RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2014, **4**, 27837

α-Dialkylamino *N,N*-diisobutylacetamides: a new class of anion exchanger with intramolecular buffering properties†

Shikha Sharma,[a] Sunil K. Ghosh,*[a] Anitha M[b] and Joti N. Sharma*[c]

A new class of ammonium based anion exchangers embedded with a terminal amide group, *viz.* α-dialkylamino *N,N*-diisobutylacetamides has been designed, synthesized and tested for their ability to extract oxometalate anions from nitric acid medium. As a representative example, the molybdate anion has been chosen for the present studies and its extraction behaviour was compared with routinely used anion exchangers like Alamine 336, Aliquat 336 and Primene JMT having no amide functionality. A higher %*E* value for molybdate was observed with α-dialkylamino *N,N*-diisobutylacetamides compared to Alamine 336, Aliquat 336 and Primene JMT, from the same HNO_3 acidity. The presence of amide group in the ligand is the key to the success of extraction from a relatively higher concentration of nitric acid medium. The amide group in the extractant leads to extra acidity through the intramolecular buffering effect thus enabling the ligand to extract the molybdate anion at higher acidities. Stoichiometry of the ion pair formed during extraction was ascertained by the slope analysis method. The composition of the complex was found to be $(LH)_2MoO_4 \cdot HNO_3$. FTIR and NMR of the loaded extractant indicated that MoO_4^{2-} is associated with the ammonium site while binding of HNO_3 occurred at the amide group.

Received 4th April 2014
Accepted 16th June 2014

DOI: 10.1039/c4ra03020f

www.rsc.org/advances

1. Introduction

Oxometalates such as MoO_4^{2-}, $Mo_7O_{24}^{6-}$, $H_2Mo_7O_{24}^{4-}$, $UO_2(CO_3)_3^{4-}$, $UO_2(SO_4)_3^{4-}$, TcO_4^- are usually present in various nuclear waste streams.[1,2] Amines are widely used as extractants for these kinds of anions.[2–12] Trioctylamine (TOA), a major component of Alamine 336 is known to extract oxometalates from nuclear waste by an anion-exchange mechanism.[13–17] Aliquat 336 and Primene JMT are also used for the same purpose.[13,18,19] A combination of kerosene and alcohols or ketones is usually used as the diluent with these amines.[20,21] While the extraction is based on anion exchange mechanism, the distribution ratio strongly depends on the concentration of cations, anions and acidity of the aqueous phase. Alamine 336 and other amine based anion exchangers works well at lower acidity but shows poor efficiency at higher acidity of aqueous phase.[2] Recently, imino analogs of TODGA (also known as iminodiamides), have been introduced as extractants for oxometalates from nitric acid medium.[22–24] The ether oxygen of TODGA has been replaced by secondary and tertiary imino groups which acts as the anion exchanger site. Some of them[24] have shown good extraction behavior for oxometalates even from higher nitric acid medium. However, the role of amide groups in these extractants has not been discussed.

It is known that the amide group in CMPO can suppress the effect of competing HNO_3 and retains its ability to work at higher acidity.[25,26] This behaviour is termed as intramolecular

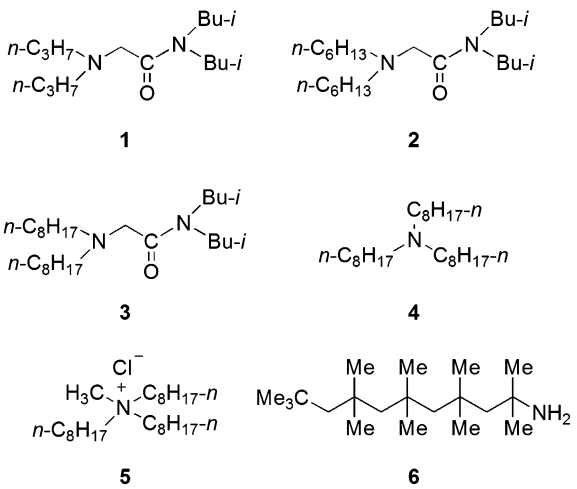


Fig. 1 Structure of α-dialkylamino *N,N*-diisobutylacetamides **1–3**, TOA (major component of Alamine 336) **4**, Aliquat 336 **5** and Primene JMT **6**.

