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Short communication

Development of negligible depletion hollow fiber membrane-protected liquid-phase microextraction for simultaneous determination of partitioning coefficients and acid dissociation constants

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ABSTRACT

A new method based on negligible depletion hollow fiber-protected liquid-phase microextraction coupled with high-performance liquid chromatography (HPLC) was developed for the simultaneous determination of partitioning coefficients (K_{OW}) and acid dissociation constants (pK_a), by using phenol, 4-chlorophenol and 2,4-dichlorophenol as model compounds. A 37-mm length polypropylene hollow fiber membranes (600 μm inner diameter, 200 μm wall-thickness, 0.2 μm pore size, ~70% porosity) with two-end sealed were filled with 1-octanol by ultrasonic agitation to prepare the extraction device. The extraction device was deployed in sample solutions, prepared by spiking target analytes in 1-octanol saturated aqueous solutions (500 mL), for negligible depletion extraction. After equilibrium was reached (~5 h), the 1-octanol in the lumen of the hollow fiber membrane was collected for HPLC determination of the target analytes. As the depletion of the analytes in aqueous samples was negligible, the distribution coefficient (D_{OW}) could be calculated based on the measured equilibrium concentration in 1-octanol (C_O) and the initial concentration (C_W) in the aqueous sample of the target analyte ($D_{OW} = C_O/C_W$). The D_{OW} values measured at various pH values were nonlinearly regressed with pH to obtain the K_{OW} and pK_a values of a compound. Results showed that the measured values of the K_{OW} and pK_a of these model compounds agreed well with literature data.

1. Introduction

The distribution coefficient between 1-octanol and water (D_{OW}) and acid dissociation constant (pK_a) of an ionizable compound are key parameters that are related to pharmacokinetic and environmental behaviors, i.e., sorption, distribution, metabolism, elimination, and toxicity [1,2]. Since the D_{OW} of an ionizable compound is pH dependent, the pH independent partitioning coefficient of its neutral molecular form (K_{OW}) is generally reported in the literature. Though various methods have been developed for the determination of K_{OW} [3] and pK_a [4] values, alternatives for high efficient determination of these parameters are still of interests. New approaches by using magnetic nano-absorbent [5], and two-phase hollow fiber-based liquid-phase microextraction procedures with 1-octanol filled in the lumen of a hollow fiber [6] or supported in the pores of hollow fiber membrane wall [7] were adopted for the measurement of D_{OW} and K_{OW}, whereas negligible depletion solid-phase microextraction (nd-SPME) was reported to be applicable for the measurement of pK_a [8].

Although methods for simultaneous determination of K_{OW} and pK_a are of great interest, they are sparingly studied. Reversed-phase high-performance liquid chromatography (HPLC) was recently reported to be a unique tool for the determination of both pK_a and K_{OW} of multicomponent mixtures [1]. In our previous study [9], K_{OW} and pK_a values were simultaneously determined by using hollow fiber supported liquid-phase microextraction coupled with HPLC. The extraction procedure was performed by using a sampling device with ~0.16 μL of 1-octanol supported in the pores of hollow fiber membrane wall, which required small sample volume to avoid sample depletion. However, this sampling device has the disadvantage of very long equilibration time (72 h), probably due to 1-octanol in the 1-octanol saturated sample solution was gradually adsorbed onto the sample device. The long equilibration time limited the application of this method as degradation of the target analytes might occur during the equilibration.

In this present study, a negligible depletion hollow fiber-protected liquid-phase microextraction (nd-HF-LPME) procedure with 1-octanol filled in the lumen of a hollow fiber was developed

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for simultaneous determination of D_{OW} and pK_a. This proposed procedure markedly reduced the equilibration time, and was successfully applied to determine the K_{OW} and pK_a values of phenol, 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP), which were used as model compounds.

2. Experimental

2.1. Reagents and materials

Phenol, 4-CP and 2,4-DCP purchased from Sigma–Aldrich (Milwaukee, WI, USA) were dissolved in HPLC-grade methanol to prepare individual standard stock solutions (2000 mg/L), respectively. Working solutions were prepared daily by appropriate dilution of the stock solution with 1-octanol saturated sodium dihydrogenphosphate buffer. HPLC-grade acetonitrile and methanol were purchased from Scharlau Chemie (Barcelona, Spain). Other chemicals such as sodium dihydrogenphosphate, hydrochloric acid, sodium hydroxide, acetone, and hydrochloric acid were obtained from Sinopharm Chemical Reagent Beijing (Beijing, China). All the chemicals used in the experiments were analytical reagent grade, and ultrapure water (18.3 MΩ cm) produced by a Barnstead Easy-Pure LF system (Dupuque, IA, USA) was used throughout.

The Q3/2 Accurel PP polypropylene hollow fiber membranes (600 μm inner diameter, 200 μm wall-thickness, 0.2 μm pore size, ~70% porosity [10]) were obtained from Membrana (Wuppertal, Germany).

2.2. Pre-saturation of 1-octanol and phosphate buffer

In 1000 mL separatory funnel, 1000 mL of 1 mM sodium dihydrogenphosphate buffer and 4 mL of 1-octanol were added, and then the mixture was shaken for several minutes. After 12 h, the sodium dihydrogenphosphate buffer and 1-octanol were separated and used in the experiments.

