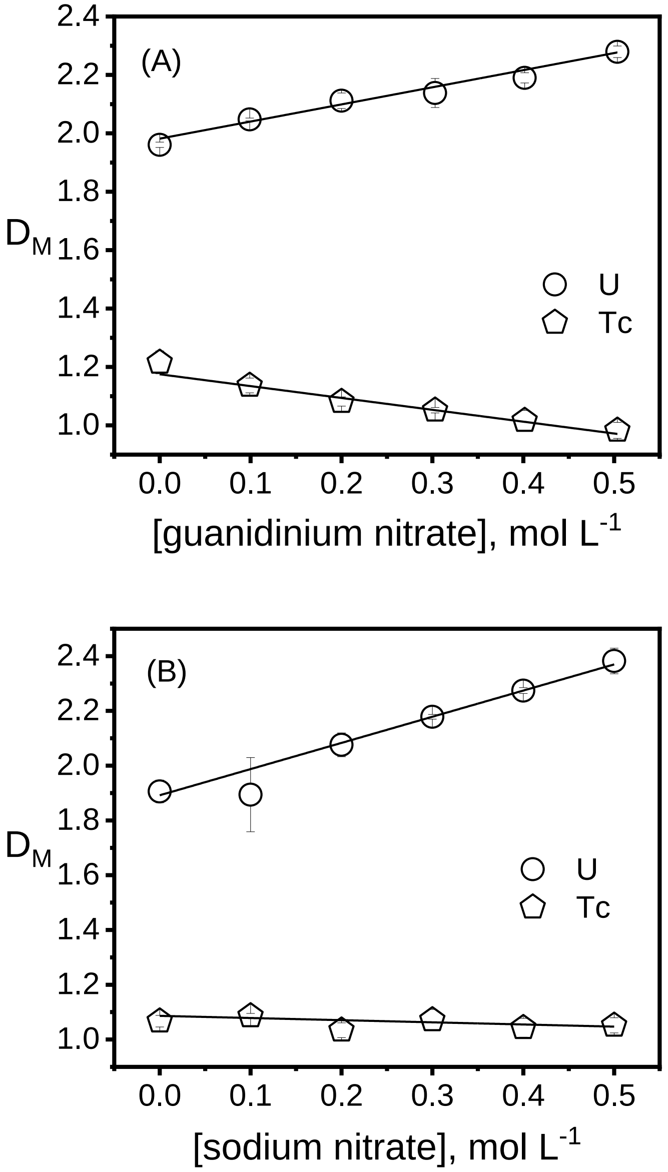

Figure 3. Effect of (A) guanidinium nitrate, (B) sodium nitrate on the distribution of U-233 and Tc-99. Organic phase: 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane was initially equilibrated with 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3, spiked with U-233 and Tc-99. Aqueous phase: 0 – 0.5 mol L^{-1} guanidinium nitrate or sodium nitrate in 2 mol L^{-1} HNO_3.

Figure 4 shows the uranium and technetium distribution studies in the presence of diaminoguanidine (4A) and the accompanying control experiment (Dag isolated as HCl salt). Uranium distribution trends are minimally influenced by the presence of Dag, showing that the uranium in the organic phase is well maintained. The distribution of technetium consistently decreases as the aqueous concentration of Dag increases. The control experiment shows no influence of HCl on the partitioning of U and Tc. This finding again indicates that an increasing efficiency of Tc removal from a loaded organic phase adheres to a growing content of Dag in an aqueous phase. Relative to Gn, the efficiency of Tc stripping increases for Dag, pointing to a stronger interaction with TcO_4^- ion.

Table 1. Experimental distribution values for U and Tc acquired when 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane, pre-equilibrated with 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3, spiked with U-233 and Tc-99, was contacted with aqueous mixtures containing guanidinium nitrate, carbohydrazide or diaminoguanidine in 2 mol L^{-1} HNO_3. T = 20.5 ± 0.5 °C. Uncertainties reported at ±1σ.

Gn, mol L^{-1}	D_U	D_{Tc}	$NaNO_3$, mol L^{-1}	D_U	D_{Tc}
0	1.96±0.01	1.22±0.04	0	1.91±0.04	1.07±0.02
0.099	2.05±0.01	1.14±0.03	0.100	1.89±0.14	1.09±0.01
0.200	2.11±0.03	1.08±0.02	0.201	2.08±0.04	1.03±0.03
0.303	2.14±0.05	1.05±0.01	0.301	2.18±0.01	1.07±0.04
0.401	2.19±0.02	1.02±0.03	0.401	2.27±0.01	1.04±0.03
0.504	2.28±0.02	0.98±0.03	0.502	2.38±0.05	1.05±0.03
Dag, mol L^{-1}	D_U	D_{Tc}	HCl, mol L^{-1}	D_U	D_{Tc}
0	1.91±0.03	1.16±0.01	0	1.84±0.05	1.14±0.01
0.104	1.85±0.01	0.96±0.01	0.10	1.92±0.03	1.15±0.03
0.205	1.82±0.04	0.77±0.01	0.20	1.88±0.01	1.16±0.01
0.307	1.77±0.01	0.66±0.01	0.30	1.93±0.01	1.17±0.02
0.408	1.75±0.02	0.53±0.01	0.40	1.94±0.01	1.19±0.01
0.510	1.73±0.01	0.44±0.01	0.50	1.95±0.01	1.17±0.01
Ch, mol L^{-1}	D_U	D_{Tc}	Odh, mol L^{-1}	D_U	D_{Tc}
0	1.90±0.02	1.15±0.01	0	1.89±0.05	1.14±0.04
0.105	1.87±0.02	0.90±0.01	0.052	1.93±0.01	0.07±0.02
0.204	1.86±0.01	0.75±0.01	0.101	1.87±0.02	< 0.001
0.308	1.79±0.01	0.63±0.01	0.199	1.84±0.02	< 0.001
0.407	1.78±0.09	0.55±0.01	0.299	1.82±0.02	< 0.001
0.512	1.74±0.01	0.51±0.01	0.400	1.79±0.01	< 0.001