[a]*Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. E-mail: ghsunil@barc.gov.in; Fax: +91-22-25505151; Tel: +91-22-25595012*

[b]*Rare Earths Development Section, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*

[c]*Nuclear Recycle Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. E-mail: jnsharma@barc.gov.in; Fax: +91-22-25505151; Tel: +91-22-25592959*

† Electronic supplementary information (ESI) available: See DOI: 10.1039/c4ra03020f

buffering effect.[27] Therefore, there is a need to evaluate the role of an adjunct amide group in an anion exchanger for oxometalate extraction. We speculated the buffering effect principle of amide group might be useful to design new class of anion exchangers having simpler structures like dialkylamino-monoamides that might work at higher HNO_3 concentrations. This paper describes the synthesis and extraction behaviour of α-dialkylamino *N*,*N*-diisobutylacetamides **1–3** (Fig. 1), a new class of ammonium based extractants embedded with a terminal amide group. The extraction behavior of these amides was compared with more commonly used anion exchangers like Alamine 336 **4**, Aliquat 336 **5** and Primene JMT **6** (Fig. 1) devoid of amidic groups.

2. Experimental

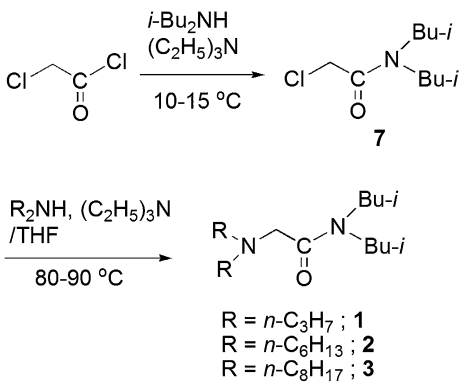
2.1 Chemicals

Nitric acid, *n*-dodecane and isodecyl alcohol (IDA) were obtained from local sources. Alamine 336, Aliquat 336, Primene JMT, diisobutylamine, dioctylamine, dihexylamine, dipropylamine, ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ and other chemicals used were of analytical grade. The solvents were dried and distilled from the indicated drying agents: THF from sodium/benzophenone; triethyl amine from CaH_2 and then stored over calcium metal. Analytical thin layer chromatography was performed using silica gel plates (about 0.5 mm) and column chromatography was performed using silica gel of 230–400 mesh. Characterization of synthesized compounds was done by ^{1}H NMR, ^{13}C NMR and elemental analyses.

2.2 Synthetic procedures for 1–3

α-Dialkylamino *N*,*N*-diisobutylacetamides **1–3** were synthesized in our laboratory as described in Scheme 1. For this, chloroacetyl chloride was reacted with diisobutylamine to give the amide **7** which was subsequently reacted with different dialkyl amines to give the desired α-dialkylamino *N*,*N*-diisobutylacetamides **1–3** in very good overall yields.

***N*,*N*-Diisobutylchloroacetamide (7).** A solution of diisobutylamine (525 μL, 1 equiv., 3 mmol) in dry CH_2Cl_2 (3 mL) was dropwise added to a stirred solution of chloroacetyl chloride (290 μL, 1.2 equiv., 3.6 mmol) in dry CH_2Cl_2 (6 mL) followed by dropwise addition of dry triethylamine (420 μL, 1 equiv., 3 mmol) at 10–15 °C. The reaction mixture was allowed to attain to room temperature and stirred for 24 h. The reaction mixture was diluted with water and extracted with ethyl acetate–petroleum ether mixture. The organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by distillation to give chloroacetamide **7** (523 mg, 85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.82–1.0 (12H, m, 2 × CH*Me*$_2$), 1.80–2.16 (2H, m, 2 × C*H* Me$_2$), 3.14 (2H, d, J = 7.6 Hz, NC*H*$_2$CH), 3.20 (2H, d, J = 7.6 Hz, NC*H*$_2$CH), 4.08 (2H, s, COC*H*$_2$Cl).



Scheme 1 Synthesis of α-dialkylamino *N*,*N*-diisobutylacetamides.

