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Coordination abilities of Good's buffer ionic liquids toward europium(III) ion in aqueous solution

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Good's buffer ionic liquids (GB-ILs) are new class of ILs with self-buffering capacity at the physiological pH range for biological research. GB-ILs are formed by the combination of Good's buffers as anions and various organic bases as counter ions. In this work, the complexation of europium(III) ion with tricine and tricine-based GB-ILs, tetramethylammonium tricinate, tetraethylammonium tricinate, tetrabutylammonium tricinate, cholinium tricinate, and 1-ethyl-3-methylimidazolium tricinate in aqueous solution were determined potentiometrically at $T = 298.2$ K and ionic strength $I = 0.1\ \text{mol} \cdot \text{dm}^{-3}$ $NaNO_3$. The protonation constants of the studied ligands (L) and their overall stability constants (lgβ) with Eu(III) were determined. The best model that fit the potentiometric data was consisted of six main species, EuL^{2+}, EuL_2^+, EuL_3, $EuH_{-1}L^+$, $EuH_{-2}L_2^-$, and $EuH_{-3}L_3^{3-}$. The $\lg\beta_{Eu(tricine)}$, $\lg\beta_{Eu(tricine)_2}$, and $\lg\beta_{Eu(tricine)_3}$ are 5.75, 9.51, and 12.79, respectively. The overall stability constants (lgβ) of tricine-based GB-ILs were found to be greater than those of tricine. The species distribution diagrams of these complexes were calculated and discussed in terms of percent Eu(III) and pH. We present a density functional theory (DFT) study to understand tricine chelating to Eu(III).

1. Introduction

Ionic liquids (ILs) are a large class of salts with a low melting temperature below the boilingpoint of water at ambient pressure [1]. They usually consist entirely of ions, large organic cations (e.g., *N*-alkylimiazolium, *N*-alkylpyridinium, or tetraalkylamonium) and different inorganic (e.g., Cl^-, Br^-, I^-, $[BF_4]^-$ or $[PF_6]^-$) or organic (e.g., $[CF_3SO_3]^-$, $[CF_3CO_2]^-$, or $[N(SO_2CF_3)_2]^-$) anions with delocalized or shielded charges [1]. ILs are considered to be green alternatives to the volatile organic compounds (VOCs) volatile organic compounds (VOCs) because of their specific properties such as negligible vapor pressure, high chemical/thermal stability, high ionic conductivity, and high solvation ability for inorganic and organic compounds [1–4]. The most important feature of the ILs is their remarkable structural tenability, slight changes in the cationic and/or anionic groups have observed to produce different physicochemical properties, such as density, viscosity, polarity, and hydrophobicity; consequently, it is possible to designed ILs with some desired properties and classified as functionalized ILs or task-specific ILs (TSILs) [4]. The applications of ILs in all areas of chemical science are becoming increasingly popular in nearly the last 20 years, as reported in some recent reviews [1–4].

Application of ILs to substitute conventional solvents in (liquid + liquid) extraction of lanthanides and actinides has shown encourage results [5–9]. The IL-based extraction systems avoid many environmental problems related to the use of VOCs, which leads to safer processes. Another advantage of using ILs is that the metal ion can be recovered by electrodeposition [10]. However, the metal salts are poorly soluble in the traditional ILs. Several strategies to overcome this drawback have been attempted such as (1) the use of strong chelating agents, (2) the use of TSILs with chelating function groups on their cations and/or (3) the use of ILs with strong coordinating anions [11,12].

The formation of stable complexes of europium(III) are of great interest due to their wide applications in optical devices and medical applications in magnetic resonance imaging, luminescence probes, and cancer treatment [13–17]. The affinity of some TSILs to Eu(III) has been also investigated and evaluated for Eu(III) extraction from aqueous solution [5].

Recently, we have synthesized novel ILs with buffer characteristics, in the physiological pH range, comprising anions derived from Good's buffers (e.g., tricine, TES, HEPES, MES, and CHES) and several cations such as 1-ethyl-3-methylimidazolium ($[C_2mim]^+$), tetramethylammonium ($[N_{1111}]^+$), tetraethylammonium ($[N_{2222}]^+$),

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TABLE 1
The specification of chemical samples.

Chemicals	Source	Purification method	Mass fraction purity	Melting point (K)
Europium(III) nitrate pentahydrate	Sigma–Aldrich	None	>0.999[a]	
Tricine	Sigma–Aldrich	None	>0.990[a]	
[C_2mim][OH] (10 wt% in H_2O)	Sigma–Aldrich	None		
[N_{1111}][OH] (25 wt% in H_2O)	Sigma–Aldrich	None		
[N_{2222}][OH] (25 wt% in H_2O)	Sigma–Aldrich	None		
[N_{4444}][OH] (40 wt% in H_2O)	Sigma–Aldrich	None		
[Ch][OH] (46 wt% in methanol)	Sigma–Aldrich	None		
[C_2mim][tricine]	Present work	None	0.983[b]	Viscous liquid
[N_{1111}][tricine]	Present work	Recrystallization and vacuum evaporation	0.990[b]	388.9
[N_{2222}][tricine]	Present work	Recrystallization and vacuum evaporation	0.989[b]	441.8
[N_{4444}][tricine]	Present work	Recrystallization and vacuum evaporation	0.985[b]	370.8
[Ch][tricine]	Present work	Recrystallization and vacuum evaporation	0.990[b]	336.8
Sodium hydroxide	Eka Chemicals	None		
Nitric acid (65 wt%)	Panreac (Barcelona, Spain)	None		
Potassium hydrogen phthalate	Panreac (Barcelona, Spain)	None	>0.998[a]	
Sodium nitrate	Himedia Labs	None	>0.995[a]	
Methanol		None	>0.999[a]	
Acetonitrile	Lab-Scan (Ireland)	None	>0.997[a]	
Acetone	VWR Chemicals	None	>0.995	