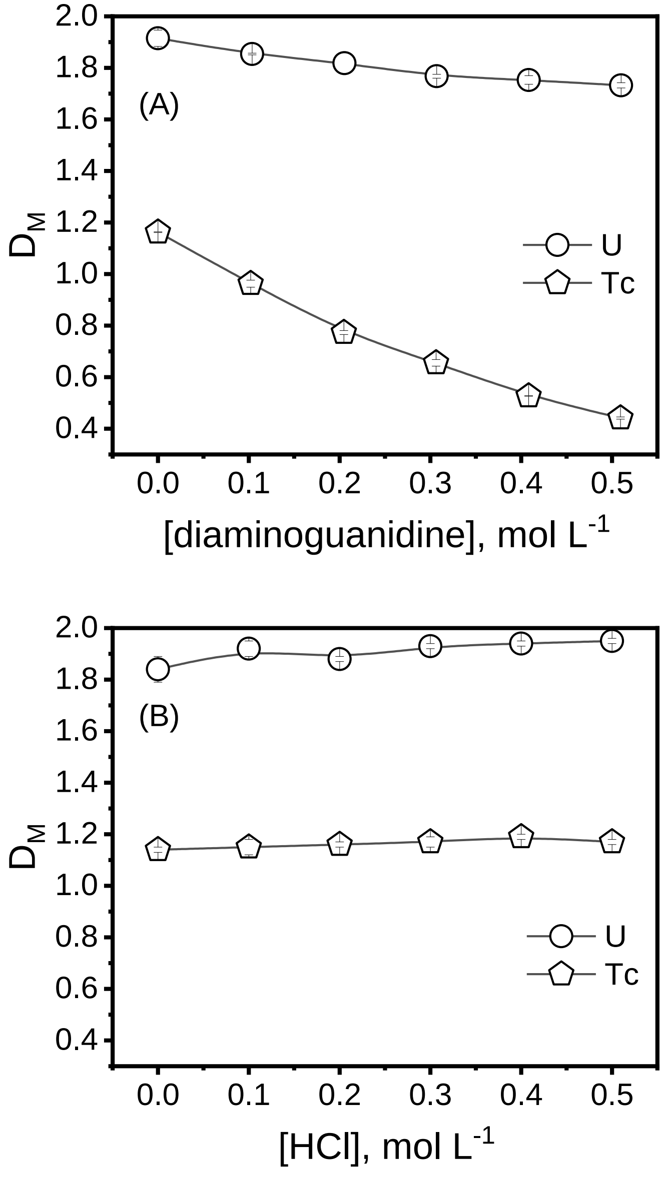

Figure 4. Effect of (A) diaminoguanidine, (B) hydrochloric acid on the distribution of U-233 and Tc-99. Organic phase: 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane was initially equilibrated with 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3, spiked with U-233 and Tc-99. Aqueous phase: 0 – 0.5 mol L^{-1} Dag or HCl in 2 mol L^{-1} HNO_3.

Figures 5 illustrates the effect of carbohydrazide on the uranium and technetium distribution. Alekseenko *et al*. studied stripping of Tc and Pu from loaded TBP solvent with carbohydrazide, demonstrating that nearly 80 % of Tc can be removed when aqueous nitric acid concentration is 0.5 mol L^{-1}.[77] The authors indicate the efficient Tc stripping is due to the Tc-catalyzed degradation of Ch, where Tc^{7+}

is reduced to non-extractable Tc^{4+} as previously observed for hydrazine.[12,31] The U and Tc distribution trends shown in Figure 5 are rather similar to those observed for Dag.

Figure 6 compares the three Tc stripping reagents (Gn, Dag and Ch) studied in 2 mol L^{-1} HNO_3, showing their relative capacity to decrease Tc content in the uranium-loaded phase. The improvement in Tc stripping follows the Gn < Dag ≈ Ch trend following a growing content of nitrogen rich reagents.

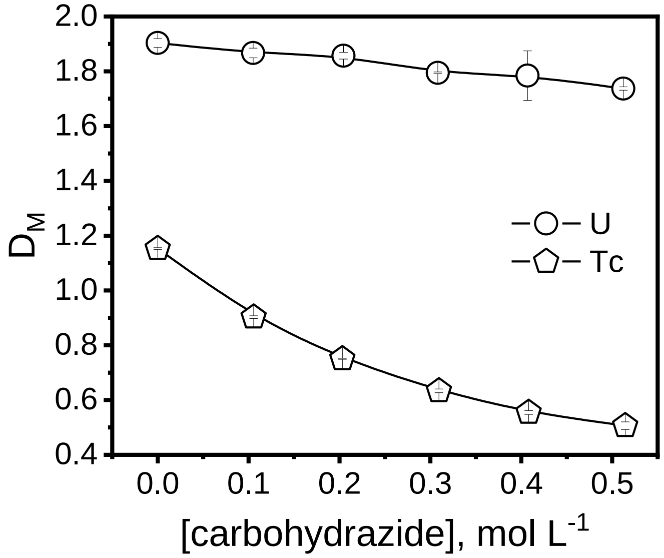

Figure 5. Effect of carbohydrazide on the distribution of U-233 and Tc-99. Organic phase: 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane was initially equilibrated with 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3, spiked with U-233 and Tc-99. Aqueous phase: 0 – 0.5 mol L^{-1} Ch in 2 mol L^{-1} HNO_3.

