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Single-drop coacervative microextraction of organic compounds prior to liquid chromatography
Theoretical and practical considerations

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ABSTRACT

Coacervates made of surfactant aggregates, namely aqueous and reverse micelles and vesicles, were firstly used as solvents in single-drop microextraction (SDME) and proposed for the extraction and concentration of chlorophenols prior to liquid chromatography. The formation of coacervate drops in the needle tip of conventional microsyringes depended on the type of intermolecular forces established between the surfactant headgroups making up the supramolecular aggregates; hydrogen bond interactions were strong enough to permit the formation of spherical drops. Stability of 1–50 μL coacervate drops was achieved by introducing the microsyringe needle tip in a PTFE rod, the end of which had been machined out with a heated flanging-tool to get circular flanges (diameters in the range 3.5–6 mm). The parameters affecting the efficiency of single-drop coacervative microextraction (SDCME) were investigated using vesicular coacervates as a solvent and 2-chlorophenol (CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) as model analytes. Coacervative microextraction dynamics fit to the general rate equation of liquid–liquid extraction. The effect of variables such as extraction time, drop volume, stirring rate, pH and temperature, on the extraction of chlorophenols was similar to that described for organic solvent drops. Electrolyte concentrations above 0.1 M caused drop instability. Under the optimum conditions, detection limits were in the range 0.1–0.3 $\mu g\,L^{-1}$. The relative standard deviation was between 4.3 and 5.6 at 20 $\mu g\,L^{-1}$ spiked level. The method was applied to the determination of the four chlorophenols in wastewater, superficial water from a reservoir and groundwater and the recoveries were in the range 79 and 106% at 5–20 $\mu g\,L^{-1}$ spiked level.

1. Introduction

The world of analytical chemistry increasingly involves smaller scales and miniature devices. In this context, microextraction techniques are the result of looking for the miniaturization of classical extraction techniques in order to expend minimum analysis time and chemicals [1]. In recent years, efforts have been made towards the miniaturization of the traditional liquid–liquid extraction. These "micro-techniques", based on the contact between two immiscible liquids, fall into two categories [2], namely microextractions using immiscible liquid films [3–5] and single-drop microextraction (SDME) [4,6–9].

The most extended drop-based configuration in SDME consists of an organic solvent drop hanging from the tip of a GC syringe needle, immersed in an aqueous sample or exposed to headspace [4,9]. SDME is a simple, inexpensive, fast, effective and virtually solvent-free sample pre-treatment technique [1]. In combination with GC, it has successfully been used to extract and concentrate a variety of organic compounds from environmental [10–17], food [10,18] and biological [16,19] samples. However, the applicability of SDME to LC has been restricted because the solvents commonly used in SDME, e.g. toluene, hexane, isooctane, carbon tetrachloride, etc., are not compatible with the reversed phase mode and, besides, the low drop volume used (typically 1 μL) causes low sensitivity in LC analysis.

Different strategies have been developed to surpass the above drawbacks. The compatibility of SDME with LC can be achieved using single-drop liquid–liquid–liquid microextraction (SD-LLLME) [20], which involves the use of three phases, namely the donor (sample), organic and aqueous acceptor phases. Another alternative is to use ionic liquids as solvents [21–23]; they are LC-compatible, water immiscible and non-volatile, thus allowing the application of longer sampling times in headspace SDME. In order to increase the drop volume permitted for extraction, different modifications of

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the needle tip have been proposed, all of them based on increasing the contact area with the drop [21–23]. Recently, a bell-mouthed device has been described that permits the use of 20 μL drops without their dislodgement from the needle [24].

In this work, coacervates are proposed, for the first time, as solvents in SDME. Coacervates are colloid-rich liquids that separate from colloidal solutions under the action of a dehydrating agent, namely temperature, pH, electrolyte or a non-solvent for the macromolecule [25]. The coacervate phase is immiscible with the colloid-poor aqueous equilibrium solution from which it separates. Coacervates based on supramolecular assemblies (e.g. surfactant micelles) have been largely used to extract and concentrate a variety of organic compounds prior to their separation by LC. The extraction technique, initially reported by Watanabe and coworkers [26], has been extensively reviewed [27–32].

Coacervates have unique properties to be adopted as solvents in SDME prior to LC. Thus, these liquids are water immiscible, despite water is a major component of coacervates (about 85%). This property has been explained on the basis of their sponge structure [33]. The macromolecules are arranged into a porous network composed of highly interconnected planar bilayers and although the network contains a huge amount of water, the bilayer walls prevent this water from comixing with the bulk water. Secondly, coacervates are compatible with LC mobile phases. In fact, main applications of conventional coacervative extractions have involved this chromatographic technique. However, the main asset of coacervates is the special structure of the macromolecules making them up. Thus, supramolecular assembly-based coacervates are formed by aggregation of amphiphiles, which provide regions of different polarities that have the potential of solubilizing solutes in a wide range of polarity/charge. Hydrophobic solutes are solubilized into the hydrocarbon region, polar/charged analytes can be solubilized in the polar region through a number of interactions (e.g. electrostatic, π-cation, hydrogen bonds, etc.), and amphiphilic solutes are incorporated to the macromolecules through both hydrophobic and polar interactions and form mixed aggregates. This property makes coacervates extremely versatile extractants.