α-Dipropylamino *N*,*N*-diisobutylacetamide (1). Dipropylamine (20 mL, 3 equiv., 146 mmol) was added to a stirred solution of chloracetamide **7** (10 g, 1 equiv., 48.7 mmol) in dry THF (20 mL) and the solution was heated at 80 °C for 3 days. The reaction mixture was diluted with water and extracted with 10% ethyl acetate–petroleum ether. The combined organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was distilled to give α-dipropylamino *N*,*N*-diisobutylacetamide **1** (10.52 g, 80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.80–0.95 (18H, m, 6 × C*H*$_3$), 1.40–1.59 (4H, m, 2 × C*H*$_2$CH$_2$N), 1.82–2.07 (2H, m, 2 × C*H*Me$_2$), 2.53 (4H, t, J = 7.4 Hz, 2 × CH$_2$C*H*$_2$N), 3.16 (2H, d, J = 7.4 Hz, NC*H*$_2$CHMe$_2$), 3.27 (2H, d, J = 7.8 Hz, NC*H*$_2$CHMe$_2$), 3.35 (2H, s, C*H*$_2$CO). ^{13}C NMR (150 MHz, $CDCl_3$): δ 11.8, 19.9, 20.1 (4C), 26.1 (2C), 27.3 (2C), 52.5, 54.3, 56.1 (2C), 57.8, 171.1. Calcd. for $C_{16}H_{34}N_2O$; C, 71.06; H, 12.67; N, 10.36%; found: C, 71.16; H, 12.67; N, 10.46%.

α-Dihexylamino *N*,*N*-diisobutylacetamide (2). A mixture of chloracetamide **7** (1 g, 1 equiv., 4.87 mmol) and dihexylamine (1.42 mL, 1.25 equiv., 6.09 mmol) in triethylamine (3 mL) was heated at 90 °C for 20 h. The reaction mixture was diluted with water and extracted with 10% ethyl acetate–petroleum ether. The combined organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography to give amide α-dihexylamino *N*,*N*-diisobutylacetamide **2** (1.31 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.83–0.93 (18H, m, 6 × CH$_3$), 1.22–1.33 (12H, m, 6 × CH$_2$), 1.39–1.47 (4H, m, 2 × C*H*$_2$CH$_2$N) 1.86–1.95 (1H, m, C*H*Me$_2$), 1.96–2.05 (1H, m, C*H*Me$_2$), 2.48 (4H, t, J = 7.5 Hz, 2 × C*H*$_2$NCH$_2$CO), 3.16 (2H, d, J = 7.5 Hz, NC*H*$_2$CHMe$_2$), 3.28 (2H, s, C*H*$_2$CO), 3.29 (2H, d, J = 9 Hz, NC*H*$_2$CHMe$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9 (2C), 20.0 (2C), 20.2 (2C), 22.6, 26.2 (2C), 27.0 (2C), 27.2 (2C), 27.4, 31.8 (2C), 52.6, 54.4 (2C), 54.5, 57.7, 171.2. Calcd. for $C_{22}H_{46}N_2O$; C, 74.51; H, 13.07; N, 7.9%; found: C, 74.46; H, 13.0; N, 7.92%.

α-Dioctylamino *N*,*N*-diisobutylacetamide (3). A mixture of chloracetamide **7** (1 g, 1 equiv., 4.87 mmol) and di-*n*-octylamine (1.84 mL, 1.25 equiv., 6.09 mmol) in triethylamine (3 mL) was heated at 90 °C for 20 h. The reaction mixture was diluted with water and extracted with 8% ethyl acetate–petroleum ether. The combined organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography to give amide α-dioctylamino *N*,*N*-diisobutylacetamide **3** (1.46 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.83–0.96 (18H, m, 6 × C*H*$_3$), 1.20–1.34

(20H, m, 10 × CH_2), 1.39–1.48 (4H, m, 2 × CH_2CH_2N), 1.86–1.96 (1H, m, $CHMe_2$), 1.96–2.07 (1H, m, $CHMe_2$), 2.48 (4H, t, $J = 8$ Hz, 2 × CH_2NCH_2CO), 3.17 (2H, d, $J = 7.5$ Hz, NCH_2CHMe_2), 3.29 (2H, s, CH_2CO), 3.30 (2H, d, $J = 7.5$ Hz, NCH_2CHMe_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1 (2C), 20.1 (2C), 20.2 (2C), 22.6 (2C), 26.3, 27.1 (2C), 27.5, 27.6 (2C), 29.3 (2C), 29.6 (2C), 31.8 (2C), 52.7, 54.4 (2C), 54.5, 57.8, 171.3. Calcd. for $C_{26}H_{54}N_2O$; C, 76.03; H, 13.25; N, 6.82%; found: C, 76.07; H, 13.01; N, 6.72%.

2.3 Molybdenum feed solutions

Ammonium molybdate solutions were prepared by dissolving appropriate amount in nitric acid. Nitric acid concentration range of our extraction studies was 0.5–2.0 M, where molybdenum mainly exists as H_2MoO_4.[28] Quantitative determination of molybdenum was carried out using ICP-AES (inductively coupled plasma atomic emission spectrophotometry technique). Detection limit for molybdenum was 1 ppm. Error in molybdenum analysis was within ±5.0%.

