

# Analytical Methods

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## Analytical Methods

## ARTICLE

## Hydrophobic-hydrophilic ionic liquids for the extraction and determination of metal ions with water-soluble reagents†

S. V. Smirnova, T. O. Samarina and I. V. Pletnev\*

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Tetraoctylammonium N-lauroyl sarcosinate and trioctylmethylammonium salicylate are water-immiscible solvents which contain a large amount of dissolved water and may be called "hydrophobic-hydrophilic" ionic liquids (HHILs). We found that several representative water-soluble reagents - Arsenazo I, Arsenazo III, Alizarin Red S, Nitroso-R salt, and Xylenol Orange - are strongly partitioned into HHIL phase from aqueous solutions over a wide pH range. Metal ions that form complexes with these reagents are extracted efficiently from aqueous solutions. We studied the details of extraction in two representative systems, Sc(III) with Arsenazo III and Co(II) with Nitroso-R salt. A sensitive, selective, and rapid procedure of the extraction-photometric determination of cobalt with HHIL and Nitroso-R salt has been developed.

### 1. Introduction

Ionic liquids (ILs) are relatively new solvents, which are increasingly used in analytical separations due to a number of advantages over conventional molecular solvents. Being molten (at room temperature) salts, ILs typically have negligible vapor pressure and are often inflammable and chemically and thermally stable over a wide range of conditions. Their polarity, hydrophobicity, viscosity, and other properties may be broadly varied by changing the nature of cationic or anionic constituents.

A number of water-immiscible ILs have been used in liquid-liquid extraction of metal ions [1–11] as well as organic compounds [12–14]. A typical scenario in conventional solvent extraction of metal ions is to use an inert diluent, to which metal cations are transferred as the complexes with a specially introduced hydrophobic reagent. If this reagent is chromogenic, this approach may be naturally combined with the subsequent spectrophotometric detection of metal. The same scenario may also be used in IL-based extraction and preconcentration. However, in contrast to any conventional molecular solvent, IL contains its own cation and anion, which may, and often do, play their own roles in extraction. Furthermore, the solvation of ionic species (including metal ion complexes) in ILs may be quite different from that in molecular solvents. As a result, employing ILs may give rise to an unusual mechanisms of extraction and an unusual efficiency/selectivity patterns. An illustrative example is a crown ether assisted extraction of strontium into dialkylimidazolium-based ILs,

characterized by extremely high distribution ratio of metal [15]. It was proven that this unprecedentedly high recovery is associated with the particular extraction mechanism, ion exchange of cation of IL to cationic crown-metal complex [16]. The role of ion exchange was established also for a number of other IL-based extraction systems.

Some ionic liquids possess their own complexing functionalities situated either at cation or anion IL part, so the solvent may act as a reagent itself. A large number of "task-specific ionic liquids" containing thiourea, thioether, urea, amine, thiol, crown ether and other groups appended to IL cation have been employed for separation of metal ions [1,3,5,9]. Another option (which is typically cheaper and more easily available) is given by ionic liquids possessing complexing anions. For example, we have recently described the use of trioctylmethylammonium salicylate, TOMAS [6], for the extraction of transition metal ions. Salicylate anion is well known for its ability to bind metal ions, in particular, Fe(III); TOMAS does extract metal ions in complexed form and the extraction efficiency is related to the stability constants of salicylate complexes. Thiosalicylate salt of the same organic cation [2], as well as many other ILs with complexing anions, have been reportedly used for metal ion extraction [2,4,7,8].

Noteworthy, however, is a still limited choice of ILs suitable for extraction. Actually, the solvents composed of a substituted imidazolium cation and a fluorinated anion are still most widely used. An important recent alternative to these "conventional" hydrophobic ILs is given by so-called aqueous biphasic systems (ABS). They employ hydrophilic ILs which are normally miscible with water but do form a separate layer in the presence of specially introduced salting-out agent, an inorganic salt. ABS systems were used in extraction for a long time, initially for organic/biomolecule separations [17,18] and then for metal ion extraction and analysis (pioneering work [19]; some subsequent examples [20–25]). However, these

Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1, Moscow, 119899 Russia Tel.: +7 495 9395464. E-mail: [pletnev@analyt.chem.msu.ru](mailto:pletnev@analyt.chem.msu.ru)

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previous applications employed water-soluble polymers like polyethyleneglycole (PEG); usage of ionic liquids instead of polymers is relatively recent invention (pioneering work [26], review [27]; some applications [28,29]). In general, "IL-rich" (or "polymer-rich") phase in ABS contains high amount of water thus presenting a comfortable environment for organic polar compounds and metal ions/hydrated ions/complexes [19,21,25]. Note that addition of salting-out agent is a prerequisite of phase separation in ABS.

Recently, we have described alkylammonium ionic liquids with non-fluorinated anions, trioctylmethylammonium salicylate, TOMAS [6, 30] and tetraoctylammonium N-lauroyl sarcosinate, TOALS [31, 32]. They contain very high amount of water, thus resembling non-aqueous phases of ABS. Yet, these ILs are water-immiscible in the absence of any salting-out agent. We found that these "hydrophobic-hydrophilic ionic liquids" (HHILs) are able to extract efficiently various relatively hydrophilic organic compounds from aqueous solutions. It was natural to hypothesize that they are also able to extract water-soluble complexing reagents and their complexes with metal ions.

In this paper we demonstrate that ionic liquids TOALS and TOMAS are suitable for the hosting water-soluble reagents containing one or more sulfonate groups and for the extraction of metal ions with such reagents from aqueous solutions. These separation systems are useful for analytical pre-concentration as illustrated by the developed procedure for sensitive extraction-photometric determination of Co(II) with water-soluble reagent, Nitroso-R salt.

