NOVEL METHOD FOR ANALYSING PHASE DIAGRAMS USING PERVAPORATION

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ABSTRACT

We propose a novel approach, based on microfluidic technology, dedicated to the exploration of phase diagrams of binary and ternary aqueous systems. The system consists in concentrating solutions in independent microchambers by pervaporating water through PDMS membranes. On the chip, we implement a novel optical technique that allows to monitor in real time the concentration in each chamber. The approach is applied to binary and ternary mixtures, including salts and surfactant solutions. The system allows to detect the formation of crystals along with measuring supersaturations and the solubility level.

KEYWORDS: Pervaporation, Phases Transition, Concentration, Supersaturation

INTRODUCTION

Pervaporation (i.e evaporation of the solvent through a membrane) is currently used in the industry to concentrate or purify solutions. Recently, the process has been implemented in PDMS microsystems [1]. Here we extend this approach by elaborating more complex devices that allow screen phase diagrams of binary mixtures under a real time monitoring of the solute concentration. The monitoring is based on a novel optical technique, that uses the microchamber walls as optical elements.

EXPERIMENTAL

The experimental system uses two-layer soft lithography technology (Fig 1.). Two entries distribute aqueous solutions into six chambers at different concentrations [2]. The chambers ($300 \times 300 \times 20 \mu m$) are separated by thin membranes ($20\text{-}25 \mu m$) from a microchannel along which air is driven ($500\text{-}700 \mu m$ high, between 0 and 500 $\mu L/min$); this channel pervaporates water through the PDMS membranes. Six integrated valves [3] isolate the chambers from the distributor and avoid any mass exchange between neighbor chambers.
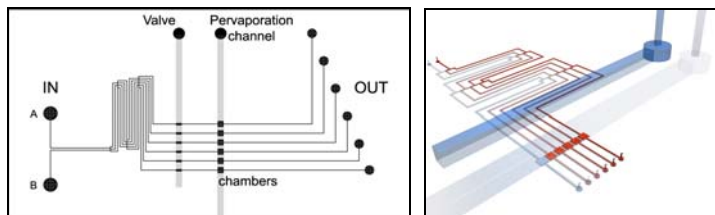

Figure 1. Layout of the system. We distribute solutions A and B among six chambers with equal concentration increments between each chamber.

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781

After the chambers are filled with the solutions, the valves are closed and the air flow is switched on; the solutions thus concentrate by pervaporating water through the membrane. Figure 2 demonstrates this feature with fluorescein solutions.
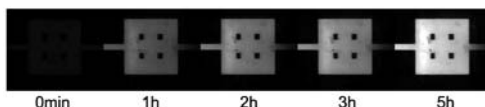

Figure 2. Fluorescein solutions pervaporated through 25µm thickness membrane.

THEORY

The measurement of the chamber concentration is made by using the chamber walls as optical elements. According to the microfabrication process we used (based on grayscale technology), the walls are inclined with respect to the horizontal plane and therefore deviate the incident light. In the model of Fig 3, the amplitude of the effect depends on the optical index of the solution and geometrical quantities. In some range of the solution optical index, the light is entirely deflected and the chamber walls appear as dark lines. In practice, the light intensity collected by the microscope is a continuous function of the solution index; the function can be calibrated with the solute concentration. This technique thus provides a real time monitoring of the solute concentration inside each chamber as they concentrate.
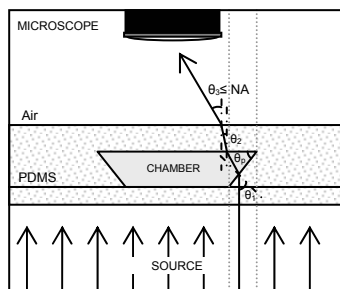

Figure 3. Sketch of the system using microchambers walls as optical elements to monitor solute concentrations inside each chamber.

RESULTS AND DISCUSSION

We applied this technique to a binary system. The six chambers were filled with NaCl solutions with different concentrations, varying from 0 to 3M. Fig 4 shows two chambers where crystals appear as the solutions concentrate and Fig 5 shows the variation of salt concentration with time for one chamber. A sudden jump appears when the crystal nucleates, after which the chamber concentration levels off at the solubility level. In this case, the crystal nucleation is detected and the supersaturation is accurately measured.
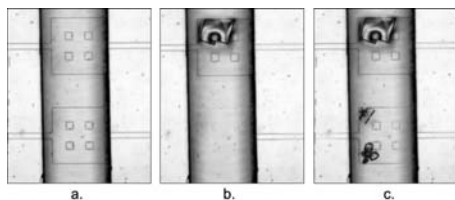
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782

Figure 4. View of two chambers filled with two NaCl solutions: a. initial state t=0 ; b. t=58 min (a crystal is visible in the upper chamber; the walls of the lower chamber are barely visible; c. t=59 min (crystals are visible in the two chambers; the walls of the lower chamber are visible).
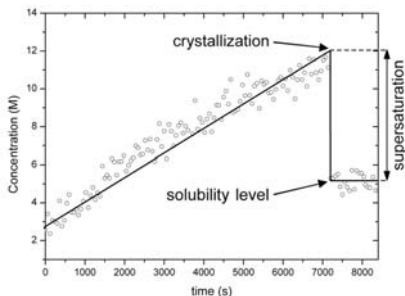

Figure 5. Concentration temporal evolution inside a chamber. NaCl crystallization occurs after 7000s at a concentration of 12M; supersaturation is estimated at 7M, a value consistent with the literature.

We used the same system to determine the phases of AOT solutions at different concentrations. The results are shown in Fig 6. We identified lamellar, cubic and hexagonal phases for different AOT concentrations. The sequence of phases is well correlated with the temporal evolution of the optical signal. The system can thus be used to analyze phase diagrams of complex systems, with an optical monitoring.
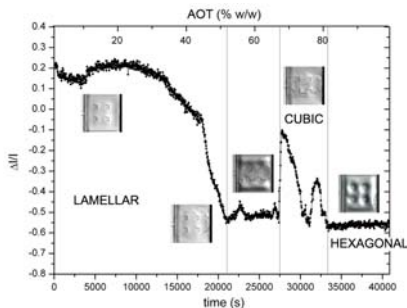

Figure 6. AOT solution observed in a range of concentrations varying from 1% w/w to close to 100% w/w. Three phases are observed: lamellar, cubic and hexagonal, and the transitions are well correlated with the evolution of the optical signal.

CONCLUSIONS

In summary, we present a novel method that allows to concentrate and monitor solutions in microchambers. This system can be used to screen ternary phase diagrams and highly viscous solutions that must be diluted prior to being transported in microchambers for physical analysis.

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783