

FTIR Spectra of *N,N,N',N'*-Tetraoctyl Diglycolamide Complex in Room Temperature Ionic Liquids

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The interaction of an octyl derivative of diglycolamide extractant complex in three different types of room temperature ionic liquids (RTILs) was studied by ATR-FTIR spectroscopic method. The shift in stretching vibrational frequencies for the functional groups (C=O and C-O) in the nitrate ion-extractant complexes and metal ion-extractant complexes in room temperature ionic liquids namely, 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([C₄mim][NTf₂]), 1-butyl-1-methylpyrrolidinium *bis*(trifluoromethanesulfonyl)imide ([C₄mpyr][NTf₂]) and 1-butyl-1-methylpiperidinium *bis*(trifluoromethanesulfonyl)imide ([C₄mpip][NTf₂]) was compared. These results were also compared with that obtained for molecular diluent system, *n*-dodecane.

Keywords: FTIR, Ionic liquid, Europium, TODGA, Complex.

INTRODUCTION

Room temperature ionic liquids (RTILs) have been investigated for various applications such as separation technology [1], catalysis [2] and electrochemistry [3], *etc.* Moreover, in the past few decades, RTILs are being extensively studied as diluents for the separation of actinides and fission products and it would be expected to change the physical and chemical properties of organic phase [4]. Generally, RTIL based extractant system provides superior extraction of metal ions as compared to the molecular diluent based system. Even a small concentration of extractant dissolved in ionic liquid is sufficient to extract of the target metal ions [5]. Actually, imidazolium based ionic liquids have been studied broadly as diluents for metal ion extraction as compared to the other ionic liquid (IL) diluents based on pyrrolidinium and piperidinium cations, *etc.*

In recent past, *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) has been studied greatly in molecular diluent (*n*-dodecane) medium for the nuclear fuel cycle applications [6-9]. But, disadvantage of this extractant in molecular diluent is third phase formation [10,11]. But when we use ionic liquid instead of molecular diluent, third phase could be avoided. Recently, we have reported the extraction of Eu(III) in TODGA/ [C₈mim][NTf₂] and no third phase formation was

noticed even at high metal ion loading condition ([Eu(III)] = ~ 100 g/L) [12].

Fourier transform infrared (FTIR) spectroscopy could be used to investigate the nature of the complex. In this study, we wish to report the complexation in room temperature ionic liquids (RTILs) based systems. Hence, the spectroscopic changes of TODGA complex in imidazolium, pyrrolidinium and piperidinium cations based RTILs have been analyzed. Generally, the concentration of nitric acid in nuclear waste could vary from 3 to 4 M and trivalent metal ion concentration could vary from 0.5 g/L to 3 g/L. Hence in the present study, we used 15 g/L of Eu(III) ion solution in 3 M HNO₃.

EXPERIMENTAL

The chemicals used in the present study were of analytical grade. 1-Methyl-3-butylimidazolium *bis*(trifluoromethanesulfonyl)imide ([C₄mim][NTf₂]) [13], 1-butyl-1-methylpyrrolidinium *bis*(trifluoromethanesulfonyl)imide ([C₄mpyr][NTf₂]), 1-butyl-1-methylpiperidinium *bis*(trifluoromethanesulfonyl)imide ([C₄mpip][NTf₂]) [14] and *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) [11] were prepared by the reported procedure as described elsewhere. Eu(NO₃)₃ solution was prepared by dissolving Eu₂O₃ in concentrated nitric acid. Structure of ionic

liquids and TODGA used in this present study are shown in Fig. 1.

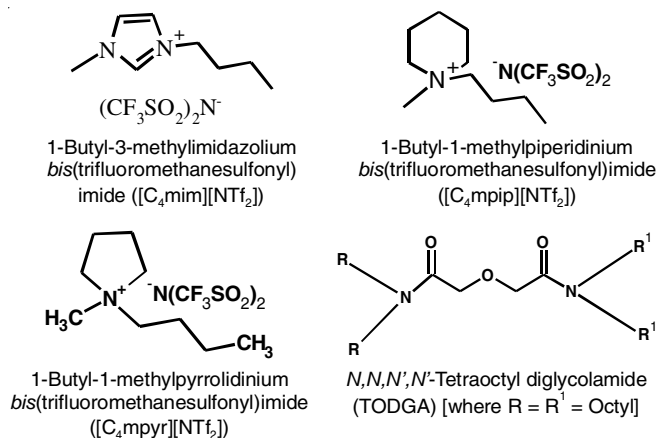


Fig. 1. Structures of ionic liquids and extractant

Procedure for equilibration and recording ATR-FTIR spectrum:

The infrared spectrum of the sample was recorded using BRUKER TENSOR II FT-IR spectrometer containing an ATR (attenuated total reflectance) diamond crystal. Ionic liquid phase (0.01 M TODGA/ $[\text{C}_4\text{mim}][\text{NTf}_2]$ or 0.01 M TODGA/ $[\text{C}_4\text{mpyr}][\text{NTf}_2]$ or 0.01 M TODGA/ $[\text{C}_4\text{mpip}][\text{NTf}_2]$ or 0.01 M TODGA in *n*-dodecane) was equilibrated with 3 M nitric acid (with and without Eu(III)). Equilibration experiments were performed by the mixing of each 1 mL of aqueous and ionic liquid phases in a 10 mL capacity test-tube immersed in a constant temperature water bath. The tubes were rotated in upside down manner for about 1 h. After equilibration, it was allowed for clear separation of ionic liquid and aqueous phases. Few drops of ionic liquid phase were collected to record IR spectrum.

RESULTS AND DISCUSSION

ATR-FTIR spectrum of prepared ionic liquids and extractant:

The ATR-FTIR spectra of neat ionic liquids ($[\text{C}_4\text{mim}][\text{NTf}_2]$, $[\text{C}_4\text{mpyr}][\text{NTf}_2]$, $[\text{C}_4\text{mpip}][\text{NTf}_2]$) and *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) are shown in Fig. 2. The spectrum

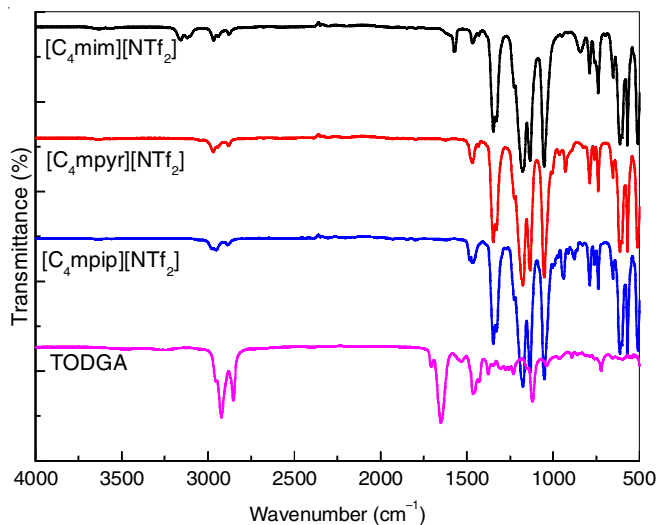


Fig. 2. ATR-FTIR spectra of neat ionic liquids and TODGA

of neat TODGA shows a stretching frequency band at 1651 and 1122 cm^{-1} , which corresponds to C=O and etheric C-O group respectively [13]. The FTIR spectrum of neat TODGA and TODGA in ionic liquids are shown in Fig. 3. A solution of 0.01 M TODGA dissolved in ionic liquids also shows the band of