## 2. Experimental

### 2.1. Material, reagents and standards

The Aliquat® 336 (trioctylmethylammonium chloride, Aldrich), sodium salicylate (Panreac, USP), tetraoctylammonium bromide (Sigma, 98%), N-lauroylsarcosine sodium salt (Sigma, 98%), chloroform (Ekros, Russia) were used as supplied. Organic reagents Alizarin Red S, Nitroso-R salt, Xylenol Orange, Arsenazo III, Arsenazo I (Reakhim, Russia) were all of analytical reagent grade. Aqueous solutions of Co(II) were prepared using the certified reference sample GSO 7784-2000, 1 mg/cm<sup>3</sup>. Solutions of scandium nitrate were prepared by dissolving a weighted amount of solid salt (chem. pure) in distilled water. Hydrochloric acid (2 and 0.1 mol L<sup>-1</sup>), sodium hydroxide (0.5 and 0.1 mol L<sup>-1</sup>), borate (0.05 mol L<sup>-1</sup>, pH 9.18) and citrate (0.1 mol L<sup>-1</sup>, pH 3.0) buffer solutions, and sodium acetate (1 mol L<sup>-1</sup>) were used for pH adjustments.

The ionic liquids were synthesized by Dr. V. Baulin (Institute of Physiologically Active Compounds RAS, Chernogolovka) by methods based on procedures developed previously [6, 32].

### 2.2. Instruments

Spectrophotometric measurements were carried out using a U-2900 UV-vis recording Spectrophotometer (Hitachi, Japan) with 1 cm glass cells. A pH-410 acidity meter (Akvilon, Russia)

with combined glass microelectrode ELSK-13.7 was used for pH measurement. The centrifuge (Hettich EBA 20, Tuttlingen, Germany), generating a speed in the range from 500 to 6000 rpm, was employed for phase separation after extraction procedure. The mixing of two-phase systems was performed with «ELMI S – 3» orbital shaker (ELMI, Latvia).

### 2.3. Extraction procedure

Extraction was performed at room temperature (21±2°C). An aliquot of water-saturated HHIL, 0.2 ml, was added to 4.0 ml of pH-adjusted aqueous solutions of the organic reagent (concentration range 1×10<sup>-4</sup>–1×10<sup>-2</sup> mol L<sup>-1</sup>). The pH of the aqueous phase was adjusted with HCl and NaOH. In the case of extraction of metal ions, 0.5 ml of HHIL was added to 5.0 ml of the aqueous phase containing Co(II) (1×10<sup>-5</sup> - 1×10<sup>-4</sup> mol L<sup>-1</sup>) and Nitroso-R salt (1×10<sup>-4</sup> - 1×10<sup>-3</sup> mol L<sup>-1</sup>) or Sc(III) (8×10<sup>-5</sup> mol L<sup>-1</sup>) and Arsenazo III (1×10<sup>-4</sup> - 2×10<sup>-3</sup> mol L<sup>-1</sup>). For Co(II) extraction with Nitroso-R salt, 0.2 ml of 1 wt% solution of ascorbic acid was added to the aqueous phase to prevent oxidation of Co(II) to Co(III). The two-phase system was shaken for the time necessary to reach the extraction equilibrium. Aqueous and organic phases were separated; if necessary, centrifugation for up to 15 min was performed. An equilibrium pH value was measured. Then the solute was determined in the aqueous phase.

The distribution ratio (*D*) and the extraction efficiency (*E*,%) of water-soluble reagents and metal ions were calculated using the Eqs (1) and (2):

$$D = \frac{(c_w^o - c_w)}{c_w} \times \frac{V_w}{V_{HHIL}} \quad (1)$$

$$E(\%) = \frac{100 \times D}{D + \frac{V_w}{V_{HHIL}}} \quad (2)$$

where *c*<sub>w</sub><sup>o</sup> and *c*<sub>w</sub> are initial and final (equilibrium) concentrations of the solute in the aqueous phase, *resp.* (M); *V*<sub>w</sub> and *V*<sub>HHIL</sub> denote the volumes of aqueous and HHIL phases, *resp.*

The reagents and metal ions were monitored using spectrophotometric methods [33]. The concentrations of water-soluble reagents in the aqueous phase were determined after adding 0.5 ml of 0.5 mol L<sup>-1</sup> NaOH by their own absorbance at 550 nm (Arsenazo I), 590 nm (Arsenazo III), 370 nm (Nitroso-R salt), 575 nm (Xylenol Orange), 560 nm (Alizarin Red S). For the determination of Co(II), 1.0 ml of sodium acetate (1 mol L<sup>-1</sup>) and 0.5 ml of Nitroso-R salt (1×10<sup>-2</sup> mol L<sup>-1</sup>) were added to the aqueous phase obtained after the extraction of cobalt; the absorbance was measured at 490 nm. For the determination of Sc(III), 0.3 ml HCl (2 mol L<sup>-1</sup>) and 0.4 ml Arsenazo III (1×10<sup>-2</sup> mol L<sup>-1</sup>) were added to the aqueous phase after the extraction, and the absorbance was measured at 676 nm.

### 2.4. Sample treatment

Liquid fertilizer «Florist-M» (Florist, Russia; this is a solution containing metal ions and humic acids) was purchased from

local supermarket. The treatment of the sample was performed as follows. An aliquot of 1.00 ml of mineral fertilizer was placed in a glass, and 10 ml of citric-acetic buffer solution (pH 4.8) was added. The glass was heated on a sand bath until the solution became yellow. Then 2 ml of HCl (2 mol L<sup>-1</sup>) was added, and the resulting solution was transferred quantitatively into a volumetric flask and diluted to 50 ml with distilled water.