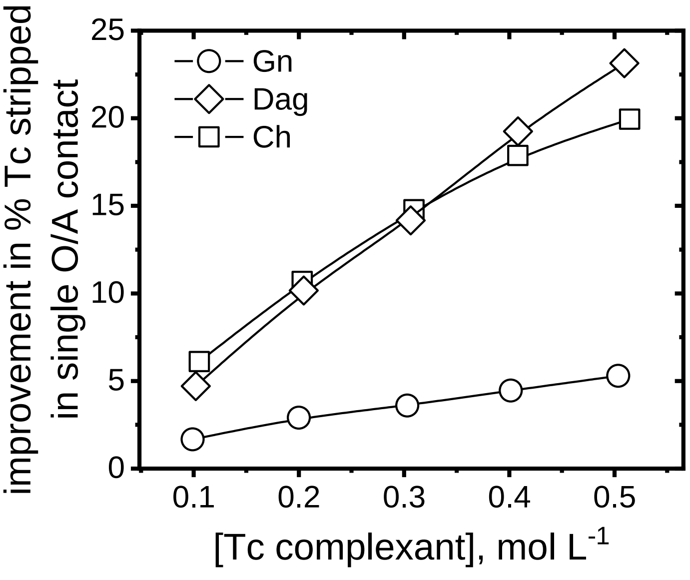

Figure 6. Improvement of Tc stripping (%) as facilitated by the aqueous presence of Gn (circle), Dag (diamond) and Ch (square). Aq: complexant in 2 mol L^{-1} HNO_3, Org: 70 g L^{-1} U, tracer Tc-99, 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane.

A small (4 %) improvement in Tc stripping efficiency was observed for Gn, but it was more efficient with carbohydrazide (15 % increase) and diaminoguanidine (18 %) at 0.5 mol L^{-1} concentration. This is a very positive result, yielding a liquid-liquid formulation capable of removing nearly 70 % of loaded Tc from an organic phase in a single contact. The observed improvement in the Tc stripping with diaminoguanidine and carbohydrazide, relative to guanidinium nitrate, may possibly be related to the increased presence of positively charged sites due to protonation in 2 mol L^{-1} HNO_3. Successive protonation of amine groups will occur in aqueous mixtures of increasing concentrations of hydrogen ion.

Trends observed for Dag and Ch are nearly identical in the 0.1 – 0.4 mol L^{-1} range, with Dag gaining small advantage (3 %) at 0.5 mol L^{-1}. The observed similarity between a guanidinium- and dihydrazide-based reagents was unexpected as the mechanisms of Tc stripping are predicted to be different.

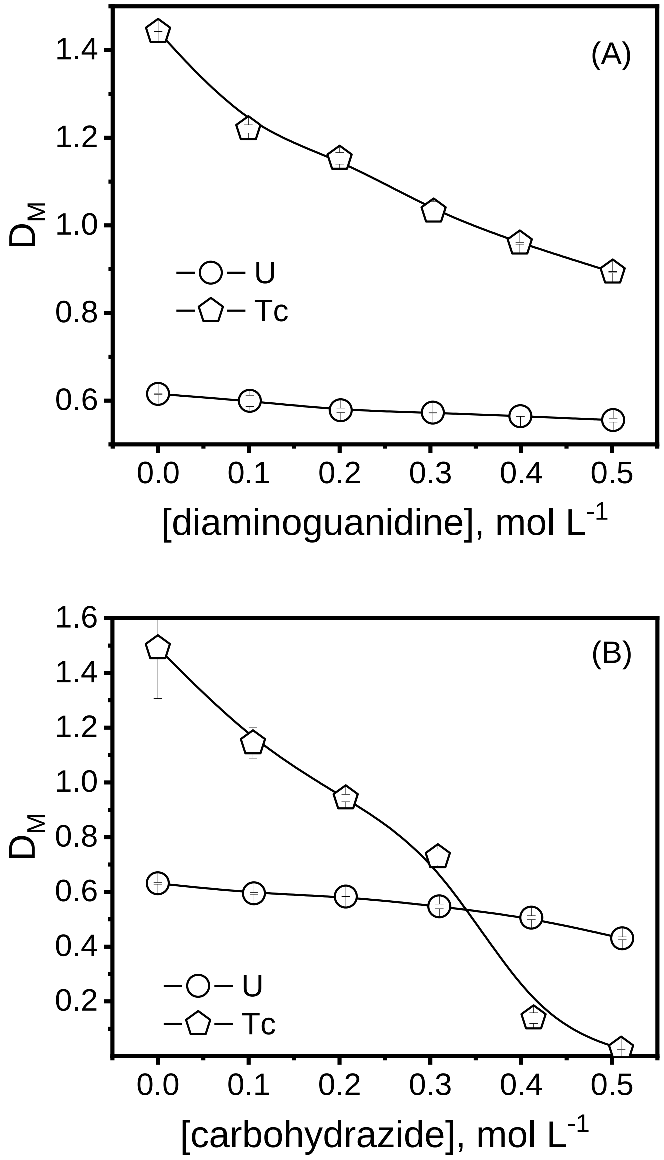

Figure 7. Effect of (A) diaminoguanidine, (B) carbohydrazide on the distribution of U-233 and Tc-99 after the reduction of aqueous acidity. Organic phase: 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane was initially equilibrated with 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3, spiked with U-233 and Tc-99. Aqueous phase: 0 – 0.5 mol L^{-1} Dag or Ch in 0.5 mol L^{-1} HNO_3.

Gallaway *et al.*, and later Kemp *et al.*, when studying Tc-catalyzed degradation of hydrazine, reported the rate of oxidation is inversely proportional to nitric acid concentration.[12,31] Accordingly, the efficiency of Tc stripping will increase for Ch if the autocatalytic redox equilibrium also occurs with this reagent. Figure 7 shows the influence of Dag (A) and Ch (B) on the distribution of U and Tc when the acidity of the aqueous environment was reduced to 0.5 mol L^{-1}. The experimental distribution ratios for this study are listed in Table 2. While the organic phase uranium loading was substantially reduced (as expected from reduced nitrate content) the technetium stripping efficiency was decreased for Dag and increased for Ch. Figure 8 shows the relative change in Tc stripping efficiency induced upon changing the aqueous acidity from 2.0 to 0.5 mol L^{-1}.

