Physicochemical and radiolytic degradation properties of dihexyloctanmide-imidazolium ionic liquid

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A B S T R A C T

N,N-dihexyloctanmide (DHOA) in ionic liquid medium has been proposed for the solvent extraction of actinides from nitric acid solutions. This paper reports the physicochemical and hydrodynamic properties of the solvent system containing N,N-dihexyloctanmide (DHOA) in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_4mim][NTf_2]$) ionic liquid, for the first time. The properties such as density, viscosity, phase disengagement time etc. were measured for irradiated and unirradiated liquids composed of DHOA, $[C_4mim][NTf_2]$ and 1.1 M solution of DHOA in $[C_4mim][NTf_2]$. The results were compared with the values obtained for the nitric acid equilibrated–organic phases. ATR-FTIR spectroscopy and dynamic light scattering (DLS) measurement of the ionic liquid phase was employed for characterizing interaction between the ionic liquid-DHOA-nitric acid, and the aggregate size of the adduct formed in the solution.

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1. Introduction

Ionic liquids (ILs) can be regarded as a sustainable alternative to the conventional molecular diluent, n-dodecane (n-DD), in solvent extraction applications [1–3]. Since the ILs consist entirely of ions they have several fascinating properties such as near zero vapor pressure, high ionicity, good thermal and radiation stability, tunable properties (ionic liquid property could be changed by changing the cation –anion combination), high solvating capability etc., suitable for industrial exploitation. Replacement of volatile organic solvents by ionic liquids in solvent extraction could lead to inherently safer processes [4]. Several studies have been reported in literature on the use of ionic liquids as diluents and extractants in solvent extraction applications [5–15]. Employment of ionic liquids in solvent extraction applications usually led to high distribution ratios as compared to conventional molecular diluents, despite ionic liquids having high viscosity. This was obviously attributed to the favorable interaction occurring between the metal ion and the extractant dissolved in ionic liquid phase, resulting in the extraordinary stability of metal – solvate complex in ionic liquid phase.

In nuclear fuel reprocessing, N,N-dialkyl aliphatic amides have been extensively studied as an alternate to the traditional organophosphorous extractants for the separation of actinides from nitric acid medium [16–18]. Among the various ligands, N,N-dihexyloctanamide (DHOA)

has been identified as a promising extractant for the separation of actinides [16,18,19] from simulated wastes and reprocessing feeds. The merits of DHOA over other extractants are simple ease of synthesis, incenerability (completely CHON based), less secondary waste generation (degraded products are water soluble), efficient extraction of Pu(IV) over U(VI) at higher feed acidities, no third phase formation etc. [18]. In view of this, Pathak et al. extensively investigated the physicochemical and solvent extraction application of DHOA present in the conventional molecular diluent, n-dodecene (n-DD), for reprocessing of spent nuclear fuel solution [18,19]. Conversely, if ionic liquids are proposed as an alternative to the molecular diluent, n-dodecane, it is necessary to generate complete physicochemical properties and study the extractive properties of actinides in DHOA/ionic liquid solutions. However, the literature shows only few reports are available on the actinide extraction in DHOA/ionic liquid solution [20–22]. In the recent past, we also studied the extraction of plutonium(IV) using DHOA dissolved in trioctylmethylammonium bis(trifluoromethanesulfonyl)imide ($[N_{1888}][NTf_2]$) ionic liquid and reported the superiority of DHOA/$[N_{1888}][NTf_2]$ system over the other solvent systems such as TBP/$[N_{1888}][NTf_2]$ and DHOA/n-DD [26]. However, the physicochemical properties of DHOA – ionic liquid mixture were not reported by us. The literature also indicates that only few reports are available that describes the physicochemical properties of different types of ionic liquids pertaining to solvent extraction applications [23–25].

In view of this, the present paper reports the physicochemical and hydrodynamic properties of the solvent system composed of DHOA

and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([C_4mim][NTf_2]) ionic liquid. The properties such as density, viscosity, phase disengagement time etc. were measured for irradiated and unir-radiated liquids. The results were compared with the values of obtained for the nitric acid equilibrated- organic phases. Spectroscopic techniques such as ATR-FTIR spectroscopy and dynamic light scattering measurements were employed for understanding the interactions between DHOA–ionic liquids.

2. Experimental

2.1. Materials and reagents

All the chemicals and reagents used in this study were of analytical grade and they were used without any purification. Nitric acid, sodium hydroxide, methyl imidazole (99%), chloro butane (>99%), bis(trifluoromethanesulfonyl)imide lithium salt (LiNTf$_2$) (99%) were purchased from Sigma-Aldrich. DHOA was kindly supplied by Heavy Water Board, India. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mim][NTf_2]) was synthesized according to the literature procedure [4]. [C_4mim][NTf_2] was characterized by IR, NMR and elemental analysis. The NMR spectra and other characterization data for [C_4mim][NTf_2], presented in the supplementary information file, confirmed that the product was >99% pure and the impurities were negligible.