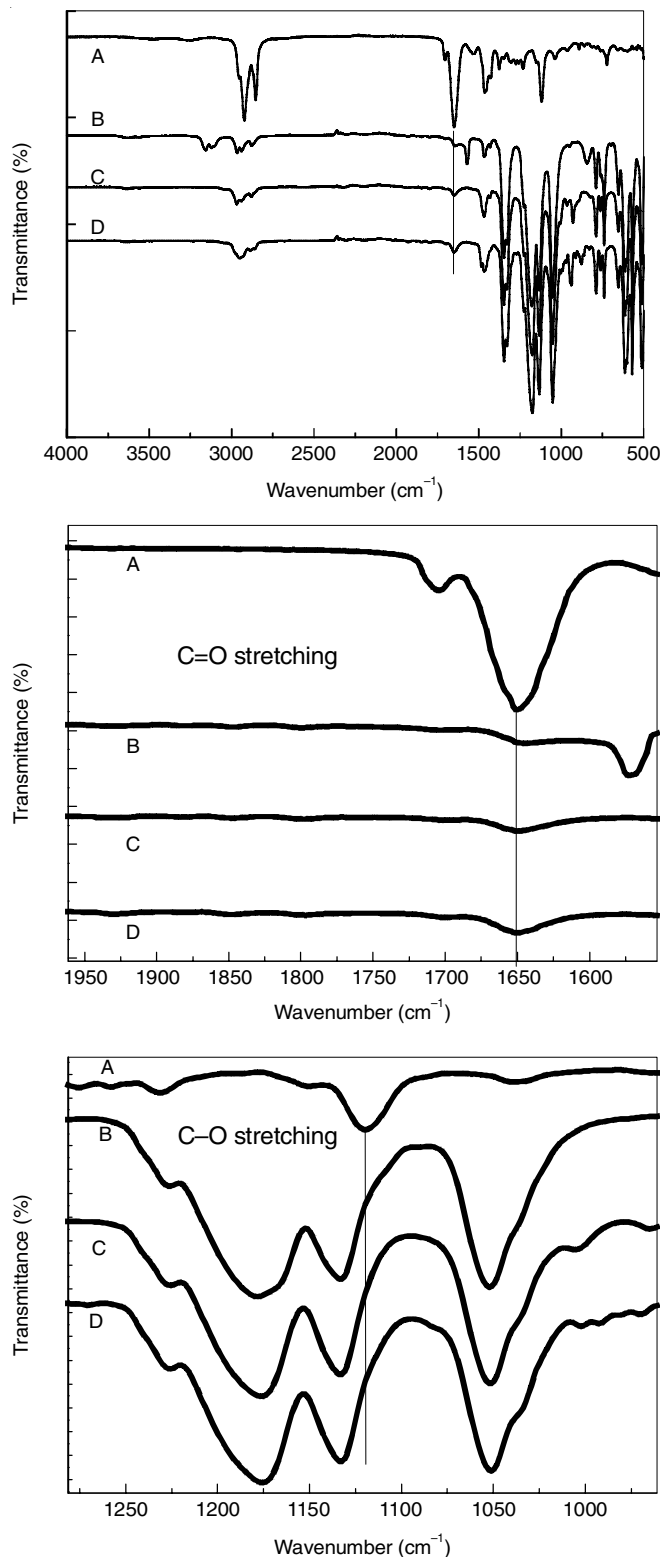


Fig. 3. ATR-FTIR spectra of neat extractant and ionic liquid containing extractant (A) neat TODGA, (B) TODGA in $[\text{C}_4\text{mim}][\text{NTf}_2]$, (C) TODGA in $[\text{C}_4\text{mpyr}][\text{NTf}_2]$, (D) TODGA in $[\text{C}_4\text{mpip}][\text{NTf}_2]$. $[\text{TODGA}] = 0.01 \text{ M}$. The initial position of band is noted by vertical dash in the figure

amidic C=O (1651 cm^{-1}) group with reduced intensity because of dilution. But for etheric C-O group (1122 cm^{-1}), no band was seen after diluting the TODGA with ionic liquid and it could be due to the merging with the neighbouring transmittance bands of ionic liquids.

ATR-FTIR spectra of TODGA/[C₄mim][NTf₂], TODGA/[C₄mpyr][NTf₂] and TODGA/[C₄mpip][NTf₂] contacted with nitric acid: Figs. 4-7 show the ATR-FTIR spectra of ionic liquid based extractant phase, TODGA/[C₄mim][NTf₂], TODGA/[C₄mpyr][NTf₂] and TODGA/[C₄mpip][NTf₂] recorded after contacting the ionic liquid phase with 3 M nitric acid. It can be seen that after equilibrating TODGA/IL phase with 3 M HNO₃, there is a change in position of transmittance band of C=O group from 1651 cm^{-1} to 1615 cm^{-1} , 1625 cm^{-1} , 1629 cm^{-1} for the systems, TODGA/[C₄mim][NTf₂], TODGA/[C₄mpyr][NTf₂] and TODGA/[C₄mpip][NTf₂], respectively (red shift). The reason for this shift could be attributed due to the protonation of amidic C=O group in TODGA by the extraction of nitric acid in ionic liquid phase from aqueous phase [15,16]. Recently, Prathibha *et al.* [15] reported the FTIR spectra of TODGA/*n*-dodecane system containing modifiers, dihexyl-octanamide (DHOA) and *n*-octanol after the extraction of nitric acid and there was a shift in the stretching vibration band of C=O from 1651 cm^{-1} to 1643 cm^{-1} for 0.2 M TODGA-0.5 M DHOA/*n*-dodecane and 1659 cm^{-1} to 1643 cm^{-1} for 0.2 M TODGA-*n*-octanol/*n*-dodecane system [15]. In the present study, we have compared the acid equilibrated 0.01 M TODGA/IL systems with acid equilibrated 0.01 M TODGA/*n*-dodecane system (Fig. 4). The etheric group transmittance band shifted from 1122 to 1080 cm^{-1} . But for TODGA/IL systems, etheric group band was not seen. A very small hump of C=O group transmittance band for acid equilibrated 0.01 M TODGA/*n*-dodecane system was observed (1635 cm^{-1}). It is noted that the red shift of C=O group transmittance band in TODGA/IL systems is more than that in TODGA/*n*-dodecane. It indicates that ionic liquid based

