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Journal of Chromatography A, 1066 (2005) 19–25

JOURNAL OF
CHROMATOGRAPHY A

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Cationic surfactant-based polyfluorate salts: Phase separation and analytical applications in the extraction and preconcentration of ionic species prior to liquid chromatography

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Received 8 December 2004; received in revised form 10 January 2005; accepted 13 January 2005

Abstract

The liquid–solid phase separation originating from the formation of cationic surfactant-based polyfluorate salts (CSBPS) has been explored for extracting and preconcentrating ionic species. Two cationic surfactants were tested; one with aliphatic hydrocarbon tail [Cetyltrimethylammonium bromide (CTAB)]and the other containing a heterocyclic ring [Hexadecylpyridinium bromide (HPyBr)]. Phase separation possibility was investigated with the use of hexafluorophosphates (PF_6^-) and tetrafluoroborates (BF_4^-). The effect of added acid, base and salt on the phase separation and analyte extraction was also investigated. In all cases the obtained phase diagrams consisted of two regions: a homogeneous liquid region and a solid–liquid region. Analytes of hydrophilic and hydrophobic nature such as amines, amino acids and organic chromophores were used as test compounds in both their anionic and cationic forms. The respective recoveries ranged from over 90% for anionic species and in the proximity of 50% for cationic species, remaining below 20% for neutral species. Extracts from alkaline aqueous and plasma samples spiked with tyrosine and phenylalanine were also subjected to HPLC separation with UV detection with satisfactory results. On line application was also enabled using a flow through-solid phase extraction-HPLC hyphenated apparatus, thus adding the element of automatization and increased reproducibility.

Keywords: Cationic surfactants; Polyfuorates; Phase separation; Extraction; Preconcentration; Ionic species; Molten salts; Liquid chromatography

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1. Introduction

Aqueous solutions of non-ionic [1,2] as well as some zwitterionic [3] surfactants are well known for their ability to undergo clouding and liquid–liquid phase separation when heated above a certain temperature referred to as cloud point temperature (CPT) [4]. Phase separation can also be induced in an increased ionic strength environment, that is upon addition of salts [5]. Anionic surfactants [6,7] also exhibit similar behavior, in the presence of concentrated ($C > 2\,M$) acids, that transform the anionic head groups into protonated nonionic formations. In every circumstance the resulting surfactant rich phase creates a microenvironment consisting of a hydrophilic exterior and a hydrophobic core, where covalent, uncharged species are favorably entrapped, while ionic formations are repelled. Thus, this so-called cloud point extraction methodology has been employed, so far, for the extraction and subsequent preconcentration of hydrophobic analytes, while the extraction of hydrophilic and especially ionic species is limited, based on the neutralization of their charge.

Cationic surfactants, on the other hand, have shown limited tendency to micellization and respective phase separation through analogous schemes [8] and they have, therefore, been neglected as candidates for cloud point extraction applications. The main reason is that they require a large hydrophobic counterion (tosylate or salicylate) [9], an anionic surfactant [10], a cosurfatcant [11] or extremely large amounts (20–3 M) of common salts [12,13] to induce micellar

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0021-9673/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.chroma.2005.01.034

growth. Moreover, cationic surfactants with promising micellization properties are limited and commercially not available [12,13]. In the case of commercially popular cationic surfactants like Cetyltrimethylammonium bromide (CTAB) and Cetylpyridinium bromide (HPyBr) more than 2 or 3 M of salt [13] was necessary for phase separation and for this reason direct analytical applications are scarce.

In these applications it became obvious that the cationic surfactant-originated rich phase, still consists of charged counter ions that may well have the ability to interact with ionic species in solution, through simple electrostatic attraction, thus entrapping them into the surfactant extract.