2.3. Extraction procedure

The extraction (sampling) device for nd-HF-LPME was prepared as follows: Q3/2 Accurel PP polypropylene hollow fiber membranes were manually cut into a length of 3.7 cm and were cleaned in an ultrasonic bath for 10 min with acetone. Then, the hollow fibers were taken out and exposed to the air till the acetone in the fiber was completely volatilized. After that, the hollow fiber with two-end sealed by using a heated stainless iron tweezers was immersed in water saturated with 1-octanol and sonicated for 2 h in order to impregnate the lumen of the fiber with 1-octanol. Finally, the hollow fiber membrane was taken out and immersed into water and then shaken for about 1 min to wash out surplus 1-octanol. Generally, the prepared sampling device had an effective fiber length of ~3.5 cm with a sampling phase (1-octanol) of ~10 μL in the lumen and ~12 μL in the micropores of the wall. Measurement of the exact volume of 1-octanol was unnecessary as the analyte concentration in the 1-octanl phase was determined by HPLC with external calibration and that in the aqueous phase was kept constant.

Distribution of the target compounds into 1-octanol was performed at room temperature by completely immersing the prepared sampling device into 500 mL of sample solution, held in a capped flask with near zero-headspace, and stirred at a speed of 1200 rpm for prescribed time. The sample solutions were prepared by spiking 200 μg/L each of phenol, 4-CP and 2,4-DCP into 1-octanol saturated 1 mM phosphate buffer solutions with various pH. After equilibrium distribution of the target compounds was reached between the 1-octanol and aqueous phases, the sampling device was harvested and subsequently the two sealed ends were cut open to flush the 1-octanol into a 200-μL glass vial with a 5-mL syringe. Usually, 8 μL of 1-octanol can be harvested, of which 5 μL was manually aspirated into a HPLC microsyringe and injected into the HPLC system for the determination of analyte concentration in the 1-octanol phase (C_O). The C_O values of each analyte were calculated with external calibration curve prepared by injecting 5 μL aliquots of standard solutions. The used fiber was discarded and a fresh one was used for the next experiment. The pH of the sample solution was measured before and after extraction, and the pH value after extraction was used for data process.

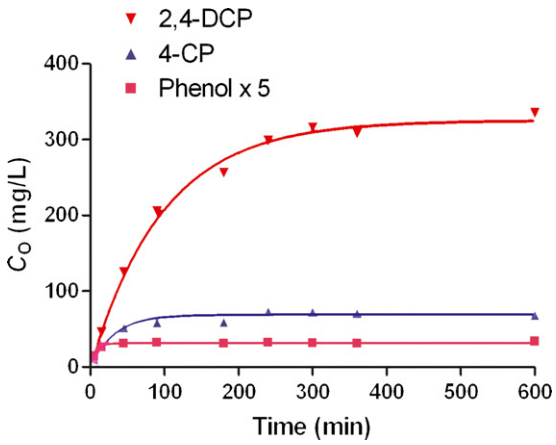

Fig. 1. Uptake profiles of phenols to the 1-octanol filled in the hollow fiber membrane liquid-phase extraction devices. The lines represent the fit of Eq. (1) to the data. Sample solution: 200 μg/L each of phenol, 4-CP and 2,4-DCP spiked in 500 mL of 1-octanol saturated 1 mM sodium phosphate buffer (pH 6.0). Note that the C_O values of phenol were multiplied 5.

2.4. HPLC determination

Determination of the target phenols was conducted with an Agilent 1100 HPLC system consists of a binary pump, a variable-wavelength detector set at 220 nm, a personal computer equipped with an Agilent ChemStation program for LC to process chromatographic data, and an Agilent Zorbax Eclipse XDB-C18 column (150 mm × 4.6 mm I.D., 5 μm particles) for separation of the analytes. Separation of phenol, 4-CP and 2,4-DCP was performed by using a mixture (45:55, v/v) of acetonitrile and sodium dihydrogenphosphate buffer (10 mM, pH 3.0) as mobile phase at a flow rate of 1.0 mL/min.

2.5. Data process

All experiments were conducted at least twice and the mean values were reported. Nonlinear regression of experimental data was conducted by using Graphpad Prism (ver. 4.1, GraphPad Software, San Diego, CA, USA).

Extraction was conducted with a negligible depletion mode, i.e., extracting less than 5% of the dissolved amount of an analyte in samples. Thus, the analyte concentration in the aqueous sample solution can be regarded as a constant that equals its initial concentration (C_W), and D_{OW} can be calculated based on the measured equilibrium concentration in 1-octanol (C_O) and the initial concentration in the aqueous sample of the target analyte ($D_{OW} = C_O/C_W$). Assuming the partitioning to the sampling phase is linear, the uptake profile of analytes can be fitted to a first-order one-compartment uptake model modified from Ref [11]:

$$C_O(t) = C_W \cdot D_{OW} \cdot (1 - e^{-k \cdot t}) \quad (1)$$

with $C_O(t)$ be the analyte concentration in 1-octanol in the hollow fiber at time t, and k the elimination rate constant of an analyte from the 1-octanol in the hollow fiber.