Table 2. Experimental distribution values for U and Tc acquired when 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane, pre-equilibrated with 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3, spiked with U-233 and Tc-99, was contacted with aqueous mixtures containing diaminoguanidine and carbohydrazide in 0.5 mol L^{-1} HNO_3. T = 20.5 ± 0.3 °C. Uncertainties reported at ±1σ.

Dag, mol L^{-1}	D_U	D_{Tc}	Ch, mol L^{-1}	D_U	D_{Tc}
0	0.62±0.01	1.44±0.01	0	0.63±0.01	1.49±0.18
0.101	0.60±0.01	1.22±0.01	0.106	0.59±0.01	1.14±0.06
0.201	0.58±0.01	1.15±0.01	0.207	0.58±0.01	0.94±0.01
0.303	0.57±0.01	1.03±0.02	0.310	0.55±0.01	0.73±0.03
0.399	0.56±0.01	0.96±0.01	0.411	0.51±0.01	0.14±0.02
0.501	0.56±0.01	0.89±0.01	0.511	0.43±0.01	0.025±0.001

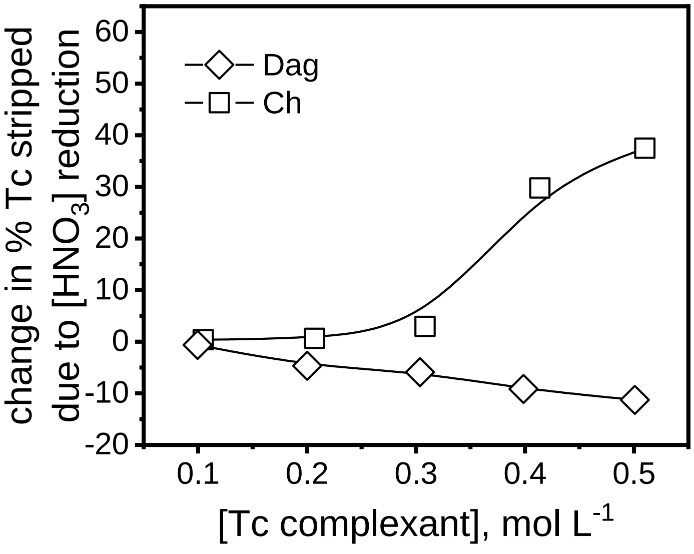

Figure 8. Relative change (%) in Tc stripping efficiency by aminoguanidine and carbohydrazide observed when aqueous concentration of nitric acid was decreased from 2.0 to 0.5 mol L^{-1}.

The opposite acid dependence for Tc stripping observed for Dag and Ch confirms that these reagents follow different mechanisms in their interaction with TcO_4^- anion. A lowered Tc stripping efficiency observed for

Dag in 0.5 mol L^{-1} HNO_3 agrees with the hypothesized changes in protonation equilibria for such amine-based reagents. The abundance of a di-protonated Dag decreases when the concentration of nitric acid is lowered, while increasing the presence of mono-protonated species. Changes in the speciation of positively charged Dag may directly influence the interaction with pertechnetate anion. Unfortunately, the acid dissociation constants of Dag cannot be measured potentiometrically (too acidic for glass electrode) or using NMR due to lack of discrete ^{1}H and ^{13}C resonances.

The Tc stripping trend observed for carbohydrazide is nearly constant for 0.1 – 0.3 mol L^{-1} concentration range, but the removal of Tc accelerates for the largest (0.4 and 0.5 mol L^{-1}) concentration of carbohydrazide. The sudden enhancement of Tc stripping could possibly be attributed to changes in redox speciation of technetium as part of Tc-catalyzed oxidation of carbohydrazide. Garraway and Wilson showed the Tc-catalyzed oxidation of hydrazine begins with an induction period when Tc^{7+} is reduced to Tc^{4+}. It is a rather slow process, where the degradation of hydrazine does not begin, depending on the aqueous conditions, until 1-2 hours after mixing. If the same redox chemistry proceeds for carbohydrazide the substantial increase in Tc stripping may be kinetic in nature. In contrast to Ch, a monotonic change observed with Dag supports the claim that Tc stripping is guided by steady-state chemistry.

Oxalyldihydrazide, Odh, (Figure 2) was also investigated. Figure 9 shows the dependency of U and Tc partitioning when aqueous stripping solution contained 2 mol L^{-1} HNO_3. The distribution ratios are listed in Table 1. The back-extraction of Tc is very effective with this reagent. The technetium extracted by DEH*i*BA was quantitatively removed from non-aqueous environment at $0.1 \leq \text{Odh} \leq 0.4$ mol L^{-1} concentration range. An additional study, conducted using 0.05 mol L^{-1} Odh, yielded a quantifiable D_{Tc} of 0.07±0.02, showing that the induction period for the reduction of Tc^{7+} is dependent on the concentration of a dihydrazide reagent. This was also demonstrated for hydrazine.[12]

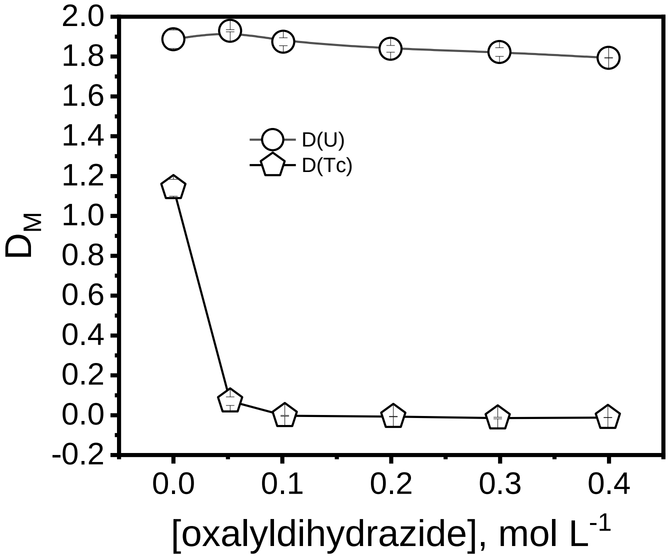

Figure 9. Effect of oxyalyldihydrazide, Odh, on the distribution of U-233 and Tc-99. Organic phase: 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane was initially equilibrated with 0.5 mol L^{-1} uranyl nitrate in 2 mol L^{-1} HNO_3, spiked with U-233 and Tc-99. Aqueous phase: 0.05 – 0.4 mol L^{-1} Odh in 2 mol L^{-1} HNO_3.

