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Short communication

An extraction technique for analytical sample preparation in aqueous solution based on controlling dispersion of ionic surfactant assemblies in isotachophoretic migration

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ABSTRACT

An extraction technique for analytical sample preparation in aqueous solution has been developed based on controlling dispersion of ionic surfactant assemblies. An extraction technique was realized based on controlling dispersion of the ionic surfactant assemblies in their isotachophoretic migration during the extraction by arranging the solutions of leading electrolyte, ionic surfactant and terminating electrolyte in order and applying voltage. Potential of the technique for analytical sample preparation in aqueous solution has been demonstrated by extracting a model sample of four alkylphenones, which were analyzed by HPLC after the extraction. The extraction showed concentration effects on all the four alkylphenones of butyrophenone, valerophenone, hexanophenone and heptanophenone in the model sample. The enrichment factors were 5.29, 7.70, 7.25 and 7.49 for the four alkylphenones of butyrophenone, valerophenone, hexanophenone and heptanophenone, respectively. Linear relationship was obtained with all the four alkylphenones between their chromatographic peak areas before and after the extraction in the range of concentration from 0.05 ppm to 1.5 ppm. The RSD of the chromatographic peak areas in triplicate extractions was 7.97%, 3.75%, 2.91% and 4.45% for butyrophenone, valerophenone, hexanophenone and heptanophenone, respectively. Advantages of the extraction technique developed include ease of operation, low reagent cost, no consumption of organic solvents and no requirement for additional phase separation.

1. Introduction

Although instrumental analysis has become an important subject in chemistry, biochemistry, materials science, as well as pharmaceutical, biological, and environmental fields, the preliminary step of sample preparation should not be overlooked in order to obtain accurate and quick analytical information in carrying out modern analytical tasks. As commented by Grob, a worldwide well-known chromatographer, sample preparation is the most error-prone and labor-intensive task in the analytical laboratory [1]. In general, sample preparation serves as two functions. One is to enrich analytes of low concentration to adequate levels of detection or quantification; the other is to isolate the desired components from sample matrices, which the instruments cannot handle directly. Because of its impact on nearly all subsequent steps, sample preparation is an essential step in an analytical process. A successful sample preparation step can improve quality of final analytical results. On the contrary, an inappropriate sample preparation step will render all efforts in vain in the later analytical steps. Hence, there has been a strong research trend of developing and improving sample preparation techniques in the field of analytical chemistry recently [2–10].

The sample preparation step in an analytical process typically involves an extraction procedure, which results in the isolation and enrichment of target analytes from a sample matrix [11]. Liquid–liquid extraction is a classical and common technique used for sample preparation of organic compounds from aqueous samples prior to chromatographic or electrophoretic analysis [12–14]. However, the main drawback of liquid–liquid extraction is that it is a time- and labor-intensive procedure and requires large amounts of high-purity solvents, which are expensive and toxic. Reviews have been published on the recent developments in non-traditional extraction technologies to address the problems mentioned above [15,16]. Solid-phase extraction (SPE) has been developed to overcome the drawbacks of classical liquid–liquid extraction and has been widely used in analytical sample preparation. Advantages of SPE include easier to automate, shorter processing times, low solvent consumption, attainable to remove matrix interferences and possible to extract polar analytes. However, SPE techniques have their own problems. The surface chemistry, and therefore sorption properties, of solid phases are not as reproducible as solvent properties. The mixed retention mechanism occurring sometimes can

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interfere with analyte recovery since elution solvents is ineffective for displacing ionically bound analytes to residual silanol groups of the silica substrate. Solid phases tend to have a higher level of contamination by manufacturing and packaging materials than is the case for solvents. Sample-processing problems in SPE related to the limited sorption capacity of sorbents and analyte displacement or plugging of sorbent pores by matrix components easily pass unnoticed, resulting in changes in analyte recovery [17]. The need to pre-filter the real-life samples to avoid clogging and the steps of cleaning and elution in SPE may lead to analyte loss and contamination.