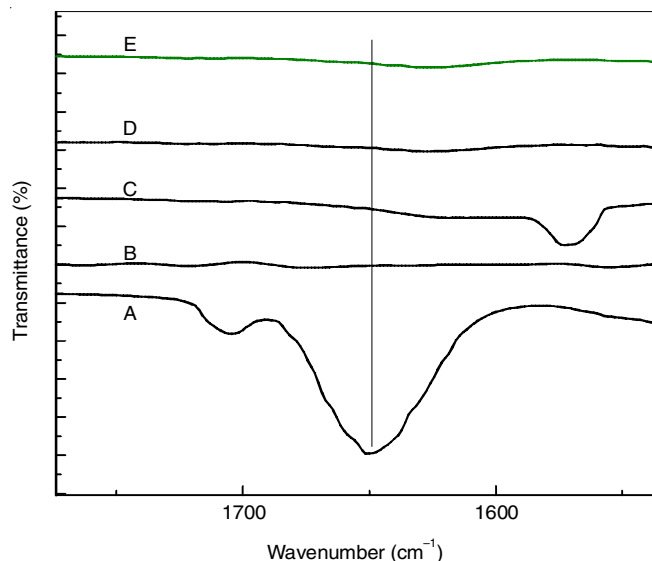


Fig. 4. ATR-FTIR spectra of TODGA/IL systems and TODGA/*n*-dodecane system recorded after contacting with 3 M nitric acid solution, (A) Neat TODGA, (B) 0.01 M TODGA in *n*-dodecane, (C) 0.01 M TODGA in [C₄mim][NTf₂], (D) 0.01 M TODGA in [C₄mpyr][NTf₂], (E) 0.01 M TODGA in [C₄mpip][NTf₂]. The initial position of band is noted by vertical dash in the figure

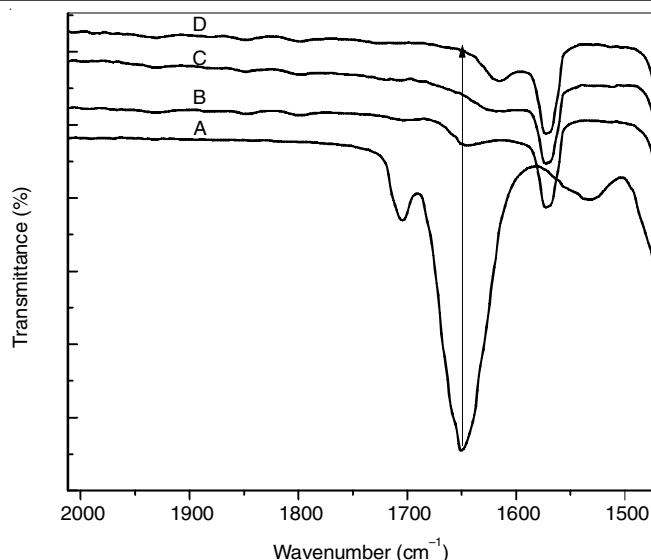


Fig. 5. ATR-FTIR spectra of TODGA/[C₄mim][NTf₂] system recorded after contacting the ionic liquid phase with nitric acid solution in the presence and absence of Eu(III) ion, (A) TODGA neat, (B) TODGA/[C₄mim][NTf₂], (C) acid equilibrated TODGA/[C₄mim][NTf₂], Aq: 3 M HNO₃, (D) Eu(III) loaded TODGA/[C₄mim][NTf₂], Aq: 3 M HNO₃. The initial position of band is noted by vertical dash in the figure