A substantial difference in Tc back-extraction observed between Ch and Odh suggests the latter reagent is more susceptible to the Tc-catalyzed oxidation, thus yielding non-extractable Tc^{4+} more efficiently. To look at this structural dependence more closely additional reagents based on the dihydrazide structure were studied. Specifically, succinic acid dihydrazide, Sdh, and adipic acid dihydrazide, Adh, (Figure 2) were compared with Ch and Odh. The distance between the two hydrazide groups was varied with an ethylene bridge for Sdh and butylene bridge for Adh separating these N-rich moieties. Figure 10 shows the results of this comparative study. All compounds were compared at 0.05 mol L^{-1} concentration. The Tc stripping performance by Ch was consistent with early observations. At the condition of the study Ch improved the Tc back-extraction only by 6 %. Sdh at 23 % and Adh at 26 % were more effective, and Odh at 47 % performed best.

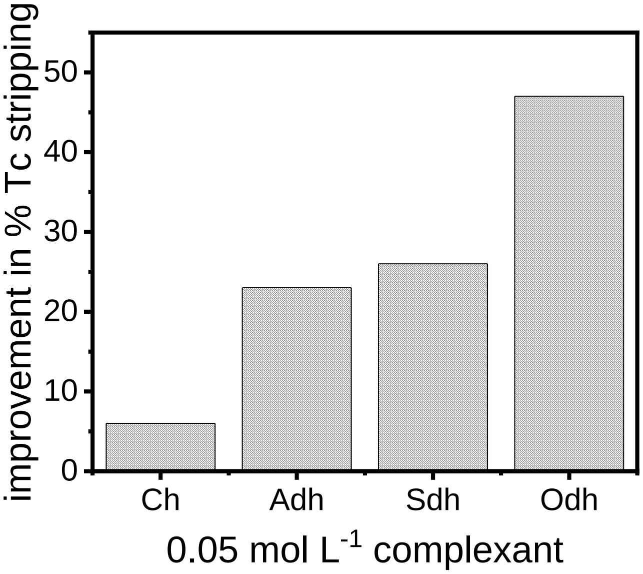

Figure 10. Relative improvement in Tc stripping efficiency by Ch, Sdh, Adh and Odh observed when 0.05 mol L^{-1} of each reagent in 2.0 mol L^{-1} HNO_3 was equilibrated with U,Tc-loaded organic phase.

The observed Ch < Adh ≈ Sdh < Odh trend for the efficiency of Tc back-extraction matches the observed acidic character of these reagents as estimated by the first protonation equilibrium, pK_2. Potentiometric titrations were performed to examine the protonation states of Ch, Odh, Sdh and Adh, seeking additional insight into the observed Tc distribution differences observed for these compounds. A glass electrode monitored changes in hydrogen ion concentration when sodium hydroxide was added to perturb the acid/base equilibria of Ch, Odh, Sdh and Adh. The experimental potentiometric curve collected for a forward titration of Ch in $(H^+,Na^+)ClO_4$ is presented in Figure 11A. The calculated equilibrium constants, listed in Table 3, correspond with the protonation reactions for two terminal nitrogens of hydrazide moieties, adhering to the proton dissociation sequence described by Equation 4.

$$\mathrm{H}_{3-a}\mathrm{L}^{+3-a} \rightleftarrows \mathrm{H}_{2-a}\mathrm{L}^{+2-a} + \mathrm{H}^{+} \qquad K_a = \frac{[H^+]\cdot[\mathrm{H}_{2-a}\mathrm{L}^{+2-a}]}{[\mathrm{H}_{3-a}\mathrm{L}^{+3-a}]} \quad a = 1, 2 \qquad (4)$$

Table 3. Acid dissociation constants, pK_a, determined for Ch, Adh, Sdh and Odh using potentiometric titration studies. Uncertainties reported at ±3σ. ND: not detected using glass electrode.

H_nL	*a*	Ch	Adh	Sdh	Odh
HL^+	2	4.44±0.01	3.89±0.01	3.84±0.01	2.70±0.03
H_2L^{2+}	1	2.55±0.02	3.24±0.01	3.14±0.01	ND

$^a I = 2.0$ M $(H^+/Na^+)ClO_4$ at 20.0°C.