2.4 Extraction studies

Prior to extraction experiments, organic phase containing the anion exchangers was pre equilibrated with equal volume of 0.5 M HNO_3 to minimize variation in nitric acid concentration during extraction. For determination of distribution ratio (D_{Mo}), organic phase was equilibrated with equal volume of aqueous phase containing molybdate anion for 1 h in a glass vial. All the extraction experiments were carried out in a thermostated water bath maintained at temperature 25 ± 1 °C. After phase separation by centrifugation, the organic and the aqueous phase was separated and the aqueous phase was analyzed for molybdenum concentration by ICP-AES after suitable dilutions. The concentration of molybdenum in the organic phase was calculated by mass balance. The distribution ratio D_{Mo} was determined as the ratio of metal concentration in organic phase to that in aqueous phase. Percentage extraction of metal ion was determined by equation:

$$\%E = (D_{Mo}/D_{Mo} + 1) \times 100 \quad (1)$$

Errors in D_M values were within ±5%. The nitric acid concentrations of aqueous and organic phases were determined by potentiometric titration with 0.1 M NaOH using a Metrohm 905 Titrando device.

3. Results and discussion

3.1 Extraction behavior of amines 1–6

A solution of 0.2 M each of extractants **1–6** dissolved in 30% IDA/*n*-dodecane was equilibrated with aqueous solution containing 450 mg L^{-1} molybdenum at varying nitric acid concentrations from 0.5 M to 2.0 M (Fig. 2). It can be seen that %*E* decreases with increase in nitric acid concentration for all the extractants, but the relative decrease in case of Alamine 336 **4**, Aliquat 336 **5** and Primene JMT **6** is much higher compared to acetamides **1–3**. At lower concentration of nitric acid, %*E* for Mo is similar and high for all the extractants except Primene JMT **6**.

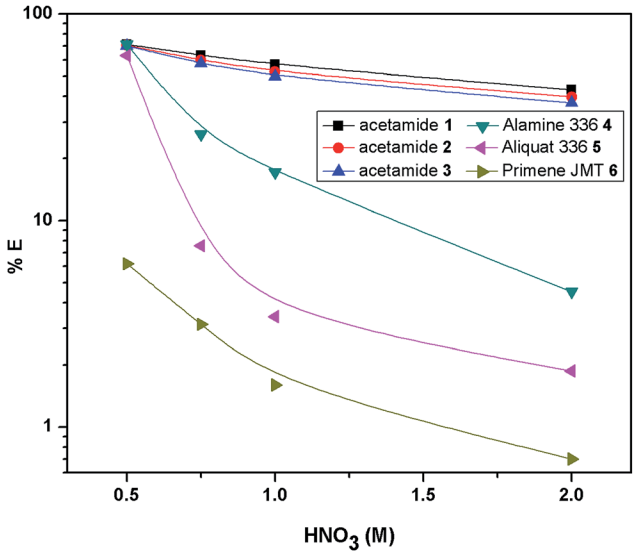


Fig. 2 %*E* for anion exchangers **1–6** at varying nitric acid concentrations.

But at higher concentrations of nitric acid, %*E* of Mo is much better for acetamides **1–3** compared to extractants **4–6**. This behavior can be explained by the presence of amidic group in acetamides **1–3**, which allowed retaining the extraction ability at high nitric acid medium by intramolecular buffering effect of amidic group. Acetamide **1** was chosen for further studies as it has shown better extraction behavior.

3.2 Determination of organic phase composition

Considering the polar nature of metal–ligand complex and their poor solubility in *n*-dodecane, IDA has been chosen as a phase modifier to mitigate the third phase formation.[29,30] In order to find out the most suitable solvent composition, extraction studies were carried out at different concentrations of phase modifier and acetamide **1**. Concentration of IDA was varied form 0–100% and acetamide **1** from 0.1–0.3 M (Fig. 3).

It was observed that with increase in IDA concentration in solvent, initially there was considerable increase in the D_{Mo} values for all extractant concentrations, but, remained unchanged beyond 30% IDA. From these observations, 0.2 M α-amino-acetamide **1** in 30% IDA/*n*-dodecane was chosen as the optimum organic phase composition for extraction studies.