Standard uncertainty of the melting point is $u(T) = 0.1$ K.
Mass fraction purity determined by:
[a] The manufacturer.
[b] Titration.

tetrabutylammonium ([N_{4444}]$^+$), and cholinium ([Ch]$^+$) [18,19]. Good's buffers were developed by Good et al. for use as biological buffers with high buffering capacity at the physiological pH range [20,21]. Buffer capacity is a measure of a buffer's ability to resist change in pH with an added acid or base to the buffer solution. According to the Henderson–Hasselbalch equation, the buffering capacity of GB-ILs is maximum at the pH equal to the protonation constant of the amine group (pK_{a2}).

We are interested in determining the protonation constants tricine-based GB-ILs ([C_2mim][tricine], [N_{1111}][tricine], [N_{2222}][tricine], [N_{4444}][tricine], and [Ch][tricine]) and their complexation behavior with Eu(III). Tricine buffer is an interesting chelating agent due to its flexibility to behave as monodentate and multidentate ligand [22]. It is an *N*-substituted glycine and usually chelates with metal ions *via* carboxylate oxygen, amido nitrogen, and one or two hydroxymethyl groups. Tricine is capable of forming stable complexes with divalent alkaline-earth and transition metal ions, as well as lanthanides and actinides [22–31]. In this work, the stability constants of the complexes of tricine and tricine-based GB-ILs with Eu(III) ion in aqueous solution were determined by potentiometric technique. The geometries Eu(III)-tricine complexes were investigated by utilizing density functional theory with TZVP basis set.

2. Materials and methods

2.1. Materials

Europium(III) nitrate pentahydrate, tricine, [C_2mim][OH], [N_{1111}][OH], [N_{2222}][OH], [N_{4444}][OH], [Ch][OH], sodium hydroxide, nitric acid, and potassium hydrogen phthalate, sodium nitrate, acetonitrile are analytical grade and obtained from commercial sources. The purity of these compounds were reported in table 1. All materials were used as received without further purification. The synthesized tricine-based GB-ILs were purified by washing with acetone several times. Recrystallization of GB-ILs, except [C_2mim][tricine], from methanol-acetone mixture gave white powder, and dried by vacuum evaporation at room temperature. The purity levels of the synthesized tricine-based GB-ILs were determined by titration; a known mass of GB-IL was dissolved in pure water and titrated with standardized HCl, using the 'Metrohm 904' Titrando auto-titration apparatus (see Section 2.3).

2.2. Synthesis of tricine-based Good's buffer ionic liquids

The tricine-based GB-ILs, [C_2mim][tricine], [N_{1111}][tricine], [N_{2222}][tricine], [N_{4444}][tricine], and [Ch][tricine], were synthesized by neutralizing a slight excess of equimolar tricine with the aqueous organic hydroxide aqueous solution as described in our earlier papers [18,19]. The water content in the synthesized tricine-based GB-ILs was measured by Karl–Fischer coulometer using (Metrohm Ltd, model 831), and it was less than 0.05 wt%.

The molecular structures of the tricine-based GB-ILs were identified by ^{1}H and ^{13}C NMR spectroscopy (Bruker AMX 300) operating at 300.13 and 75.47 MHz, respectively. Chemical shifts are given in δ (ppm) relative to tetramethylsilane (TMS). The melting points of the tricine-based GB-ILs from the peak onset position were measured by differential scanning calorimetry (DSC), a Perkin Elmer DSC-7 instrument (Norwalk, CT), with heating rate of 5 °C min^{-1} and N_2 flow of 40 mL · min^{-1}. The onset temperature was taken at the intersection of a line tangent where the DSC heat flow peak starts to develop, to the initial base-line. The DSC curves of [N_{1111}][tricine], [N_{2222}][tricine], [N_{4444}][tricine], and [Ch][tricine] are given in figure 1. It was observed that [N_{4444}][tricine] and [Ch][tricine] are hygroscopic compounds which absorb water during the DSC measurements; and thus, broad peaks are observed for these two compounds (figure 1). All the calculations considering tricine-based GB-ILs concentration were carried out discounting the complexed water.

[C_2mim][tricine]–^{1}H NMR (300 MHz, D_2O/TSP): 1.39 (*t*, 3H), 3.86 (*s*, 3H), 4.20 (*q*, 2H), 7.65 (*s*, 1H), 7.85 (*s*, 1H), 9.58 (*s*, 1H), 3.18 (*s*, 6H), 2.93 (*s*, 2H); ^{13}C NMR (300 MHz, D_2O/TSP): 15.29, 35.61, 44.10, 122.10, 123.66, 136.94, 60.41, 60.56, 177.10, 46.16.

[N_{1111}][tricine]–^{1}H NMR (300 MHz, D_2O/TSP): 3.11(*s*, 12H), 3.19 (*s*, 6H), 2.87 (*s*, 2H); ^{13}C NMR (300 MHz, D_2O/TSP): 54.35, 60.55, 60.81, 176.10, 46.14.