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Review

Cloud point extraction: A sustainable method of elemental preconcentration and speciation

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ABSTRACT

Trace elements are gaining increasing attention of scientists working in various analytical fields. Presence or absence of a trace element in a system seriously modifies its intrinsic behavior. Cloud point extraction (CPE) is an upcoming technology to preconcentrate and separate many of the trace elements from different chemical and biological systems. The system is sustainable as it involves benign extractants like surfactants and that too at low concentrations at slightly elevated temperatures to form clouds that separate out from the bulk solution. In addition, the extraction behavior of many elements depends on its chemical species. Keeping in view the need to summarize the research encompassing this technique, many review articles were published which cover a selection of the literature published on this topic over several time spans. A myriad of various technological developments has been reported by several workers. These developments have prompted us to revisit the CP technology with a better understanding of its detection, mechanism and extension to species dependent extraction behavior with regard to the state of art determination of trace metals in our day to day applications. The present article summarizes mainly the results of trace metal preconcentration using CP methodology from different practical samples with an insight to the probable mechanism and speciation involved from 2006 onwards.

Contents

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1. Introduction

The cloud point (CP) of a solution is the temperature at which the solution forms two phases. Cloud point preconcentration (CPP), based on the clouding phenomena of surfactants has drawn large attention in separation science. CPP offers many advantages over traditional liquid–liquid extraction [1]. The two basic components as a prerequisite for CPP are a salt solution and a surfactant solution which separates into immiscible surfactant-rich and surfactant-poor phases [2]. In the presence of salt, long-tailed surfactants self assemble in aqueous solution at a particular temperature into long, flexible wormlike micelles, thus rendering the solution viscoelastic [3,4]. An analyte interacting with micellar systems can therefore be concentrated into the surfactant-rich phase in a small volume.

Different elements at low concentrations influence various chemical and biological systems and play vital roles in the determination of their structure and functions [5–11]. Solvent extraction is a widely used separation tool for rare earth metals [12]. However, this method has some problems, such as use of toxic and flammable organic solvents, poor extraction-speed, and low concentration efficiency for solute. Furthermore, due to the dilution in the organic phases, the mass action of the extractant is decreased compared to that potentially present in the pure compound. On the other hand, the heterogeneous extraction at cloud point based on surfactants, are simple, rapid and powerful which extract the solutes existing in the homogeneous or pseudo-homogeneous aqueous solution into the water-immiscible phase after the phase separation. Indeed, the extractant is first dispersed in the aqueous phase by sonication and left to settle at a particular temperature after reaction with the metal cation to be extracted. These methods are more inexpensive, of lower toxicity, and cause negligible environmental pollution than the conventional liquid–liquid extraction. Such methodology also provides high preconcentration factors [13,14]. The system is highly sustainable as it involves the use of benign extractants like surfactants and that too at low concentrations at slightly elevated temperatures to form clouds that separate out from the bulk solution.

2. Procedures to detect cloud point

There are several procedures to detect the cloud point, some of which are enlisted below

- Light scattering or particle counting method
- Refractometry
- Turbidimetry
- Thermo optical method
- Viscometry

2.1. Particle counting method

The particle counting method for cloud point measurement was introduced by Eliassi et al. [15]. The basis of this method is the determination of the number of particles in a mixture. When a new phase appears in a solution, a large number of small particles are produced and the solution becomes hazy. The particles scatter the light beam passing through it. By measuring the number of particles in a solution at various temperatures, it is expected that at the temperature where a new phase appears, a sudden change in number of particles would be observed and this temperature indicates the cloud point for the solution.

Imani et al., prepared several solutions of PEG with sulfate salts with varying mass ratios of PEG to salt from 0.8 to 1 and 1–2 [16]. They used a Spectrex laser particle counter with a laser diode at a wavelength of 670.8 nm. The solution was pumped to a flow cell and the temperature was measured at the entrance of the cell by a thermocouple. At each temperature, the number of particles was measured per cubic centimeter and at the cloud point, a sharp change in the number of particles was observed.

2.2. Refractometry

In designing PEG-salt cloud points, different salt solutions e.g., K_3PO_4, K_2HPO_4, Na_2HPO_4, and Na_2CO_3 along with PEG solution (MW = 10,000) were mixed. A refractometer equipped with a digital thermometer was used through which water was circulated using thermostatically controlled bath. The mixtures of solutions were directly injected into the prism assembly of the instrument using a Hamilton syringe stored at the working temperature to avoid evaporation. The refractive index measurements were done after the liquid mixtures attained the constant temperature of the refractometer. This procedure was repeated at least three times [17].

2.3. Turbidimetry

The effect of salt concentration on CP temperatures can be studied by the turbidimetry method using a reaction calorimeter. The calorimeter is attached with a glass head with turbidity sensor, temperature sensor and a stirrer along with a temperature control and programming device to measure the CP temperature with the help of the turbidity sensor. The turbidity is measured in % units (Milli-Q quality distilled water is taking as reference). The second method is to study the transmittance of the solution was with increasing temperature. A slow heating rate of 0.2 °C/min is maintained in all the measurements to minimize the thermal lag between the sample and the solution. The cloud point of each sample is determined as the average of at least two independent scans. [18].

2.4. Thermo optical method

Thermo optical analysis (TOA) provides a simple and rapid, method to determine cloud point curves of binary polymer/solvent systems. The sample is taken in a pyrex tube which is connected to a vacuum pump and evacuated. The tube is then collapsed and sealed by a vacuum when one end is heated by a flame while the content of the tube is maintained at sub-ambient temperature by liquid nitrogen. The cloud point curves are determined at the saturation vapor pressure of the solvent. A polarizing microscope is fitted to it through a photodiode and a microprocessor. The heating–cooling stage is designed for observation of the thermal behavior of a sample under the microscope. The temperature program for the given run is entered into the microprocessor. This program consists of a starting temperature, a heating and cooling