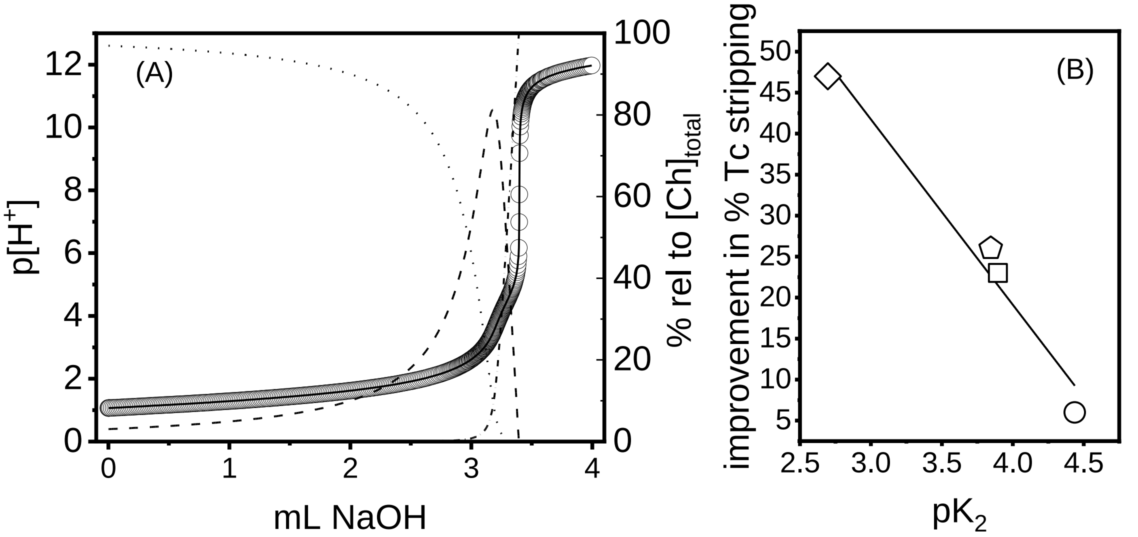

Figure 11. (A) Potentiometric p[H^+] trends collected for Ch protonation titration at $T = 20.0 \pm 0.1$°C and $I = 2.00 \pm 0.01$ M (Na^+/H^+)ClO_4. Titrand: $V_{init} = 10.077$ mL, $C_{Ch} = 5.85$ mmol L^{-1}, $C_{H+} = 0.101$ mol L^{-1}. Titrant: 0.299 mol L^{-1} NaOH and 1.70 mol L^{-1} $NaClO_4$. (○) Experimental p[H^+], (——) calculated p[H^+], (-·-) Ch, (---) HCh^+, (···) H_2Ch^{2+}. (B) A relationship between the observed enhancement in the stripping efficacy of Tc due to presence of Ch (circle), Sdh (square), Adh (pentagon) and Odh (diamond), and reagent acidity as quantified by the second proton dissociation reaction, pK_2.

Figure 11B correlates the observed Tc stripping efficiency with the first protonation reaction, pK_2, as described by equation 4, showing good agreement ($R^2 = 0.96$). This trend could not be examined for the second protonation reaction, pK_1, as the acidity of Odh does not allow the quantification of this equilibrium using the glass electrode. Garraway and Wilson hypothesized that Tc-catalyzed oxidation of hydrazine progressed via a complex formation between Tc^{4+} and hydrazine, following rapid oxidation by nitrate.[31] The authors were unable to isolate the complex, but argued that the appearance of, in some cases, intense red color signaled the complexation reaction, as previously evidenced for Tc^{4+} and hydroxylamine.[78] The observed correlation, as presented in Figure 11B, suggests that propensity to protonate and form positively charged dihydrazide ions is important to sustain the Tc-catalyzed oxidation mechanism, especially in aqueous conditions of increased acidity and presence of oxidizing nitrates. Accordingly, it may be theorized the increasing presence of protonated forms of dihydrazides attracts TcO_4^- ion more efficiently prior to initiation of redox reaction.

The impact of Odh on the liquid-liquid partitioning of Tc was also tested in a forward solvent extraction mode, where the reagent was added to aqueous mixtures containing 0.5 mol L^{-1} uranyl nitrate in 0.5, 1.0, 2.0, 3.0 and 4.0 mol L^{-1} HNO_3. In this configuration Odh may be regarded as technetium masking agent, preventing its transfer into the organic phase. Figures 12A and 12B show the collected acid dependencies for the partitioning of U-233 (A) and Tc-99 (B).

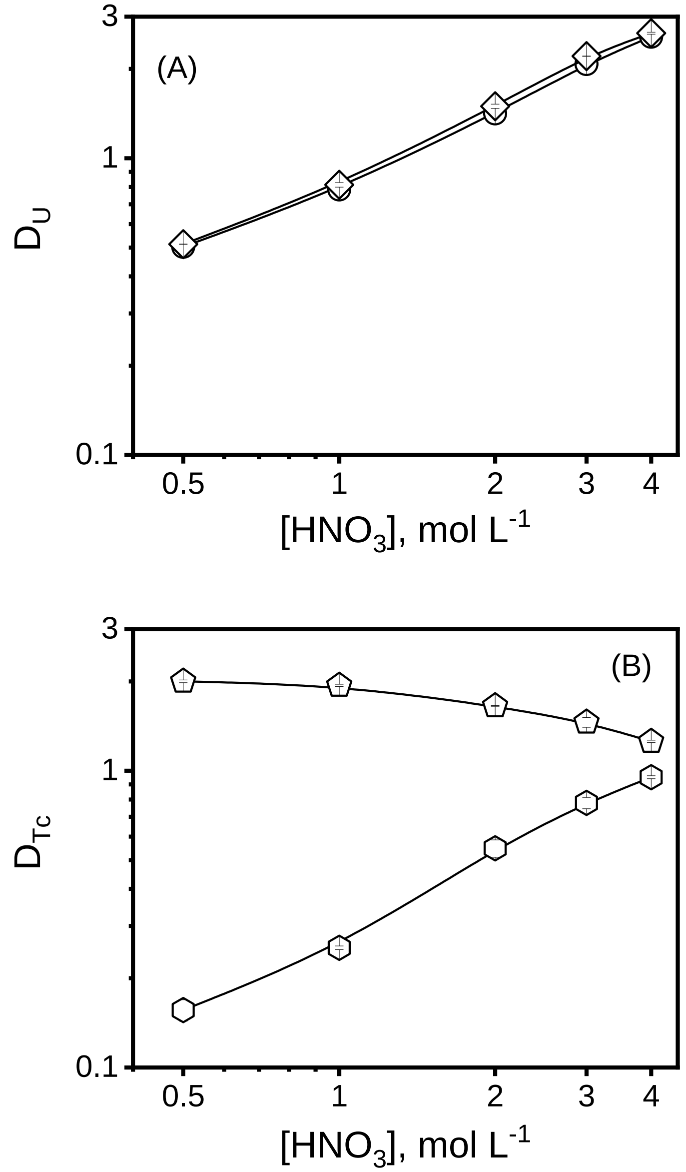

Figure 12. Influence of oxalyldihydrazide on the extraction of (A) U and (B) Tc from nitric acid. Org: 1.5 mol L^{-1} DEH*i*BA in *n*-dodecane, Aq: 0.5 mol L^{-1} depleted uranium, ~1.0E3 Bq/mL U-233, 1.0E3 Bq/mL Tc-99, 0.01 mol L^{-1} Odh in HNO_3. (circle) U, without Odh. (diamond) U, with Odh. (pentagon) Tc, without Odh. (hexagon) Tc, with Odh.