3.3 Stoichiometry of the extracted metal complex

Nitric acid uptake is a common property exhibited by amidic extractants. α-Amino-acetamide **1**, having both the amine and amidic functional groups, also expected to show similar properties. Therefore, extraction of nitric acid by 0.2 M anion exchangers Alamine 336 and acetamide **1** in 30% IDA/*n*-dodecane was studied at different initial nitric acid concentrations (0.1–4.0 M). The acid concentration in the organic and aqueous phase was estimated by potentiometric titration with 0.1 M NaOH. The variation of $[HNO_3]_{org}$ as a function of initial aqueous nitric acid concentration is depicted in Fig. 4.

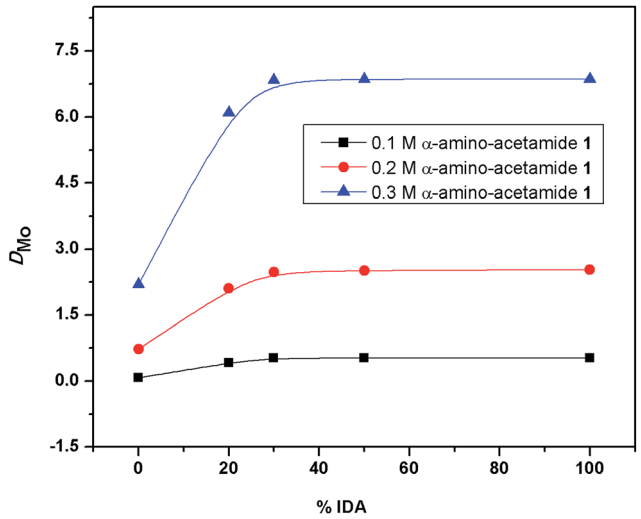


Fig. 3 Variation in D_{Mo} with IDA concentration at 0.5 M nitric acid.

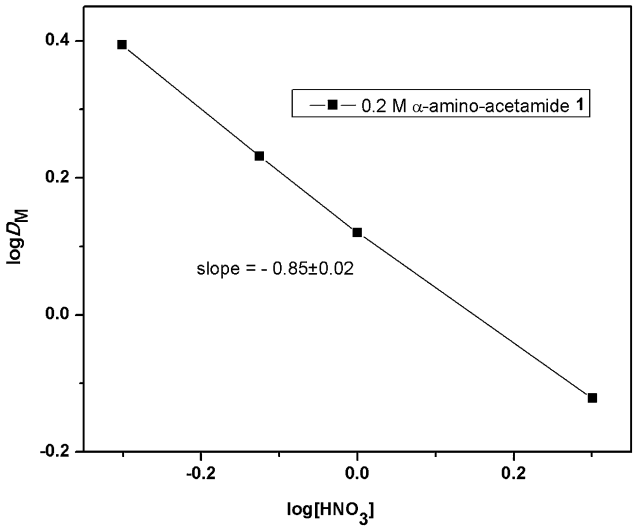


Fig. 5 Dependency of D_{Mo} on concentration of HNO_3.

For α-amino-acetamide **1**, the ratio of $[HNO_3]_{org}$ to [acetamide **1**] increases from 1 : 1 to 2 : 1 as the aqueous nitric acid concentration increases from 0.5 M to 4.0 M. At 0.5 M HNO_3 all the ammonium site of α-amino-acetamide **1** is protonated by HNO_3 and shows 1 : 1 composition, above it the amide group of α-amino-acetamide **1** starts taking up of nitric acid, partial protonation of amide group was seen at 2 M HNO_3 and complete protonation was observed at 4 M HNO_3. The above findings also indicate that during pre-equilibration with 0.5 M nitric acid the species formed in the organic phase is $L{\cdot}HNO_3$.

As evident from the Fig. 4, the ratio of $[HNO_3]_{org}$ to [Alamine 336] is 1 : 1 while that of α-amino-acetamide **1** it was 1.5 : 1 in the range of 0.5 to 2 M aqueous phase HNO_3 concentration and finally 2 : 1 above 4 M nitric acid.

The effect of HNO_3 on the D_{Mo} was established for nitric acid concentration varying from 0.5 M to 2 M (Fig. 5). The plot of log D_{Mo} *vs.* log[HNO_3] is a straight line with a slope of -0.85 ± 0.02 indicating participation of one molecule of nitric acid in the extraction process.

The stoichiometry of extracted complex with respect to α-amino-acetamide **1** (L) was determined by plotting variation of D_{Mo} as a function of concentration of **1** (Fig. 6). It was observed that D_{Mo} values increases with an increase in the concentration of **1**. The plots are straight line with slops of 2.34 ± 0.05 and 2.04 ± 0.02 for 0.5 M and 2 M HNO_3, respectively. The results indicate that in the range of 0.5 to 2 M HNO_3 concentrations, the metal ligand composition in the organic phase is $(LH)_2MoO_4{\cdot}HNO_3$ (Fig. 7).