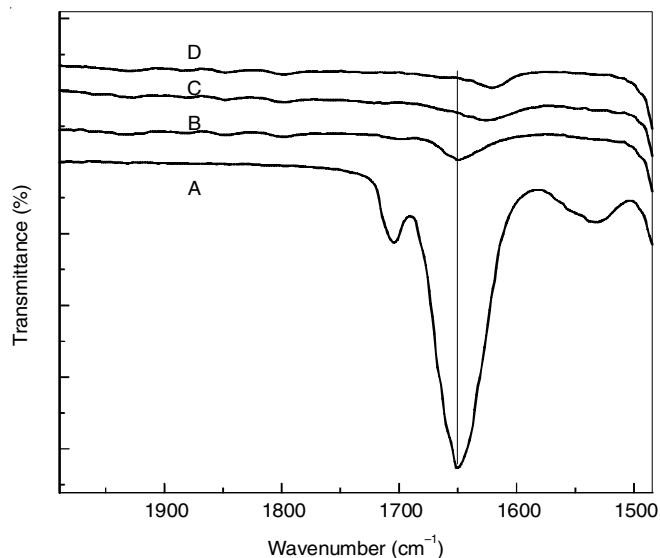


Fig. 6. ATR-FTIR spectra of TODGA/[C₄mpyr][NTf₂] system recorded after contacting the ionic liquid phase with nitric acid solution in the presence and absence of Eu(III) ion, (A) TODGA neat, (B) TODGA/[C₄mpyr][NTf₂], (C) acid equilibrated TODGA/[C₄mpyr][NTf₂], Aq: 3 M HNO₃, (D) Eu(III) loaded TODGA/[C₄mpyr][NTf₂], Aq: 3 M HNO₃. The initial position of band is noted by vertical dash in the figure

system shows more tendency towards the complexation with nitrate ion.

ATR-FTIR spectra of TODGA/[C₄mim][NTf₂], TODGA/[C₄mpyr][NTf₂] and TODGA/[C₄mpip][NTf₂] systems contacted with nitric acid containing Eu(III) ion: The FTIR spectra of 0.01 M TODGA/IL phases were recorded after contacting the ionic liquid phase with 3 M nitric acid solution containing Eu(III) ion (Figs. 5-7). It is noted that there is a red shift of C=O group transmittance bands from 1651 to 1614 , 1620 and 1623 cm^{-1} due to the formation of Eu(III)-TODGA

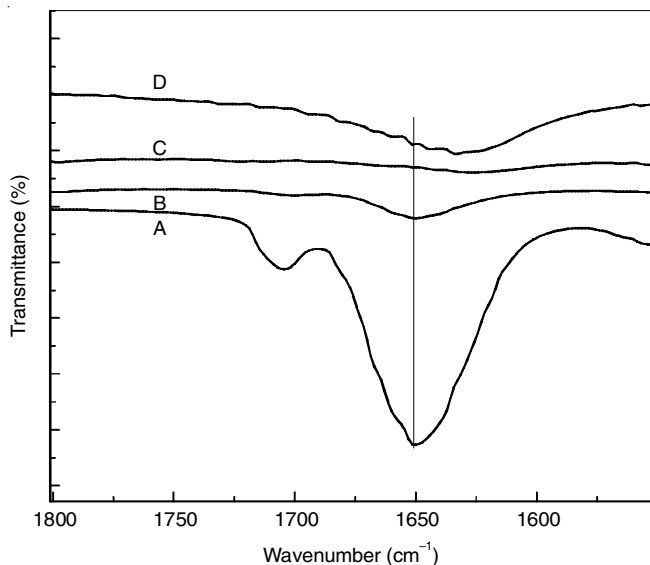


Fig. 7. ATR-FTIR spectra of TODGA/[C₄mpip][NTf₂] system recorded after contacting the ionic liquid phase with nitric acid solution in the presence and absence of Eu(III) ion, (A) TODGA neat, (B) TODGA/[C₄mpip][NTf₂], (C) acid equilibrated TODGA/[C₄mpip][NTf₂], Aq: 3 M HNO₃, (D) Eu(III) loaded TODGA/[C₄mpip][NTf₂], Aq: 3 M HNO₃