The developed procedure of analysis was as follows. A 2 ml aliquot of the analyzed aqueous solution was placed in a polypropylene centrifuge test-tube and 0.2 ml of a fresh solution of ascorbic acid (1 wt.%), 0.2 ml of Nitroso-R salt (0.01 mol L<sup>-1</sup>), 0.5 ml of sodium acetate (1 mol L<sup>-1</sup>) were added. The resulting solution was diluted to 5.0 ml with distilled water. After shaking, 0.5 ml of HHIL was added. The two-phase system was then subjected to shaking for 15 min using a mechanical shaker followed by the centrifugation for 5 min for phase separation. Then aqueous phase was discarded and 5 ml of HCl (2 mol L<sup>-1</sup>) was added to extract. After 10 min shaking, the red-colored organic phase was separated and diluted by the equal volume of chloroform (to avoid sticking of ionic liquid to the cuvette walls). The absorbance of organic phase was measured at 490 nm (*l* = 0.1 cm) against a reference solution of HHIL in CHCl<sub>3</sub> (1:1).

### 3. Results and discussion

#### 3.1. Properties of the HHILs

TOMAS and TOALS are liquid at room temperature when saturated with water; this state is assumed here and below (Fig. S1). They are lighter than water and are immiscible with it. Solubility of HHILs in water is rather low: 2.0×10<sup>-4</sup> mol L<sup>-1</sup> for TOMAS [30] and 1.1×10<sup>-5</sup> mol L<sup>-1</sup> for TOALS [31]. This is much lower than aqueous solubility of well-known hydrophobic ILs

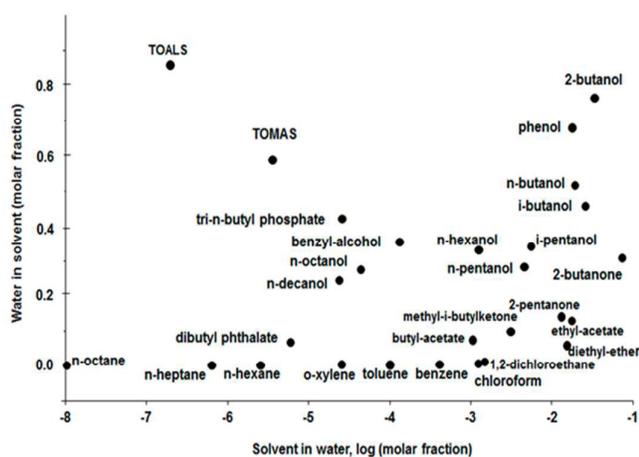


Fig. 1 Mutual solubility of water and some water-immiscible solvents (data for solvents from ref. [37]).

(e.g., 0.075 mol L<sup>-1</sup> for 1-butyl-3-methylimidazolium hexafluorophosphate and 0.018 mol L<sup>-1</sup> for 1-butyl-3-methylimidazolium bis(triflylimide) [34,35]) and is comparable to that of heptane. Low aqueous solubility is highly beneficial for the extraction separations.

At the same time, solubility of water in the HHILs is rather high. Equilibrium content of water is 13.2 wt.% [32] and 4.83 wt.% [6] for TOALS and TOMAS, *resp*; on a molar basis  $\chi_w$  is 0.86 and 0.59, *resp*. Accordingly, TOALS and TOMAS should be described as extremely “wet” [36] solvents. In fact, they contain as much water as the “wettest” of known molecular solvents ( $\chi_w$  0.42, tri-*n*-butyl phosphate; 0.52, *n*-butanol; 0.67, phenol [37]).

The unusual hydrophobic-hydrophilic character of TOALS and TOMAS is illustrated by Fig. 1 that presents an overall picture of mutual solubility of selected hydrophobic solvents and water. As is seen, TOALS and TOMAS are placed separately, far from other solvents.

Low aqueous solubility of the HHILs can be explained by relatively high hydrophobicity of their long-chain alkylammonium cations. The high solubility of water in HHILs may be attributed to relatively high hydrophilicity of the anions, salicylate and *N*-lauroyl sarcosinate. Ohno *et al.* [38] have recently reported on high water content in ILs possessing amino acid anions, whose structure is similar to TOALS. The same “wet” character was also reported for Cyphos-family ILs containing various carboxylate, phosphinate, *etc.* anions [39, 40] and tetraalkylammonium bis(2-ethylhexyl)sulfosuccinates [41]. It is worth mentioning that the exact state of water dissolved in HHILs (e.g., hydration water or water in separate aggregates/domains, *etc.*) is not completely clear at the moment.

Interestingly, biphasic HHIL-water systems may be called literally “aqueous biphasic systems”, as both their HHIL-poor and HHIL-rich phases mainly consist of water. One may expect that HHILs are suitable for unusual analytical separations involving extraction of hydrophilic reagents and their metal complexes from aqueous solutions, as it was observed for ABS [19, 21, 24, 25]. As shown below, HHILs are able indeed to extract the various representative water-soluble complexing reagents and their metal ion complexes.

#### 3.2. Distribution of water-soluble complexing reagents between water and HHILs

We studied the distribution of several water-soluble chromogenic reagents (Arsenazo I, Arsenazo III, Xylenol Orange, Alizarin Red S, and Nitroso-R salt – Fig. S2) between water and HHIL at varying pH. It was found that the time necessary to reach the extraction equilibrium is < 10 min. High phase volume ratio  $V_W : V_{HHIL} = 20:1$  was used throughout the study.

