



Dynamic pH determination at high pressure of aqueous additive mixtures in contact with dense CO₂

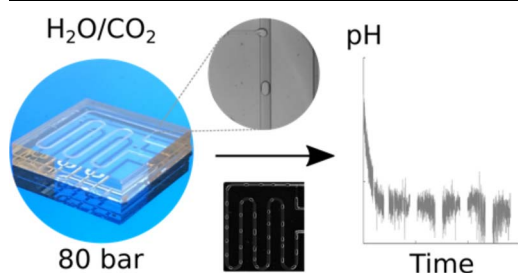


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GRAPHICAL ABSTRACT



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ABSTRACT

A system consisting of a high-pressure tolerant microfluidic glass chip, high-speed absorbance imaging, and image processing has been developed to study rapid dynamic events like pH change in a multiphase flow. The system gives both kinetic and quantitative equilibrated information. By tracking the interactions of aqueous additive mixtures and liquid CO₂, at 80 bar and 24 °C, under flow, measurement at a given P, T condition is done in 0.25 s. The acidification rate to steady state was found to be mass transport limited, occurring in less than 1 s. For 30 mM of the additives ammonium acetate and ammonium formate, equilibrium pH of 4.5 and 4.1, respectively, was seen. These additives are of key importance in common mobile phases used in SFC.

1. Introduction

High-pressure microfluidic systems have similar potential in flow-through chemical systems as what their low-pressure counterparts already have shown, e.g. by providing isothermal systems with less use of analytes, shorter time constants and, lower dead volumes [1]. For high-pressure applications, microfluidics allows for shorter measuring times and faster evaluations than setups using mL-sized batch cells, as exemplified in phase equilibria studies [2]. While batch cell techniques offer high accuracy, the methods are static and are not able to reveal local, space and time-dependent effects. With the emergence of high-

pressure microfluidics, a new tool for dynamically studying these questions is available.

Of high relevance for high-pressure microfluidics and the miniaturization of chromatographic systems is ultra-fast supercritical fluid chromatography (SFC) analysis [3]. Retention times are typically less than 1 min and there is a need to reach mobile phase stability at injection fast. Methods making it possible to study both stability and the dynamics involved when conditions change are important. The highly complex attributes of the mobile phases used in SFC makes these type of measurements challenging.

Chromatographic systems encounter a wide range of flow velocities,

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from 1 to 20 mm/s in columns to several hundred mm/s in tubing, affecting the timescales needed to reach equilibrium conditions. Also, there is a growing trend for the miniaturization of chromatographic systems [4], and as these systems decrease in size, residence times decrease. Meanwhile, SFC is becoming an increasingly competitive method for high-throughput and high-resolution separation of chiral and achiral organic compounds [3,5]. For high-throughput separations, SFC has an advantage as the high diffusivity and low viscosity of supercritical carbon dioxide (scCO₂) as the mobile phase allows for a higher efficiency at higher flow rates than for conventional liquid chromatography [3]. However, SFC using CO₂ shows difficulties with separations of highly polar compounds, and for this reason, modifications of the mobile phase by the addition of polar cosolvents and up to approximately 9% water [6], are made [7,8]. Using a similar approach to separate highly polar analytes with increased resolution, enhanced fluidity hydrophilic interaction liquid chromatography uses CO₂, methanol and water [9,10]. Dense CO₂ (less than 20 mol%) in water-methanol mixtures has been used to improve the separation of polar ionizable compounds like nucleosides [11]. In conventional liquid chromatography, the importance between pH and chromatographic performance is well established where, depending on the nature of the analyte, mobile phase composition and, stationary phase, the pH can affect retention factors, peak shape and resolution [12]. For ionizable analytes, changes in the retention factors by more than one order of magnitude over the pH scale are seen when the ionization of the analytes changes [13]. For the now common ternary component mobile phase composed of CO₂, methanol and, water, such effects are considerably more difficult to study [14,15]. As dense CO₂ and water containing cosolvents mix, carbonic acid is formed and dissociated which acidifies the resultant solution [6,16,17]. As this acidification process is connected to the amount of CO₂ present, the pressure drop over the column and variations in pressure and temperature result in dynamic conditions [18]. Further, pH is most often described for aqueous solutions. When non-aqueous components are present, both solvation energies and activity coefficients of the involved species are different [19]. This affects dissociation constants and the interpretation of pH in SFC mobile phases.