Based on the above findings the anion exchange process in the acid range 0.5 to 2 M HNO_3 may be represented as

$$H_2MoO_{4(aq)} + 2L{\cdot}HNO_{3(org)} \leftrightarrows (LH)_2MoO_4{\cdot}HNO_{3(org)} + HNO_{3(aq)} \quad (2)$$

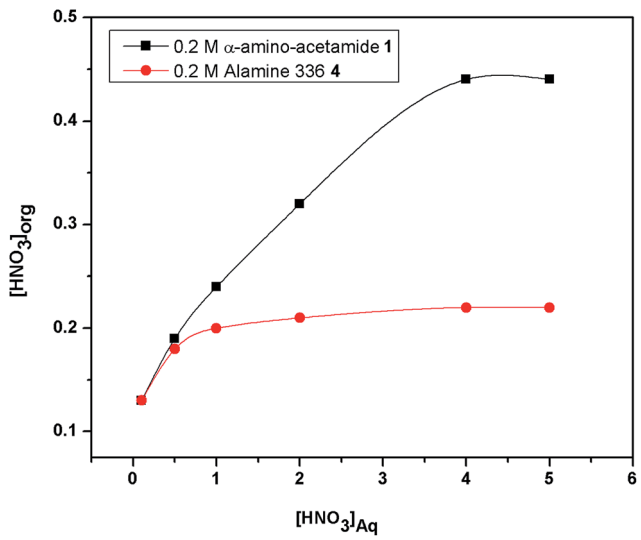


Fig. 4 Extraction of HNO_3 from aqueous solution by 0.2 M α-amino-acetamide **1** or Alamine 336 **4**.

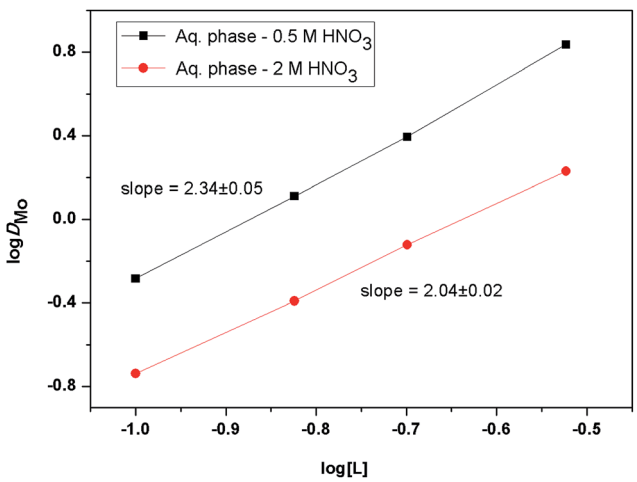


Fig. 6 Dependency of D_{Mo} on concentration of α-amino-acetamide **1** (0.1–0.3 M) at different aqueous phase HNO_3 acidity.

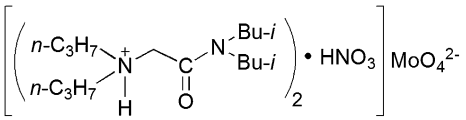


Fig. 7 Extracted metal–ligand complex in the organic phase.

The above complexation was further supported by FTIR and ^{1}H-NMR studies. FTIR of loaded organic indicated binding of HNO_3 at amide group as evidenced by lowering of $\nu_{C=O}$. The value of $\nu_{C=O}$ of the organic phase was 1639 cm^{-1} before contact to aqueous phase. After contact with 450 mg L^{-1} Mo in 1 M HNO_3, a shoulder for $\nu_{C=O}$ at 1554 cm^{-1} appeared in addition to the 1639 cm^{-1} peak (Fig. 8). This lowering in $\nu_{C=O}$ can be attributed to coordination of HNO_3 to the amide C=O.

To ascertain the binding site for Mo, organic phase containing 0.2 M α-amino-acetamide **1** in 30% IDA/*n*-dodecane was saturated with metal ion by giving sufficient number of contacts with fresh 1 M HNO_3 aqueous phase containing 450 mg L^{-1} of Mo. The resultant yellow precipitate of metal ligand complex in the organic phase was filtered and the residue was washed with chloroform. While recording ^{1}H NMR of the solution of the complex in $CDCl_3$, a downfield shift of δ values and broadening of the peaks corresponding to CH_2 α-to amine group *viz.* 2.53 (4H, t, J = 7.4 Hz, 2 × CH_2CH_2N) *vs.* 2.71–2.95 (4H, brs, 2 × CH_2CH_2N) and 3.35 (2H, s, CH_2CO) *vs.* 3.6–3.78 (2H, brs, CH_2CO) are clearly discernable indicating the exchange of MoO_4^{2-} at ammonium site (Fig. 9).