2.2. Equilibrium procedure

The equilibration experiments were performed by mixing the organic phase and aqueous phases at 298 K. The organic phase was composed of DHOA in [C_4mim][NTf_2] and the concentration of DHOA in organic phase was fixed at 1.1 M (unless otherwise mentioned). The aqueous phase was nitric acid and the concentration of nitric acid was varied from 0.5 M to 8 M. The organic phase was equilibrated with desired concentration of nitric acid prior to the physicochemical properties measurement. The equilibration procedure involved mixing of equal volumes (1 mL each) of organic and aqueous phases in a 10 mL capacity stoppered equilibration tube immersed in a constant temperature water bath. The tubes were rotated in upside down manner. After an hour of equilibration, the two phases were separated by centrifugation using a Rana centrifuge (Model No: I.A.117; SR No: 1087) in order to obtain a clear phase separation. The acid concentration of organic and aqueous phases was determined by standard acid-base titration.

2.3. Density, viscosity and PDT measurements

Densities (ρ) of neat, acid equilibrated and degraded samples were measured using Anton Paar (Austria) DMA 4500 digital vibrating U-tube densitometer (with automatic viscosity correction). Viscosities (η) were measured using Lovis 2000 ME; a rolling ball viscometer (supplied by Anton Paar), which measures the rolling time of a ball through transparent and opaque liquids according to Höppler's principle. The uncertainty in the values of density and viscosity were about ±1 × 10^{-5} g/mL and 2 × 10^{-3} cP respectively. The phase disengagement time of irradiated and unirradiated ionic liquid phases was measured by equilibrating the organic and 4 M nitric acid phases (2 mL each) in a 10 mL capacity test tube of diameter 1 cm. After agitation of the organic and aqueous phases, the equilibration tube was allowed to stand. The time required for the disengagement of phases was measured by using a stop-watch of resolution 0.01 s. The reported PDT values were the average of three independent measurements.

2.4. FTIR analysis

The infrared spectrum of the sample was recorded using BRUKER TENSOR II FT-IR spectrometer equipped with an ATR (attenuated total reflectance) diamond crystal. Few microlitres of organic phase was placed on a diamond crystal and the spectrum was recorded from 600 cm^{-1} to 4000 cm^{-1} (16 scans) with a resolution of 4 cm^{-1} for each sample. The spectrum obtained was then corrected to the background (without sample) and presented as ATR-FTIR spectrum of the sample.

2.5. Dynamic light scattering analysis

The size of aggregates in the ionic liquid phase was measured using Zetasizer-3000 (nano ZS) DLS spectrometer (Malvern Instrument Company, UK) with a 5 mW He–Ne laser beam at a wavelength of 632.8 nm. The scattering angle for measurement was set at 90° in a cell of 4 mm path length. All the experiments were carried out at 298 ± 0.05 K. The calibration of the instrument was performed using standard colloidal suspension (polystyrene latex). Each measurement was repeated at least 3 to 4 times to check the reproducibility of the data. The reported values were the average of these values and reproducibility was within ± 5%.

2.6. Radiolytic degradation studies

The radiolytic degradation studies of the ionic liquid phase component such as DHOA, [C_4mim][NTf_2] and 1.1 M DHOA/[C_4mim][NTf_2] was performed by irradiating the samples using a ^{60}Co gamma chamber facility, which provides a dose rate of 5.43 kGy/h. The irradiator was calibrated by Fricke dosimetry. The amount of absorbed γ- dose received by the sample was varied from 0 to 1000 kGy. After regular intervals of absorbed dose (50 kGy), the irradiated samples were taken out from the gamma chamber for the measurement of physiochemical properties.

3. Results and discussion

The viscosity of the 1.1 M solution of DHOA in [C_4mim][NTf_2], determined at various temperatures, are shown in Fig. 1. The viscosity 1.1 M DHOA/[C_4mim][NTf_2] is compared with pure DHOA and [C_4mim][NTf_2]. It can be seen that the viscosity of all liquids decreased with increase of temperature, as expected. The viscosity of DHOA and [C_4mim][NTf_2] decreases from 19 cP and 48 cP at 293 K to the value of 5 cP and 12 cP at 343 K, respectively. A similar trend is also observed for 1.1 M DHOA// [C_4mim][NTf_2] solution, which decreases from 54 cP at 293 K to 12 cP
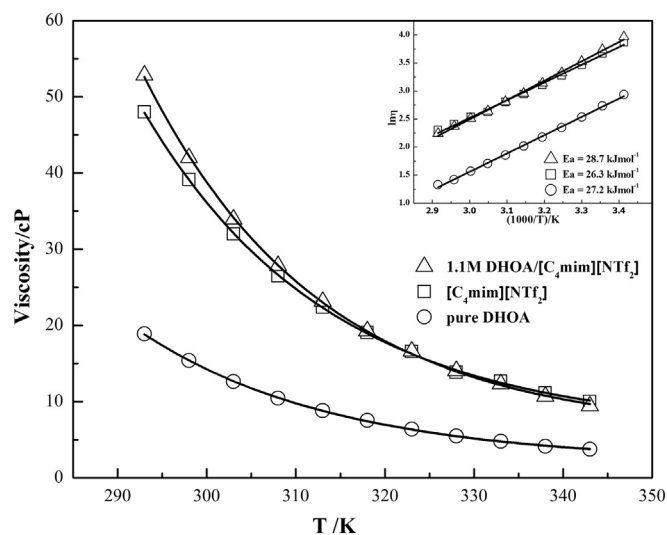

Fig. 1. Viscosity of dry organic phase composition comprising of pure DHOA, pure [C_4mim][NTf_2] and 1.1 M DHOA/[C_4mim][NTf_2]. Temperature = 293 K–343 K. Inset: Arrhenius plot.