This paper explores the potential of coacervates for SDME and for this purpose studies both the physical characteristics of 5–50 μL drops and the parameters affecting their extraction efficiency. Different experiments were carried out to determine how the formation and stability of coacervate pendent drops are influenced by the special properties of these liquids. Coacervates made of aqueous micelles, reverse micelles and vesicles were tested for this purpose. Variables influencing the efficiency of single-drop coacervative microextraction were determined using vesicular coacervate drops (10–30 μL), which were selected as a model. Their suitability to extract polar organic compounds was assessed using chlorophenols as model analytes. The effect of matrix components on this microextraction technique was studied by extracting chlorophenols from different environmental water samples. Below, the main results are outlined.

2. Experimental

2.1. Chemicals

All chemicals were of analytical reagent-grade and were used as supplied. Decanoic acid, Triton X-114 and sodium dodecyl sulfonic acid were purchased from Fluka (Buchs, Switzerland), tetrabutyl ammonium hydroxide (Bu_4NOH) and pentachlorophenol (PCP) from Aldrich (Steinheim, Germany), 2,4,6-trichlorophenol (TCP), sodium chloride, octanoic acid, Brij 52 and Brij 30 from Sigma (St. Louis, MO, USA), Triton X-100 from Serva (Heidelberg, Germany), ethylenediamine tetraacetic acid disodium salt dihydrate (EDTA), 2-chlorophenol (CP) and 2,4-dichlorophenol (DCP) from Merck (Darmstadt, Germany) and acetonitrile, tetrahydrofuran and hydrochloric acid from Panreac (Castellar del Vallès, Spain). Ultra high-quality water was obtained from a Milli-Q water purification system (Millipore, Billerica, MA, USA).

2.2. Apparatus

The microextraction apparatus (Fig. 1) consisted of a microsyringe, a PTFE rod, a vial, a stir bar, a magnetic stirrer and a jacketed vessel thermostated by means of circulating water bath. The 50-μL microsyringe, with a flat-cut tip fixed needle (glass barrel I.D.: 1.03 mm, needle I.D.: 22 gauges/0.644 mm), was supplied by SGE Analytical Science (Victoria, Australia). The syringe needle tip was introduced in a 0.5-mm I.D. PTFE rod, the end of which had been machined out with a heated flanging-tool to get circular flanges (diameters in the range 3.5–6 mm). The 20-mL glass vials (60 mm high × 20 mm I.D.) were supplied by Supelco (Madrid, Spain). Cylindrical PTFE-coated stir bars (15 mm long × 4.4 mm diameter) were purchased from Pobel (Madrid, Spain). Their speed was measured using a PCE-155 laser handheld tachometer supplied by PCE-Ibérica (Tobarra, Spain). The jacketed vessel was supplied by Metrohm (Herisau, Switzerland) and the thermostated bath (temperature uncertainty ± 0.1 °C) was supplied by Neslab (model RTE-9, Newington, USA). A Thermo/Finningan (Bellefonte, PA, USA) liquid chromatograph (P4000 quaternary pump and UV6000LP photodiode array detector) was used for quantification. Injection of coacervate drops into de chromatographic system was carried out using a Rheodyne (Rohnert Park, CA, USA) six-port manual sample injector provided with a 50-μL sample loop. The analytical column (Análisis Vínicos, Tomelloso, Spain) was a 15-mm

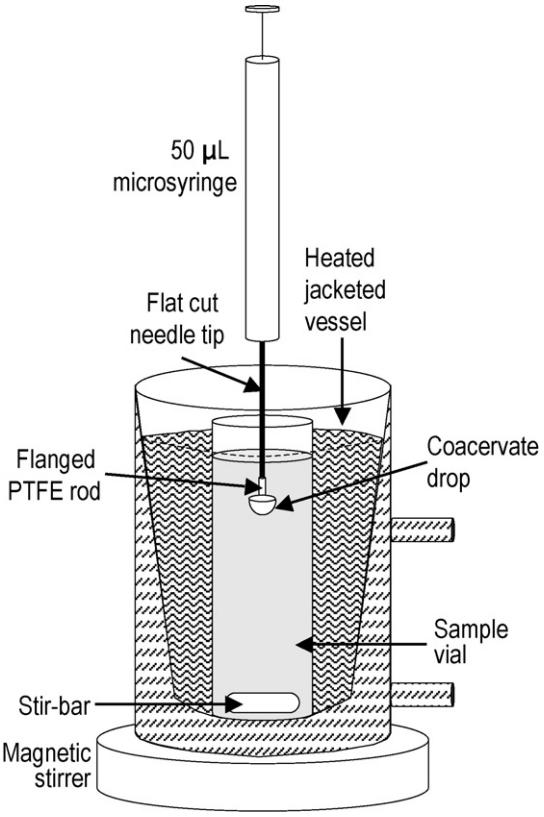

Fig. 1. Schematic illustration of the system used for coacervative microextraction.