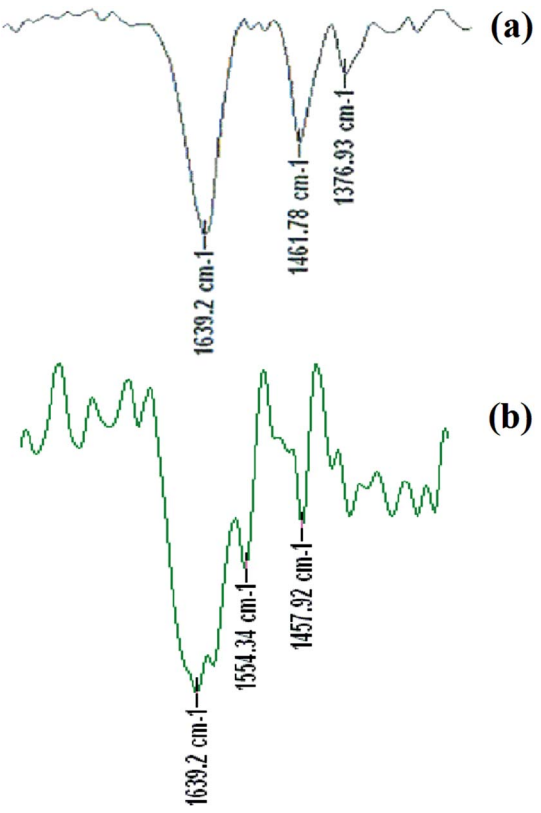


Fig. 8 IR spectra of organic phase: (a) before contact; (b) loaded organic phase.

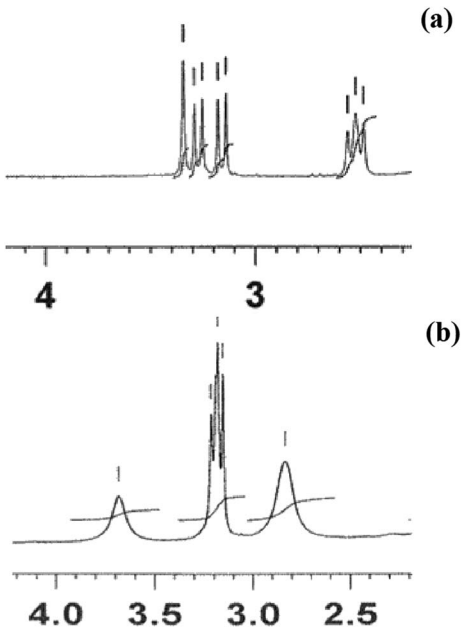


Fig. 9 (a) ^{1}H NMR of α-amino-acetamide **1**; (b) ^{1}H NMR of complex of MoO_4^{2-} with α-amino-acetamide **1**.

3.4 Back extraction studies

For back extraction studies the organic phase 0.2 M α-amino-acetamide **1** in 30% IDA/*n*-dodecane was equilibrated with aqueous phase containing 450 mg L^{-1} of Mo dissolved in 0.5 M nitric acid. Loaded organic phase was contacted with 10% NH_3 solutions. It was observed that 10% NH_3 is suitable for 90% recovery of molybdenum from loaded organic phase after three contacts.

4. Conclusions

In conclusion, α-amino-acetamides have been designed and synthesized as a new class of anion exchangers to extract molybdate anions from higher nitric acid medium. These acetamides showed better extraction behavior compared to the conventional only amine-based anion exchangers, Alamine 336, Aliquat 336 and Primene JMT. The presence of amide group was critical to this success because of its intramolecular buffering effect. This study has highlighted the exact role of the amide group in retaining the extraction ability at higher acidities. Stoichiometry of metal ligand complex was ascertained by slope analysis method and was found to be $(LH)_2MoO_4 \cdot HNO_3$. FTIR and NMR of loaded organic indicated MoO_4^{2-} exchanged at ammonium site while buffering effect takes place at amide group.

References

1 F. Poineau, J. D. Mazaubrun, D. Ford, J. Fortner, J. Kropf, G. W. C. Silva, N. Smith, K. Long, G. Jarvinen and K. Czerwinski, *Radiochim. Acta*, 2008, **96**, 527.
2 R. Shanker and K. S. Venkateswarlu, *Sep. Sci.*, 1976, **11**, 591.