While these are aspects to be further studied, the effects on chromatographic performance that mM additions of ammonium salts of simple carboxylic acids have been investigated by several researchers [20,21], showing how performance parameters, e.g. peak shape, can be improved. For SFC mobile phases with a high degree of polarity, dissociation of ionic species becomes a factor in the separation of analytes. When water is added to the mobile phase, protonation and deprotonation of ionizable compounds become increasingly possible as the ion solubility increases. Since CO₂ both have a solubility in water, that varies with temperature and pressure, and can form the ionizable species carbonic acid and bicarbonate, the situation is complex. Both mixing and hydration of CO₂ in aqueous phases takes time and should result in regions with different, local, pH when conditions change. Control of pH conditions is also essential in several other fields, e.g. in enzymatic processing [22] and extraction [23], where flowing compressed CO₂-water systems are used. The relevance of pH in water-CO₂ microemulsions is also noted, with extensive studies of additive salts having been made [24,25].

In this paper, a system has been developed consisting of a high-pressure chip for segmented flows in combination with a high-speed camera to study rapid dynamic events. To demonstrate its capabilities, the local and time-dependent variations of pH when an aqueous phase meets with dense CO₂ is explored. By utilizing the immiscibility between CO₂ and water, the aqueous phase can together with an indicator be used to probe the pH effects that dense CO₂ have. Due to the large interest in ammonium acetate (NH₄CH₃CO₂) and ammonium formate (NH₄HCO₂) in SFC, these additive salts are further added to the aqueous phase, exploring their effect on changing the pH. By this, a fast method for pH determination for high-pressure applications is demonstrated.

With the method having the ability to measure in both time and space, insight into the development of equilibrium in flow systems is generated. While not a direct measurement of the pH in a SFC mobile phase, we show how these salts are affected in a similar, but simpler, environment.

2. Materials and methods

2.1. Materials

The pH indicator BPB (sodium bromophenol blue, Abcam), having two absorption peaks at 436 and 591 nm corresponding to the protonated and deprotonated species, was used at a concentration of 2 mM in all sample and calibration solutions. The sample solutions were made from NH₄CH₃CO₂ (ammonium acetate, EMSURE®, Merck) and NH₄HCO₂ (ammonium formate, Acros Organics) at concentrations of either 2, 5, 7, 10, 20 and 30 mM; and 2, 7, 10, 20 and 30 mM, respectively. All solutions were made by weighing the corresponding amount of salt and preparing stock solutions, which then were used to prepare the sample and calibration solutions. Deionised water was used both for preparing the solutions and to record blank images of the channels in the chip. Seven calibration solutions were prepared from citric buffer salts (citric acid monohydrate, Acros Organics, and anhydrous trisodium citrate, Alfa Aesar) covering the pH range 3.0–5.2. For an early version of the setup, used to study the local dynamics at the initial contact point of the fluids, a 7.5 pH test solution containing BPB, NaOH and NaCl was used.

2.2. Experimental setup

The fluid system, Fig. 1, consisted of two separate subsystems to provide the chip with both aqueous solutions and dense CO₂. Each subsystem had a high-pressure piston pump (ISCO DM100, Teledyne) and a 1/16" stainless steel tubing line equipped with check valves and needle valves (41AF1, 11AF1 and 15AF1, High Pressure Equipment Company). Both the pump and fluid line for the CO₂ was kept at 3.5 °C using a water bath, two recirculating heaters (E100, Lauda) and a compressor chiller (RK20, Lauda), keeping the CO₂ liquid in the pump. For the aqueous solution subsystem, a 5 mL sample loop was used to inject sample solutions into the chip, using deionized water both as a pushing medium and to rinse the system between samples. Just before

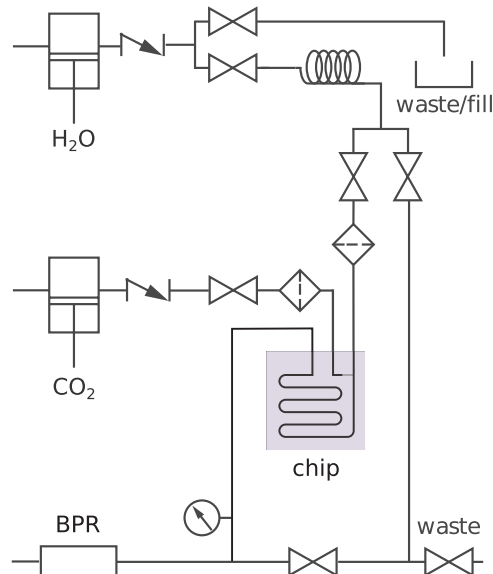


Fig. 1. Schematic drawing of the fluid system and chip. The two pumps (H₂O, CO₂), valves, filters, sample loop, pressure sensor and backpressure regulator (BPR) are shown.

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