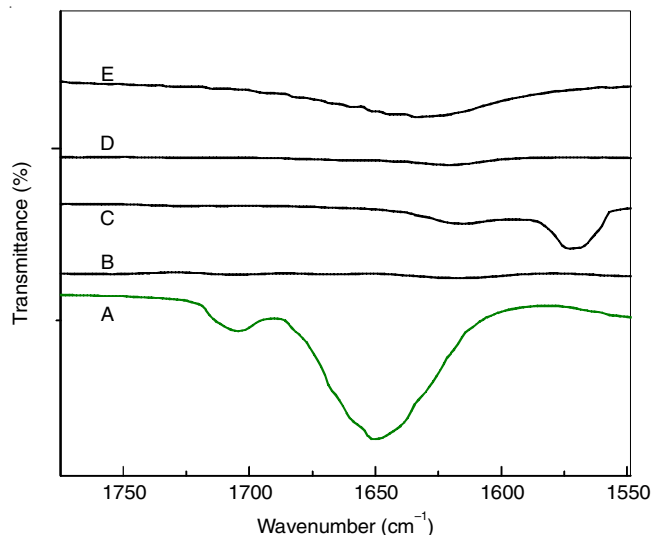


Fig. 8. ATR-FTIR spectra of TODGA/IL and TODGA/*n*-dodecane system recorded after contacting with nitric acid solution in the presence of Eu(III) ion, (A) TODGA neat, (B) Eu(III) loaded in 0.01 M TODGA/*n*-dodecane, (C) Eu(III) loaded in 0.01 M TODGA/[C₄mim][NTf₂], (D) Eu(III) loaded in 0.01 M TODGA/[C₄mpyr][NTf₂], (E) Eu(III) loaded in 0.01 M TODGA/[C₄mpip][NTf₂]; Aqu: 3 M HNO₃

complex in [C₄mim][NTf₂], [C₄mpyr][NTf₂] and [C₄mpip][NTf₂], respectively. It is noted that the red shift in imidazolium system is slightly more as compared to the pyrrolidinium and piperidinium ionic liquids based system. It indicates that there is more complexation of Eu(III) ion with TODGA in imidazolium ionic liquid as compared to piperidinium and pyrrolidinium ionic liquid based systems. Prathibha *et al.* [15] reported the red shift of carbonyl band from 1651 cm⁻¹ to 1614 cm⁻¹ due to the complexation of Nd(III) with TODGA in *n*-dodecane [15,16]. In the present study, we have compared Eu(III) loaded 0.01 M TODGA/IL systems with Eu(III) loaded 0.01 M TODGA/*n*-dodecane system (Fig. 8). The shift of C=O band due to the TODGA-metal complex in ionic liquid system is comparable with *n*-dodecane system (1615 cm⁻¹) but intensities of C=O band in ionic liquids are higher than that of *n*-dodecane system. Hence, it indicates that the complexation of TODGA with Eu(III) in ionic liquid systems is more than that in *n*-dodecane system. Even a small quantity of extractant plays significant role in the complexation. These results are in accordance with the distribution ratio obtained for Eu(III) ion in room temperature ionic liquid (RTIL) and *n*-dodecane systems. Recently, we have reported the extraction of Eu(III) using TODGA/[C₃mim][NTf₂] system and it was observed that though the concentration of TODGA employed in ionic liquid system is an order (0.01 M) less than that employed in *n*-dodecane system (0.1 M), % extraction of Eu(III) in ionic liquid and *n*-dodecane systems were comparable (> 90 %) (Table-1) [12].

Conclusion

ATR-FTIR spectra of *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) in three different ionic liquid systems ([C₄mim][NTf₂], [C₄mpyr][NTf₂] and [C₄mpip][NTf₂]) have been investigated after contacting with 3 M HNO₃ in the presence and absence of Eu(III) ion. Red shift in amidic C=O stretching bands of TODGA was observed. The results obtained for three ionic

TABLE-1
COMPARISON OF PERCENTAGE EXTRACTION OF Eu(III) ION IN 0.1 M TODGA/*n*-DD AND 0.01 M TODGA/[C₃mim][NTf₂]

[HNO ₃] (M)	Eu(III) extraction (%) [Ref. 12]	
	0.1 M TODGA in <i>n</i> -DD	0.01 M TODGA in [C ₃ mim][NTf ₂]
0.1	4.76	99.8
0.5	90.9	99.7
1.0	99.0	99.4
2.0	99.2	96.9
3.0	99.3	95.0
4.0	99.3	92.3

liquid systems have been compared and it was noted that imidazolium ionic liquid based system has more red shift for TODGA complex as compared to other two ionic liquid systems. This could be attributed due to the formation of more stable Eu(III)-complex in [C₄mim][NTf₂] compared to [C₄mpyr][NTf₂] and [C₄mpip][NTf₂] systems. The shift in C=O stretching bands observed for metal complex in TODGA/IL systems are comparable with that observed for TODGA/*n*-dodecane system but the intensities of the bands are more in ionic liquid systems than that of *n*-dodecane system. This could be attributed due to the formation of stable metal complex in ionic liquid system. Even a small concentration of TODGA in ionic liquid systems plays a significant role and these results are in accordance with the extraction results of Eu(III).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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