Under this perspective we propose the use of polyfluorates (BF_4^-, PF_6^-) in relatively low concentrations (<1 mM) to generate phase separation of CTAB and HPyBr, using them directly in cloud point extraction of charged species. Motivated by the fact that pairing of unsymetrically substituted, nitrogen-containing cations with inorganic anions has given birth to nonmolecular ionic solvents, better known as ionic liquids (ILs) or molten salts [14,15], we found that when polyfluorates are added to aqueous micellar solutions of CTAB and HPyBr, the later sustain a behavior similar to what Giokas et al. [16] called liquid coacervate extraction, formatting a surfactant-rich solid phase. Upon centrifugation this surfactant rich phase is driven either to the bottom or to the surface of the vial thus separated from the bulk aqueous phase. The ability of this solid surfactant phase – possessing both anionic and cationic components – to interact with ionic species in solution was investigated. Amines, amino acids and organic chromophores in both their anionic and cationic forms, were extracted under acidic and alkaline conditions. The obtained extracts were analyzed by high performance liquid chromatography and UV detection revealing that the proposed methodology offers high recoveries and preconcentration factors. Automatization was also performed by replacing the centrifugation step with solid phase extraction on line connected to HPLC, according to a previously developed assembly [17], thus adding the required reproducibility and handling versatility to the proposed scheme.

2. Experimental

2.1. Apparatus

A Shimadzu UV-2100 spectrophotometer with matched quartz cells of 1 cm path length was used for batch measurements. The HPLC apparatus used for chromatographic experiments consisted of a Shimadzu 10AD series for HPLC equipped with a UV–vis variable wavelength detector(Shimadzu) set at 280 nm. A LiChrospher 100 RP-18 (244 mm × 4.4 mm I.D., 5 μm) column was used for all separations. Two LiChrospher guard columns (10 mm × 4.6 mm I.D.) were also used, one as the SPE cartridge used for the on-line approach, and the other for column protection. The whole system was thermostated at 40 °C in a CTO-10A Shimadzu column oven. Data collection and manipulation were performed by means of a CLASS-VP Shimadzu automated software for chromatography. A multi-channel peristaltic pump (Ismatec, Glattburg-Zurich, Switzerland) and Tygon solvaflex tubing were used for the propulsion of reagents to the SPE cartridge in the automatized on-line application. A Vortex Velp Scientifica mixer was used for thorough mixing of solutions. Phase separation was assisted using a centrifuge (Hettich, Universal).

2.2. Reagents

All reagents were of analytical grade or of the highest grade available. Tyrosine, Phenylalanine, 8-Hydroxyquinoline, tyramine hydrochloride and 1,4-dichlorobenzene were obtained from Sigma Aldrich Chemical Company(USA). Water and Acetonitrile (Merck, Darmstadt Germany) used for chromatographic separation were HPLC grade. Cetyltrimethylammonium bromide (Aldrich, Cat. No. 85,582-0) and Hexadecylpyridinium bromide (Fluka, Cat. No. 52340) were used, without further purification, to prepare 10 g L^{-1} aqueous stock solutions. Potassium tetrafluoroborate (Aldrich, Cat. No. 45,590-3) and Potassium hexafluorophosphate (Aldrich, Cat. No. 51,597-3) were used to prepare 10 g L^{-1} aqueous stock solutions of the respective polyfluorates. As a safety note, proper precautions should be taken when handling surfactants and hexafluorophosphate (use of gloves and masks, or working under a ventilated area) because they are hazardous upon inhalation and skin contact. It should also be taken under consideration, that polyfluorate anions are slowly hydrolyzed towards the formation of hazardous and corrosive hydrofluoric acid, as well as poisonous phosphorous oxides and phosphine, especially in the presence of strong acids. Therefore the wastes produced following the proposed methodology should be collected and properly disposed off.

2.3. Procedures

2.3.1. Molten salt potential investigation

In order to test our assumption that the surfactant rich phase consists of an ionic pair with ionic liquid potential, equimolar amounts of each compound were dissolved in 50 mL of doubly distilled water. The mixture was mixed thoroughly under magnetic stirring for 1 h and left to stand for another 24 h. The resulting solids were filtered under vacuum through a Whatman No.1 filter paper and washed thoroughly with a 10 g L^{-1} NH_4NO_3 solution, until full removal of remaining bromide ($AgNO_3$ negative reaction). Then they were recrystallized from methanol and left to air-dry. Finally they were subjected to thermal analysis (DSC). Table 1 shows the melting points of the derived solids against their precursor compounds. Scanning electron microscopy (SEM) pictures of CTA-PF_6 surfactant rich phase (Fig. 1) reveal lamellar bilayers typical of ion-pairs, analogous to those obtained by Giokas et al. [16].