3 P. K. Parhi, K. H. Park, H. I. Kim and J. T. Park, *Hydrometallurgy*, 2011, **105**, 195.
4 J. Marchese, F. Valenzuela, C. Basualto and A. Acosta, *Hydrometallurgy*, 2004, **72**, 309.
5 J. Y. Lee, J. R. Kumar, H. S. Jeon and J. S. Kim, *Chem. Eng.*, 2010, **54**, 27.
6 L. E. Noronha, G. S. Kamble, S. S. Kolekar and M. A. Anuse, *Radiochim. Acta*, 2013, **3**, 15.
7 J. R. Kumar, J. S. Kim, J. Y. Lee and H. S. Yoon, *J. Radioanal. Nucl. Chem.*, 2010, **285**, 301.
8 C. J. Kim, J. R. Kumar, J. S. Kim, J. Y. Lee and H. S. Yoon, *J. Braz. Chem. Soc.*, 2012, **23**, 1254.
9 N. I. Gerhardt, A. A. Palant, V. A. Petrova and R. K. Tagirov, *Hydrometallurgy*, 2001, **60**, 1.
10 R. R. Rao and S. M. Khopkar, *Analyst*, 1983, **108**, 346.
11 V. R. Bhandiwad, R. Swarup and S. K. Patil, *J. Radioanal. Nucl. Chem.*, 1979, **52**, 5.
12 M. Ghadiri, S. N. Ashrafizadeh and M. Taghizadeh, *Hydrometallurgy*, 2014, **144–145**, 151.
13 E. A. Mezhov, V. V. Druzhenkov and A. N. Sirotinin, *Radiochemistry*, 2002, **44**, 146.
14 D. Desideri, L. Feduzi, M. A. Meli and C. Roselli, *Microchem. J.*, 2011, **97**, 264.
15 H. Ramebäck, Y. Albinsson, M. Skålberg, U. B. Eklund, L. Kjellberg and L. Werme, *J. Nucl. Mater.*, 2000, **277**, 208.
16 A. Senol, *Sep. Purif. Technol.*, 2014, **131**, 35.
17 Y. Xu, S. Y. Kim, T. Ito, H. Tokuda, K. Hitomi and K. Ishii, *J. Chromatogr. A*, 2013, **1312**, 37.
18 P. Nekovář and D. Schrötterová, *Chem. Eng. J.*, 2000, **79**, 229.
19 P. Neková[rbreve] and D. Schrötterová, *Solvent Extr. Ion Exch.*, 1999, **17**, 163.
20 T. Cosar and R. Ziyadanogullari, *Turk. J. Chem.*, 1998, **22**, 379.
21 E. Goralska, M. T. Coll, A. Fortuny, C. S. Kedari and A. M. Sastre, *Solvent Extr. Ion Exch.*, 2007, **25**, 65.
22 M. C. Ali, T. Kawasaki, M. Nogami, M. Saeki, Y. Sasaki and Y. Ikeda, *Prog. Nucl. Energy*, 2011, **53**, 1005.
23 M. C. Ali, T. Suzuki, Y. Tachibana, Y. Sasaki and Y. Ikeda, *Sep. Purif. Technol.*, 2012, **92**, 77.
24 Y. Sasaki, M. Ozawa, T. Kimura and K. Ohashi, *Solvent Extr. Ion Exch.*, 2009, **27**, 378.
25 E. P. Horwitz, A. C. Muscatello, D. G. Kalina and L. Kaplan, *Sep. Sci. Technol.*, 1981, **16**, 417.
26 E. P. Horwitz, K. A. Martin, H. Diamond and L. Kaplan, *Solvent Extr. Ion Exch.*, 1986, **4**, 449.
27 V. Kumar, J. N. Sharma, P. V. Achuthan and R. C. Hubli, *RSC Adv.*, 2014, **4**, 805.
28 M. A. Olazabal, M. M. Orive, L. A. Fernández and J. M. Madariaga, *Solvent Extr. Ion Exch.*, 1992, **10**, 623.
29 A. S. Kertes, in *Solvent extraction chemistry of metals*, ed. H. A. C. McKey, T. V. Healy, I. L. Jetkins and A. Naylor, MacMillan, London, 1965, p. 377.
30 A. Keshav, K. L. Wasewar, S. Chand and H. Uslu, *Fluid Phase Equilib.*, 2009, **275**, 21.