The reagents selected for the study contain at least one highly hydrophilic sulfonate group not mentioning other ionogenic and polar groups. They are well soluble in water and are hardly compatible with common water-immiscible solvents.

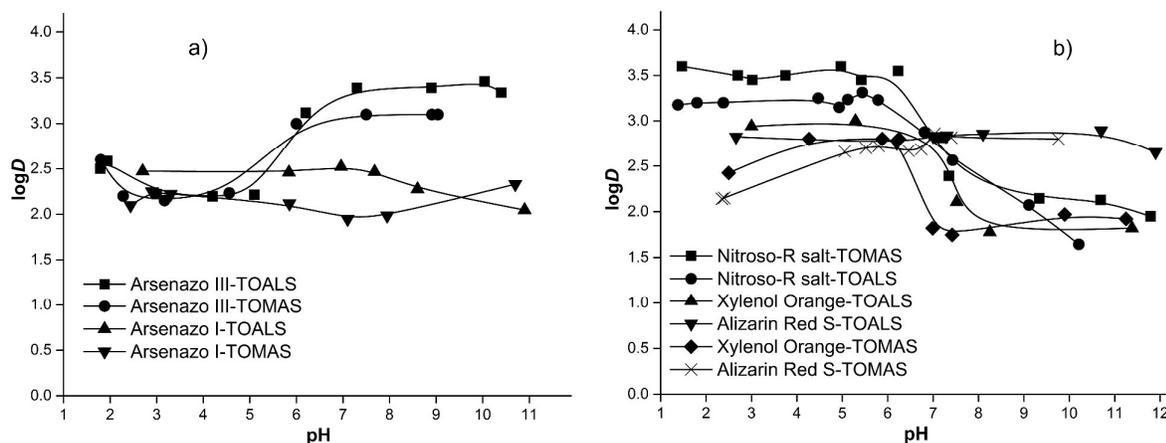


Fig. 2 Extraction of water-soluble reagents into HHILs vs. pH ( $V_{\text{HHIL}}:V_{\text{W}}=1:20$ ): a) Arsenazo I, Arsenazo III ( $1 \times 10^{-4} \text{ mol L}^{-1}$ ); b) Xylenol Orange ( $1 \times 10^{-4} \text{ mol L}^{-1}$ ), Alizarin Red S ( $2 \times 10^{-4} \text{ mol L}^{-1}$ ), Nitroso-R salt ( $1 \times 10^{-3} \text{ mol L}^{-1}$ ). In all cases, estimated error in measured  $\log D$  is not greater than  $\pm 3\%$  ( $n=3$ ,  $P=0.95$ ).

Arsenazo I, Arsenazo III, Xylenol Orange, Alizarin Red S, and Nitroso-R salt are well-known chromogenic reagents for the spectrophotometric determination of metal ions in aqueous solutions [33].

There are rare examples of extraction of their metal ion complexes; they assume either the use of an active solvent and special counter-ion [42] or utilizing a polymer-based ABS [20].

We observed that TOMAS and TOALS effectively extract **Arsenazo I** and **Arsenazo III** from aqueous solutions. Arsenazo III is quantitatively extracted into TOMAS at pH 5.9–9.1 ( $\log D=3.1 \pm 0.1$ ), and into TOALS at pH 6.2–10.4 ( $\log D=3.4 \pm 0.1$ ), see Fig. 2a. At pH >6, the extraction efficiency of Arsenazo III into both TOALS and TOMAS is ca. 99% over a wide concentration range of solute,  $5 \times 10^{-5}$ – $1 \times 10^{-2} \text{ mol L}^{-1}$  (for Arsenazo I, the extraction efficiency is 80–95%). For lower pH values, up to 1.8, the extraction does not decrease significantly,  $\log D$  values remaining greater than 2 (Fig. 2a).

In other words, Arsenazo reagents are preferably partitioned into HHIL, practically independent on the change of the ionic state of ligand in aqueous solution. Interestingly, the distribution ratios for Arsenazo III in TOALS- and TOMAS-based extraction systems ( $\log D$  is 2.20 and 2.15, *resp.*, at pH 3.5) are close to 2.30 reported for PEG-based aqueous biphasic systems [19].

**Xylenol Orange** is efficiently extracted into both HHILs (Fig. 2b). The extraction efficiency is almost quantitative at pH 2.5–6.3 for TOMAS and 3.0–6.5 for TOALS; the distribution ratios  $\log D$  are  $2.8 \pm 0.2$  and  $3.0 \pm 0.2$ , *resp.* (*cf.* previously reported  $D > 100$  in a PEG-based ABS [19]). Evidently, the single, double and triple-charged anions of Xylenol Orange that are abundant at pH 2.5–6.5 are extracted well. Upon an increase of pH above 6.5, the higher charged anions are formed, and extraction of Xylenol Orange decreases; however, the extraction efficiency is still 75–80% at pH >7.5.

The pH profile of **Alizarin Red S** distribution between water and ionic liquids is shown on Fig. 2b. The reagent is quantitatively extracted into both HHILs in the whole studied pH range 2.5–12.0 for TOALS and pH 5.0–9.8 for TOMAS. That

is, the distribution of reagent is again practically insensitive to the ionization state. The distribution ratios  $\log D$  are  $2.7 \pm 0.1$  and  $2.8 \pm 0.1$  for TOMAS and TOALS, *resp.* The quantitative extraction of Alizarin Red S is observed in wide range of its concentrations,  $2 \times 10^{-4}$ – $1 \times 10^{-2} \text{ mol L}^{-1}$ .