The partitioning of uranium was not affected by the presence of Odh throughout the investigated range of aqueous acidities. As initially observed for back-extraction experiments, the influence of Odh on the liquid-liquid distribution of Tc is profound, especially in conditions of low nitric acid concentrations. The dependence of Tc partitioning on the nitric acid concentration underscores the importance of aqueous acidity and nitrate ion content on the mechanism of Tc-catalyzed degradation of dihydrazides.

3.2 Tc-catalyzed degradation studies

It is hypothesized that an efficient Tc separation from U in liquid-liquid systems containing dihydrazide reagents can be attributed to Tc-catalyzed oxidation of such compounds, leading to the formation of non-extractable Tc^{4+}.[12,31] It is also foreseen that mechanism responsible for Tc partitioning is not redox based for guanidinium reagents, leaving technetium as TcO_4^- ion throughout the separation process. Nuclear magnetic resonance, NMR, studies were performed to further elucidate this distinct chemistry for dihydrazide- and guanidinium-based complexants. The study monitored the changes in a ^1H NMR singlet peak which originates from 4 equivalent protons on the ethylene bridge of Sdh and Eddg. Figure 2 shows the structures of these reagents. Changes of this resonance peak indicate the compound undergoes decomposition, which, in presence of Tc, should accelerate for Sdh as a member of dihydrazide class. Figure 13A tracks the normalized area under the curve for 1H NMR peak of Sdh with and without Tc in solution. The evidence for a rapid acceleration of Sdh decomposition is clear in presence of Tc. Minor degradation is observed in 2 mol L^{-1} deuterated nitric acid environment (~10 %). Figure 13B illustrates the observed evolution of ^1H NMR peak. The singlet at 2.59 ppm decreases and a new singlet at 2.55 ppm grows in, indicating Sdh is decomposing into a product where all protons are equivalent. The addition of Tc initiates a fast signal change, which slows down after ~3 hours when the chemistry reaches a steady state, indicating a plateau at ~50 % degradation. A very similar degradation trend was observed by Kemp *et al.* for hydrazine in 2 mol L^{-1} HNO_3.[12] A comparison of Sdh degradation trends with guanidinium-based Eddg was not possible in 2 mol L^{-1} DNO_3 due to a very limited solubility of this reagent. A direct comparison of Sdh and Eddg was only possible in mildly acidic environment (pH ~ 2). Figure 14 summarizes the results of ^1H NMR study for Sdh and Eddg with and without presence of Tc-99. The changes in the ^1H NMR peak area were less pronounced for Sdh in the mildly acidic environment, relative to 2 mol L^{-1} HNO_3 condition. Kemp *et al.* studied the Tc-catalyzed oxidation of hydrazine in 0.1 mol L^{-1} HNO_3, showing that HZ decomposition was rapid, resulting in ~50 % degradation within initial 60 minutes.[12] The authors did show that the rate of HZ destruction slows down in mildly acidic conditions. This impediment may be even more pronounced in 0.01 mol L^{-1} DNO_3 present in this study. Despite the slower degradation rate observed for Sdh a clear increase in ^1H NMR peak change is evident in presence of

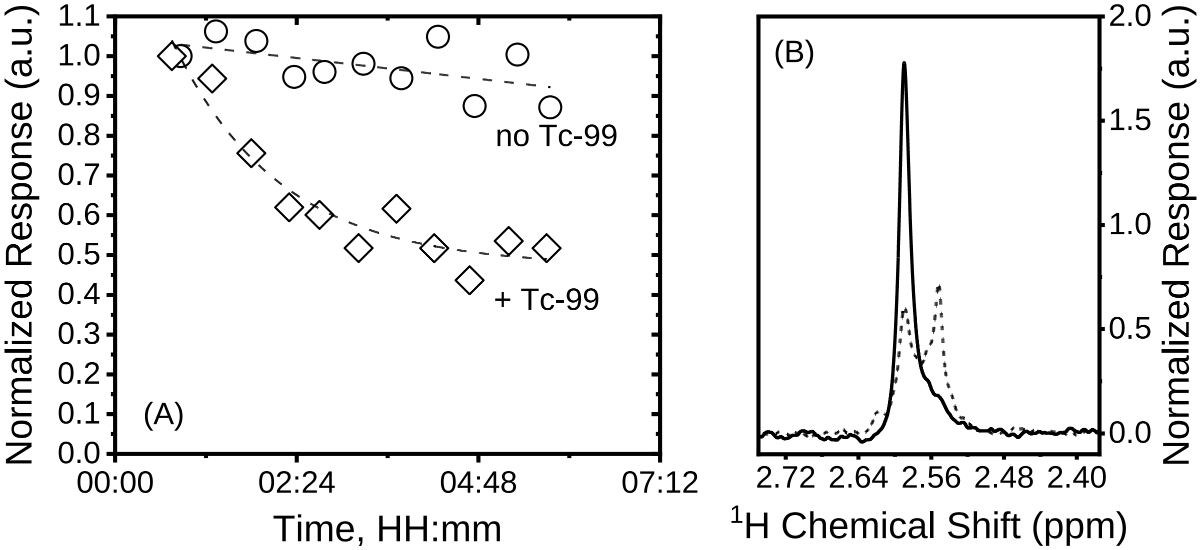

Figure 13. (A) Comparison of normalized ^1H NMR peak area for 0.050 mol L^{-1} Sdh in 2.08 mol L^{-1} DNO_3. (circle) no Tc added. (diamond) 0.003 mol L^{-1} Tc-99. (B) Evolution of ^1H NMR peak for Tc-containing mixture of Sdh. (—) t = 00:45, (·····) t = 05:12.