Surfactants have been extensively used in various analytical techniques [18,19]. Among many others, micellar electrokinetic chromatography (MEKC) [20] together with its on-line concentration scheme of sweeping [21] is a good example, of successful application of surfactants in analytical chemistry. Surfactant mediated extractions are environmentally friendly and cost effective [22–24]. In a surfactant mediated extraction, either phase separation after the extraction or control of dispersion of the surfactant assemblies during the extraction can be employed in principle. Generally, phase separation after extraction are realized by evoking a chemical or physical perturbation in surfactant mediated extraction systems [25,26]. For example, phase separation in cloud point extraction is typically made by heating above the cloud point temperature. A nonionic surfactant micelle solution will separate after a certain time into two phases: a surfactant-rich layer and a bulk aqueous phase [27]. Phase separation in coacervation of ionic surfactant assemblies can be achieved by changing pH [28,29] or adding concentrated aqueous ionic salt solution and introducing organic solvents [30]. In this short communication, we explore potential of the extraction based on controlling dispersion of ionic surfactant assemblies for sample preparation of neutral compounds in aqueous solution. Controlling dispersion of the ionic surfactant assemblies in their isotachophoretic migration during the extraction was realized by arranging the solutions of leading electrolyte, ionic surfactant and terminating electrolyte in order and applying voltage. Comparing with the conventional organic-solvent-based liquid–liquid extraction, advantages of the sample preparation technique presented in this communication like other surfactant mediated extractions include: reduction in costs associated with organic solvent purchase, storage, and disposal, as well as the associated worries regarding toxicity or hazards such as fire and explosion; the capacity to concentrate a plethora of analytes with almost quantitative recoveries; the preconcentration factors to be comparable or superior to other schemes, and adjustable by varying the amount of surfactant [24].

2. Experimental

2.1. Chemicals

Butyrophenone, valerophenone, hexanophenone and heptanophenone were obtained from TCI (Tokyo, Japan). Sudan I was a product of Dr. Ehrenstorfer (Augsburg, Germany). The other chemicals were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Sodium chloride, phosphoric acid, sodium dodecyl sulfate (SDS), sodium octane sulfonate and sodium gluconate (NaGlu) were of analytical grade. Acetonitrile, methanol and ethanol were of HPLC-grade. Distilled water was used throughout the experiments.

2.2. Standard solutions and samples

Stock solutions (1.00 mg/mL) of individual alkylphenones were prepared in ethanol and were stored at 4 °C in a refrigerator when not in use. Working solutions containing mixtures of the alkylphenones were prepared by mixing appropriate quantities of the stock solutions and diluting to desired concentrations with 100 mM H_3PO_4.

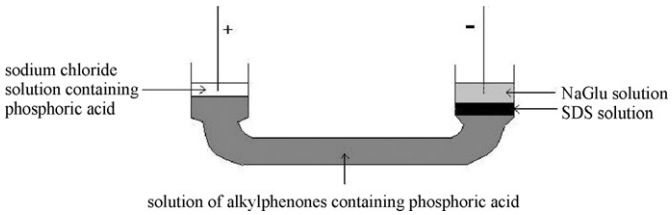

Fig. 1. Schematic of the extraction device.

2.3. Apparatus

A d.c. power supply used was a model of ES 0300–0.45 from Delta Power Supplies (Delta Electronika, Zierikzee, The Netherlands) with programmable voltage in the range of 0–300 V, providing currents in the range of 0–450 mA. A laboratory-built electrolytic cell consisted of two 1.5 mL glass vials connected with a 24 cm U-shaped glass tube of an internal diameter of 13.8 mm. Platinum wires were used for both the anode and cathode. The HPLC system used in this work consisted of an LC-10 AT pump (Shimadzu Kyoto, Japan) and a Linear UVIS 200 ultraviolet/visible (UV/vis) detector (Alltech, USA). The HPLC separation was performed on a 250 mm × 4.6 mm I.D., 5 μm, VP–ODS column (Shimadzu, Kyoto, Japan).

2.4. Procedure of the surfactant extraction

The following solutions were filled sequentially into the electrolytic cell in order with medical syringes (as shown in Fig. 1): 0.2 mL 1400 mM sodium chloride solution containing 100 mM phosphoric acid as leading electrolyte; 2.5 mL mixed solution of the alkylphenones containing 100 mM phosphoric acid as sample; 0.2 mL (equal to zone length of 33 mm) 100 mM SDS, and 0.5 mL 800 mM NaGlu as terminating electrolyte. After the solutions were filled into the electrolytic cell, a voltage of 300 V was immediately applied to the cell with the anode in contact with the leading electrolyte solution and the cathode in contact with the terminating electrolyte solution. After applying voltage for 35 min, a surfactant-rich zone of about 2 mm in length was collected into a centrifuge tube with a syringe and diluted with the same volume of acetonitrile for the HPLC analysis (acetonitrile was added to destroy the surfactant assemblies and to facilitate the HPLC analysis). Then, the power supply was turned off.

2.5. HPLC analysis

Mobile phase consisting of methanol and water (80%:20%, v/v) was used. Flow rate of the mobile phase was set at 1.0 mL/min. Sample introduction was carried out using a Rheodyne six-port switching valve with a 20 μL loop. Detection was made at a wavelength of 245 nm. Chromatographic data were collected and recorded using CSW (Chromatography Station for Windows) (DataApex, Prague, Czech Republic).

3. Result and discussion

3.1. Dependence of dispersion of the ionic surfactant assemblies on the concentration of the leading electrolyte

As long ago as 1897, the theoretical groundwork for isotachophoresis was laid down by Kohlrausch [31]. Fundamentals of