**Nitroso-R salt** is a well-known chromogenic reagent for cobalt bearing two sulfonate groups. The influence of pH on the distribution of Nitroso-R salt ( $1 \times 10^{-3} \text{ mol L}^{-1}$ ) between water and HHIL is shown on Fig. 2b. The distribution ratio  $\log D > 3$  is attained at pH 1.5–6.2 for both TOMAS and TOALS. The extraction slightly decreases in neutral and mildly alkaline media; this fact may be related to the increasing negative charge of the molecule due to dissociation of quinone/oxime group.

In general, all the studied water-soluble reagents are effectively extracted into both HHILs. Often, the extraction over a broad pH range depends on pH only slightly (*i.e.*, it is not sensitive to the reagent ionization state in the aqueous solution). Given that all reagents contain at least one sulfonate group, we can conclude that anionic form(s) of reagents are partitioned to HHIL phase (by ion exchange mechanism).

### 3.3. Extraction of metal ions with water-soluble reagents into HHILs

The ability to solubilize chromogenic reagents and the hydrophilic character of the HHILs strongly suggest that TOMAS and TOALS are able to extract metal ions complexed by such reagents. This is indeed the case, as illustrated below with two representative examples: the extraction of Sc(III) with Arsenazo III, and the extraction of Co(II) with Nitroso-R salt.

Noteworthy is that TOMAS and TOALS do contain coordinating anions and may, to some extent, extract metal ions without any reagents; in the discussion below this “blank” extraction is specifically reported and the effect of the reagent is examined. High phase volume ratio  $V_{\text{W}}:V_{\text{HHIL}} = 10:1$  was used throughout the study.

**Sc(III)/Arsenazo III.** Scandium can be extracted with Arsenazo III into both studied HHILs. The pH profiles of Sc(III) distribution are presented on Fig. 3.

One may note that TOMAS extracts the metal ion from neutral aqueous solutions almost quantitatively even without the reagent. Undoubtedly, this is related to the complexing properties of IL anion, salicylate. This efficient extraction, however, strongly depends on pH and sharply diminishes in more acidic solutions; the extraction efficiency from the acidic media does not exceed 20%. In the presence of Arsenazo III, the extraction pH profile changes drastically: the extraction efficiency of Sc(III) from acidic aqueous solutions becomes almost quantitative,  $\log D_{Sc} = 2.1$  at pH 1.3–6.7. A similar behavior is also observed for the extraction into TOALS (Fig. 3).

To determine the stoichiometry of Sc(III)-Arsenazo III interaction, we studied the dependence of Sc(III) extraction on Arsenazo III concentration. The slope of the linear part of the bilogarithmic plot  $\log D_{Sc} = f(\log C_{\text{Arsenazo III}})$  is close to 1 for both HHILs (Fig. S3a); this means that the ratio Sc:Arseazo III in the extracted species is equal to 1:1. The time of phase contact necessary to achieve the extraction equilibrium for both systems is shorter than 15 min.

Noteworthy is that the extraction of scandium with Arsenazo III to conventional polar organic solvents was previously reported as hardly possible, even in the presence of a bulky counter-cation [40]. Also, the extraction of Sc(III) from acidic media with Arsenazo III in previously described PEG-based ABS was reported to be negligible [43].

**Co(II)/Nitroso-R salt.** In the absence of reagent, Co(II) is practically not extracted from aqueous solutions into HHILs at pH 1.1–6.0. In the presence of Nitroso-R salt, Co(II) is extracted quantitatively ( $E = 98 \pm 2\%$ ) into both TOALS ( $\log D = 2.5 \pm 0.1$ , pH 1.5–5.5) and TOMAS ( $\log D = 2.4 \pm 0.1$ , pH 1.1–6.3). The time of phase contact necessary to achieve the quantitative extraction of the metal ion is not more than 10 min.

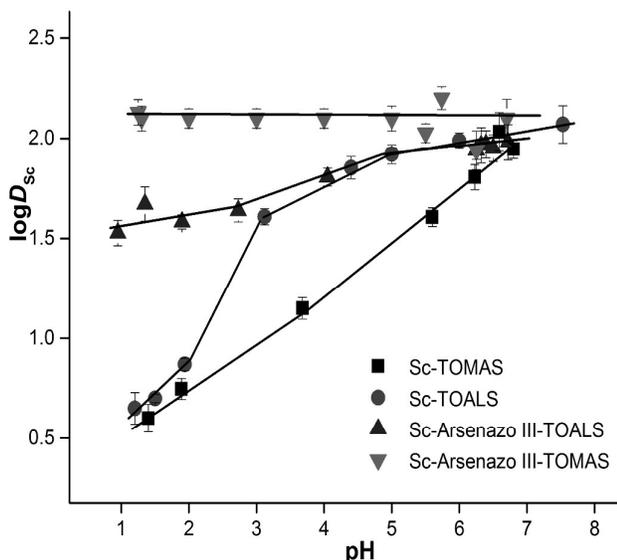


Fig. 3 The effect of pH on the extraction of Sc ( $8 \times 10^{-5}$  mol L<sup>-1</sup>) into HHILs with and without Arsenazo III ( $8 \times 10^{-4}$  mol L<sup>-1</sup>) ( $V_{\text{HHIL}}:V_{\text{w}}=1:10$ ).

We studied the dependence of Co(II) extraction on Nitroso-R salt concentration at pH 4.8 (optimal for the formation of Co(II)-Nitroso-R salt complex in aqueous solution). The slope of the linear part of the bilogarithmic plot  $\log D = f(\log C_{\text{Nitroso-R salt}})$  is ca. 2 for both HHILs (Fig. S3b); this means that the ratio Co:reagent is equal to 1:2. Such a stoichiometry is known for anionic complex of Co(II) with Nitroso-R salt in aqueous solution. Note that extraction of this complex to HHILs does not require any specially introduced counter-ion or salting-out agent [44].