Tc-99 (Figure 14A). This is not observed for Eddg. The collected ^{1}H NMR data indicates Eddg is stable throughout, with and without presence of Tc.

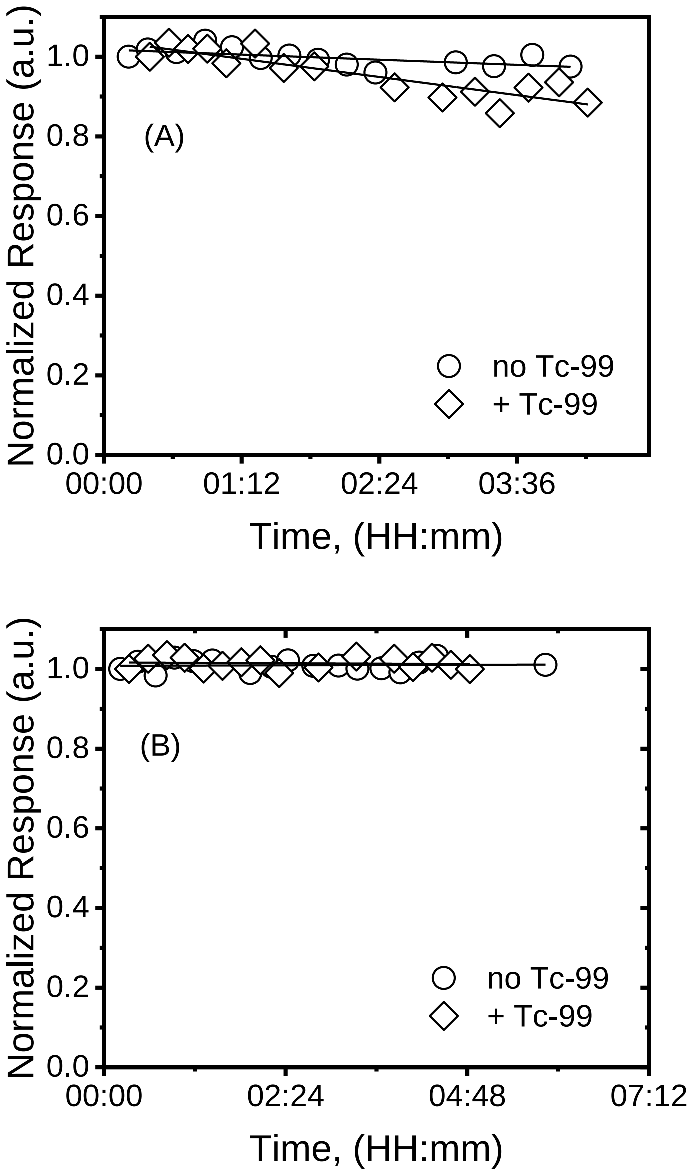

Figure 14. Time-dependent monitoring of normalized ^{1}H NMR peak area for (A) 0.026 mol L^{-1} Sdh and (B) 0.029 mol L^{-1} Eddg in 0.01 mol L^{-1} DNO_3. (circle) no Tc added, (diamond) 0.003 mol L^{-1} Tc-99.

The observed differences in the time-dependent ^{1}H NMR signatures of Sdh and Eddg support a conclusion that dihydrazide compounds are similar to hydrazine in its redox-based reactivity with technetium. The observed decomposition of Sdh can be attributed to its oxidation by Tc^{7+}. This autocatalytic process yields TcO_2, which is rejected by U·DEH*i*BA solvate and partitions back into aqueous environment in a liquid-liquid process. Figure 14B demonstrates the stability of guanidinium class of reagents as no changes are observed with or without Tc in solution. The lack of response to Tc presence suggests the observed dependence of Tc partitioning on Gn and Dag is guided by anion recognition due to ion-pair and hydrogen bond formation.

4. Conclusions

Effective management of pertechnetate anion must be a priority for single-cycle uranium recovery options at the back end of nuclear fuel cycle. The lower energy of hydration of this ion, relative to nitrate, drives its inclusion in uranium solvates of neutral solvent extraction reagents. Historically, for the PUREX process, scrubbing a loaded solvent with aqueous hydrazine inadvertently, but efficiently, diverted technetium away from uranium. Hydrazine is oxidized by heptavalent technetium in an autocatalytic process which results in the production of ammonium nitrate and nitrogen gas. This redox reaction yields a non-extractable tetravalent technetium. Liquid-liquid partitioning of technetium can also be influenced using anion recognition reagents. Molecular recognition of pertechnetate by aqueous complexants based on guanidinium moieties was compared to redox manipulation of technetium using dihydrazide reagents.

Solvent extraction, potentiometric and nuclear magnetic resonance spectroscopy studies were performed. The influence of guanidinium reagents on the liquid-liquid partitioning of technetium is less pronounced, relative to dihydrazides. As previously observed for hydrazine, strong impact exerted by dihydrazides originates from the technetium-catalyzed decomposition of such compounds which reduces technetium to a tetravalent, non-extractable state. Although this route of technetium management is very effective the destruction of dihydrazides is undesirable due to the formation of explosive ammonium nitrate and vigorous nitrogen gas generation. Guanidinium complexants show a more tempered influence on technetium. The effect on the liquid-liquid partitioning of pertechnetate is evident and likely guided by anion recognition due to ion-pair and hydrogen bond formation. Guanidiniums are stable in presence of technetium as evidenced by nuclear magnetic resonance studies. The steady state chemistry of guanidiniums identify this class of aqueous complexants as solid candidates for structure-function pertechnetate recognition studies.

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