The maximum absorbance of extracted Nitroso-R salt complex with Co(II) in both HHILs is observed at 490 nm. This agrees well with the value observed for the complex in aqueous solutions. However, the molar absorptivity of cobalt complexes in HHIL is significantly higher than in aqueous solutions [33]:  $2.78 \times 10^4$  (TOMAS) and  $2.31 \times 10^4$  (TOALS). This fact is evidently beneficial for analytical applications.

### 3.4. Extraction and spectrophotometric determination of Co(II) with Nitroso-R salt and HHIL

We developed a procedure for the extraction and spectrophotometric determination of cobalt(II) with Nitroso-R salt as a chromogenic reagent and HHIL (TOALS or TOMAS) as an extraction solvent. The analytical performance of extraction and spectrophotometric method of cobalt determination including linear range, precision, enhancement factors and LODs were studied under the optimal conditions. LODs calculated at S/N of 3 are 11 and 17  $\mu\text{g L}^{-1}$  for TOMAS and TOALS *resp.* Regression equations were  $A = 0.238 c + 0.045$  with correlation coefficients ( $r$ ) > 0.993 in the range 0.3–5.0 mg L<sup>-1</sup>, for TOMAS;  $A = 0.195 c + 0.047$  with correlation coefficients ( $r$ ) > 0.995 in the range 0.5–5.0 mg L<sup>-1</sup>, for TOALS. The relative standard deviation (R.S.D.%) calculated for three replicates ( $n=3$ ,  $P=0.95$ ) for the determination of 1.5 mg L<sup>-1</sup> of Co(II) were 2.7 and 3.4 % for TOMAS and TOALS *resp.* The extraction efficiency under the optimal conditions was 99% for TOMAS and 98% for TOALS. The enhancement factors were 5.0 and 4.9 for TOMAS and TOALS *resp.*

Table 1 compares the proposed method with the existing procedures of extraction-spectrophotometric determination of cobalt. The proposed method has LODs near or lower than in other methods [20, 21, 24, 25, 45, 46]. The only exception is very low LOD reported in the work [47] where a sophisticated mathematical procedure was employed. At the same time, the proposed method has a significant advantage in that it avoids the use of any additives like salting-out agents [21, 25]. It should be noted that coupling of extraction with modern AAS or ICP-OES techniques allows to attain much lower LODs ( $\mu\text{g L}^{-1}$ ): 0.008 [48] and 0.06 [49] (ETAAS), 0.2 [50] (ICP-OES), 0.4 [51] (FAAS). However these techniques do require much more expensive instrumentation.

We also studied the selectivity of extraction-spectrophotometric determination of cobalt with TOMAS. It is well known that in case of direct determination of cobalt with Nitroso-R salt in aqueous solutions the ions of Cu(II), Ni(II), Fe(III) can interfere as they also form stable complexes with

**Table 1** Comparison of the proposed method with other extraction-spectrophotometric methods reported for the determination of cobalt

Sample pretreatment procedure	Method	Sample	Type of extraction solvent, complexing reagent	LOD ( $\mu\text{g L}^{-1}$ )	Reference
PEG-based ABS	UV-vis	-	$(\text{NH}_4)_2\text{SO}_4$ - PEG-2000 - $\text{H}_2\text{O}$ , Nitroso-R salt	10	[21]
PEG-based ABS	TLS	-	$(\text{NH}_4)_2\text{SO}_4$ - PEG-2000 - $\text{H}_2\text{O}$ , Nitroso-R salt	20	[25]
DLLME	UV-vis	vitamin B12, water	Toluene, acetonitrile, carbon tetrachloride, dimethylindocarbocyanine dye	9	[45]
CPE	UV-Vis	water	Tween 80, 1-nitroso-2-naphthol	16	[46]
IL-DLLME	UV-vis	water, food	[HMIM][Tf <sub>2</sub> N], 1-(2-pyridylazo)-2-naphthol	0.65	[47]
HHIL-LLE	UV-Vis	mineral fertilizer	TOMAS, Nitroso-R salt	11	This work

Note: PEG-based ABS, polyethylene glycol-based aqueous biphasic systems; TLS, thermal-lens spectrometry; IL-DLLME, ionic liquid dispersive liquid-liquid microextraction; DLLME, dispersive liquid-liquid microextraction; CPE, cloud-point extraction; HHIL-LLE, hydrophobic-hydrophilic ionic liquid liquid-liquid extraction; [HMIM][Tf<sub>2</sub>N], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imid.

the reagent. Such interferences should be expected in extraction scheme also. Indeed, the interference of copper(II) appears noticeable already at Cu:Co(II) ratio equal to 1:1 (the apparent absorbance of Co(II) complex decreases by 7%). Nickel(II) does not interfere at ratio 1:1. Iron(III) is known to form stable complexes with both Nitroso-R salt and salicylate so it is expected to interfere.

A typical approach to eliminate interferences from Cu, Ni, Fe, Mn in direct aqueous determination of cobalt with Nitroso-R salt is a decomposition of undesirable complexes by heating in acidic media (HCl or HNO<sub>3</sub>); the complex of Co(II) is stable in these conditions. However, extraction-based scheme provides easier means to eliminate interferences: complexes of interfering ions are easily back-extracted by 2 mol L<sup>-1</sup> HCl, while cobalt complex remains in the extract.

### 3.5. Application of the method

The practical applicability of proposed approach was verified by the analysis of test samples with complex matrix compositions: (i) standard mixture of metal ions with different amounts of Ni(II), Cu(II), Fe(III) and Co(II); (ii) liquid fertilizer containing metal ions and humic acids. The content of cobalt in the spiked samples was determined, and the results are listed in Table 2.

Also, the determined amount of Co(II) was compared with the content certified by manufacturer: 60±3 mg L<sup>-1</sup> was found by proposed method, 50±10 mg L<sup>-1</sup> is stated by the manufacturer.

## 4. Conclusions

This study presents the use of hydrophobic-hydrophilic ionic liquids (HHILs) in separations. High content of dissolved water results in unusual properties of HHILs and allows to extract ionized forms of organic compounds without the use of specially introduced counter-ions and/or specific salting-out agents.

Accessibility, simplicity of preparation, and biodegradability of TOMAS and TOALS make them suitable for developing new "green" separations and analytical procedures.

We have demonstrated the possibility of extraction for a number of water-soluble ligands and their complexes with metal ions. The particular examples are the extraction of scandium and cobalt. The use of the water-soluble chromogenic reagent in combination with HHIL allows to develop sensitive and simple extraction-spectrophotometric method for determination of cobalt.

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**Table 2** Analytical and statistical parameters of the proposed method<sup>a</sup> for the determination of Co(II) in standard mixed solution and in composite mineral fertilizer ( $n=3$ ,  $P=0.95$ )

Sample	Spiked ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	Recovery <sup>e</sup> (%)	RSD
Standard mixture <sup>b</sup>	1.50	1.52±0.07	101.3	0.04
Fertilizer	0	2.40±0.12 <sup>d</sup>	-	0.06
«Florist-M» <sup>c</sup>	0.50	2.87±0.09	94.0	0.05
	1.50	3.77±0.16	91.3	0.08

<sup>a</sup> $V_{\text{TOMAS}}:V_{\text{W}}=1:10$ ,  $C_{\text{Nitroso-R salt}}=1\times 10^{-4}$  M, pH 4.8,  $t=15$  min;

<sup>b</sup>Contains ( $\mu\text{g}$ ): Ni(II) – 1.5, Cu(II) – 1.5, Fe(III) – 5.0;

<sup>c</sup>Manufacturer's certified concentrations ( $\text{mg L}^{-1}\pm 20\%$ ): Ni(II) – 20, Co(II) – 50, Cu(II) – 320, Fe(III) – 3000; also contains humic acids;

<sup>d</sup>Initial concentration;

<sup>e</sup> $100 \times [(\text{found} - \text{initial})/\text{spiked}]$ .

## References

- A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, and J.H. Davis, *Environ. Sci. Technol.*, 2002, **36**, 2523–2529.
- R.S. Kalb and M.J. Kotchan, *Aldrich ChemFiles*, 2005, **5**, 17.
- J. Harjani, T. Friscic, L. MacGillivray and R. Singer, *J. Chem. Soc., Dalton Trans.*, 2008, **34**, 4595–4601.
- D. Kogelnig, A. Stojanovic, M. Galanski, M. Groessl, F. Jirsa, R. Krachler, and B.K. Keppler, *Tetrahedron Lett.*, 2008, **49**, 2782–2785.

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- 5 J. M. Reyna-González, A.A.J. Torriero, A.I. Siriwardana, I.M. Burgar and A.M. Bond, *Anal. Chem.*, 2010, **82**, 7691–7698.
- 6 V.M. Egorov, D.I. Djigailo, D.S. Momotenko, D.V. Chernyshov, I.I. Torocheshnikova, S.V. Smirnova and I.V. Pletnev, *Talanta*, 2010, **80**, 1177–1182.
- 7 X. Sun, Y. Ji, F. Hu, B. He, J. Chen, and D. Li, *Talanta*, 2010, **81**, 1877–1883.
- 8 A. Rout, K.A. Venkatesan, T.G. Srinivasan and P.R.V. Rao, *Solvent Extr. Ion Exch.*, 2011, **29**, 602–618.
- 9 P.K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens and W. Verboom, *Chem. Eur. J.*, 2013, **19**, 3230–3238.
- 10 M.L. Dietz, *Sep. Sci. Technol.*, 2006, **41**, 2047–2063.
- 11 A. Stojanovic and B.K. Keppler, *Sep. Sci. Technol.*, 2012, **47**, 189–203.
- 12 S. Carda–Broch, A. Berthod and D.W. Armstrong, *Anal. Bioanal. Chem.*, 2003, **375**, 191–199.
- 13 I.V. Pletnev, S.V. Smirnova and V.M. Egorov, *Ionic liquids in chemical analysis*, CRC Press, USA, 2008, pp. 243–267.
- 14 P. Zhang, L. Hu, R. Lu, W. Zhou and H. Gao, *Anal. Methods*, 2013, **5**, 5576–5385.
- 15 S. Dai, Y.H. Ju and C.E. Barnes, *J. Chem. Soc., Dalton Trans.*, 1999, **8**, 1201–1202.
- 16 M.L. Dietz and J.A. Dzielawa, *Chem. Commun.*, 2001, **20**, 2124–2125.
- 17 P.-A. Albertsson, *Partition of cell particles and macromolecules*, John Wiley, New York, 1986.
- 18 D. Forciniti, Preparation of aqueous two-phase systems, in: Hatti-Kaul, Rajni (Eds.), *Aqueous two-phase systems. Methods and protocols*, Springer, New York, 2000, pp. 23–33.
- 19 T. Zvarova, V. Shkinev, B. Spivakov and Y. Zolotov, *Doklady Akademii Nauk SSSR*, 1983, **273**, 107–110.
- 20 V. Shkinev, N. Molochnikova, T. Zvarova, B. Spivakov, B. Myasoedov and Y. Zolotov, *J. Radioanal. Nucl. Chem.*, 1985, **88**, 115–120.
- 21 T. Zvarova, V. Shkinev, G. Vorobeva, B. Spivakov and Y. Zolotov, *J. Anal. Chem.*, 1988, **43**, 29–37.
- 22 R.D. Rogers, A.H. Bond and C.B. Bauer, *Sep. Sci. Technol.*, 1993, **28**, 1091–1126.
- 23 M. Shibukawa, N. Nakayama, T. Hayashi, D. Shibuya, Y. Endo and S. Kawamura, *Anal. Chim. Acta.*, 2001, **427**, 293–300.
- 24 T.G. Dzherayan, V.M. Shkinev, L.K. Shpigun, P.M. Kamilova and K.E. Geckeler, *Talanta*, 2002, **57**, 7–13.
- 25 D.S. Tsar'kov, E.S. Ryndina, M.A. Proskurnin and V.M. Shkinev, *J. Anal. Chem.*, 2011, **66**, 166–170.
- 26 K.E. Gutowski, G.A. Broker, H.D. Willauer, J.G. Huddleston, R.P. Swatoski, J.D. Holbrey and R.D. Rogers, *J. Am. Chem. Soc.*, 2003, **125**, 6632–6633.
- 27 M.G. Freire, A.F.M. Cláudio, J.M.M. Araújo, J.A.P. Coutinho, I.M. Marrucho, J.N.C. Lopes and L.P.N. Rebelo, *Chem. Soc. Rev.*, 2012, **41**, 4966–4995.
- 28 Y. Akama, M. Ito and S. Tanaka, *Talanta*, 2000, **53**, 645–650.
- 29 Y. Akama and A. Sali, *Talanta*, 2002, **57**, 681–686.
- 30 V.M. Egorov, S.V. Smirnova and I.V. Pletnev, *Sep. Pur. Tech.*, 2008, **63**, 710–715.
- 31 N.V. Shvedene, S.A. Krasnov, M.Y. Nemilova, A.V. Grigor'eva, K.M. Sotnezova and I.V. Pletnev, *J. Anal. Chem.*, 2012, **67**, 834–841.
- 32 S.V. Smirnova, T.O. Samarina, D.V. Ilin and I.V. Pletnev, *Moscow Univ. Chem. Bull.*, 2015, **56**, 32–37.
- 33 Z. Marzenko and M. Balcerzak, *Separation, preconcentration and spectrophotometry in inorganic analysis*, Elsevier, Amsterdam, 2000.
- 34 N.V. Shvedene, S.V. Borovskaya, V.V. Sviridov, E.R. Ismailova and I.V. Pletnev, *Anal. Bioanal. Chem.*, 2005, **381**, 427–430.
- 35 M.G. Freire, P.J. Carvalho, R.L. Gardas, L.M.N.B.F. Santos, I.M. Marrucho and J.A.P. Coutinho, *J. Phys. Chem.*, 2008, **112**, 1604–1610.
- 36 B.A. Moyer and Y. Sun in: Marcus, Y., Marinsky, J.A. (Eds.), *Solvent extraction of alkali metal ions, ion exchange and solvent extraction*, New York, 1997, pp. 295–391.
- 37 Y. Marcus, *The properties of solvents*, Wiley, Chichester, New York 1998.
- 38 J. Kagimoto, S. Taguchi, K. Fukumoto and H. Ohno, *J. Mol. Liq.*, 2010, **153**, 133–138.
- 39 M.G. Freire, P.J. Carvalho, R.L. Gardas, L.M.N.B.F. Santos, I.M. Marrucho and J.A.P. Coutinho, *J. Chem. Eng. Data*, 2008, **53**, 2378–2382.
- 40 A.C. Grijalba, L.B. Escudero and R.G. Wuilloud, *Anal. Methods*, 2015, **3**, 490–499.
- 41 N. Nishi, T. Kawakami, F. Shigematsu, M. Yamamoto and T. Kakiuchi, *Green Chem.*, 2006, **8**, 349–355.
- 42 S.B. Savvin, *Organic reagents of Arsenazo group (in Russian)*, Atomizdat, Moscow 1971.
- 43 V.M. Shkinev, *Water-soluble polymers for separations and pre-concentration of compounds*, D.Sc., thesis, Vernadsky inst. geochem. anal. chem., Moscow, 2013.
- 44 J. Adam and R. Přibil, *Talanta*, 1971, **18**, 733–737.
- 45 L. Eleckova, I.S. Baloghi, J. Imrich and V. Andruch, *J. Anal. Chem.*, 2015, **70**, 298–304.
- 46 J. Yun and H. Choi, *Talanta*, 2000, **52**, 893–902.
- 47 R. Khani and F. Shemirani, *Food Anal. Meth.*, 2013, **6**, 386–394.
- 48 P. Berton and R.G. Wuilloud, *Anal. Methods*, 2011, **3**, 664–672.
- 49 M. Hosseini, N. Dalali and S. Moghaddasifar, *J. Anal. Chem.*, 2014, **69**, 1141–1146.
- 50 L. Ranjbar, Y. Yamini, A. Saleh, S. Seidi and M. Faraji, *Microchim. Acta*, 2012, **177**, 119–127.
- 51 M. Mirzaei and N. Amirtaimoury, *J. Anal. Chem.*, 2014, **69**, 503–508.

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Water-immiscible water-rich ionic liquids + water-soluble analytical reagents = novel extraction-based platform for the determination of metal ions

