REVIEW PAPER

Cloud Point Extraction as a Method for Preconcentration of Metal Ions

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Abstract

Cloud point extraction (CPE) is an attractive technique that reduces solvent consumption and exposure, disposal costs, and process time. This method has an important practical application and is used to separate and concentrate the analyte as a step before its determination, and after the formation of a poorly water-soluble complex. Use of nonionic surfactants as "green solvents" which represent an effective alternative to toxic organic solvents (in classical extraction), along with other advantages, such as low cost and low flammability, makes this method attractive and worth further research and optimization. This paper presents a detailed description of the principles, procedure, advantages, disadvantages and application of CPE.

Keywords: Cloud point, surfactant-rich phase, nonionic surfactants, metal extraction, "green" method.

1. INTRODUCTION

Cloud point extraction (CPE) is a unique extraction method that provides economical sample preparation with high extraction efficiency. In this method, the separation of the two phases is based on the aggregation behavior of the surfactant in aqueous solution, which depends primarily on the temperature and then on the concentration of the surfactant (Hagarová, Kubová, Matúš, & Bujdoš 2008). If a solution in which the surfactant concentration is above the critical micellar concentration (CMC) is heated to a certain temperature (cloud point temperature, T_{CPE}), then the surfactant molecules form micelles that create an additional phase, which is manifested by turbidity of the solution, i.e. a cloud point is reached (Shokrollahi & Ahmadi 2017). This phase is called the surfactant-rich phase because it contains most of the surfactant, is heavier than the aqueous phase, and therefore separates the phases as shown in Figure 1.

Unlike the surfactant-rich phase, the diluted aqueous phase contains a low concentration of the surfactant corresponding to the critical micellar concentration (CMC) (Haddou, Canselier, & Gourdon 2014). Non-polar molecules can enter the micelles and thus be co-extracted,

Figure 1. Separate phases in CPE.

while polar substances and ions will remain in the aqueous phase (Reffas, Benabdallah, Youcef, & Ilikti 2010). In this way, CPE using non-ionic surfactants attracts significant attention as an alternative to conventional extraction processes for separation and preconcentration of substances(Shokrollahi, Joybar, Haghighi, Niknam, & Niknam 2013).

2. CLOUD POINT

The cloud point is the temperature at which the surfactant solution, whose concentration is close to or above its critical micellar concentration (CMC), becomes cloudy and separates into two phases (Bader, Edbey, & Telghederb 2014). Under these conditions, the micelles aggregate to form a turbid phase with a high concentration of surfactant that separates from the aqueous phase (Arnold & Linke 2007). The term cloud point refers to the dispersion of light created by the formation of a colloidal system, the so-called Tyndall effect. The Tyndall effect is the name for the scattering of light on colloidal particles (Kraemer & Dexter 2002). Rays of light, colliding with colloidal particles, are reflected in all directions. If a narrow beam of light is passed through a colloidal solution and the solution is observed perpendicular to that beam, the light in the solution appears to be cloudy (Heidorn 2006). The turbid portion of the surfactant solution, also called the surfactant rich phase, may be present as the upper or lower phase of the solution, as shown in Figure 2 (Garavito & Ferguson-Miller 2001).
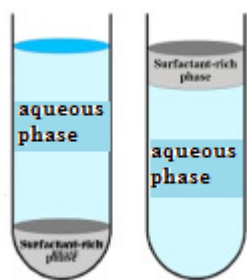

**Figure 2.** Position of the surfactant solution phases at the cloud point.

The most experimentally modified condition to reach the cloud point is temperature. The temperature at which the phase separation occurs is a function of the surfactant concentration (Muslim 2015). Some empirical links between surfactants and their cloud points can be found in several published papers. In their work, scientists Gu and Sjöblom (1992) showed that there is a linear relationship between the cloud point and the logarithm of the number of oxyethylene units for surfactants, such as alkyl oxyethyl ethers, as well as a linear relationship between the cloud point and the number of carbon atoms in the hydrophobic chain. Further, Schott (2003) also determined a linear relationship between the cloud point of water-soluble polyoxyethylated nonionic surfactants with the average number of oxyethylene units per molecule. The cloud point of polydispersed surfactants may be related to their hydrophilic and lipophilic balance (Materna, Cote, & Szymanowski 2004). Huibers, Shah, and Katritzky (1997) developed a general empirical connection for estimating

the turbidity of pure nonionic surfactant from the alkyl ethoxylate class. For a set of 62 structures composed of linear alkyl, branched alkyl, cyclic alkyl and alkyl ethoxylate chains, the cloud point can be estimated with an accuracy of + 6.38 °C using the logarithm of the number of ethylene oxide residues. At lower temperatures, the molecules of each nonionic surfactant form hydrogen bonds with the water layer using their polar groups (polar heads) and polyoxyethylene units (Shokrollahi & Refahi 2019). When the temperature increases, there is an increase in entropy, which causes dehydration of the polyoxyethylene chains and destroys the layer of water molecules. From this point, Van der Waals forces weaken between the molecules, which makes an important contribution to the micellar formation of agglomerates, and, consequently, the separation of the solution phases occurs (Kori 2019). The cloud point can be changed by the addition of electrolytes, the presence of alcohol, other surfactants, polymers and some organic and inorganic compounds that can cause an increase or decrease in the cloud point temperature. These effects are known as "salting-out" (Bezerra, Arruda, & Ferreira 2005).

3. PHASE SEPARATION MECHANISM

The cloud point phenomenon occurs when a solution containing nonionic or zwitterionic surfactants, i.e. surfactants, by heating to the appropriate temperature, divide or separate into two phases (Jamali, Gholinezhad, Balarostaghi, Rahnama, & Rahimi 2013). The concentration of surfactants in the solution must be above their critical micellar concentration (CMC) in order for micelles to form or later to separate the phases (El-Naggar, Lasheen, Nouh, & Ghonaim 2010). Anionic surfactants can also be used to preconcentrate metal ions by the CPE method. This type of surfactant requires the presence of a high concentration of acids to reach its cloud point (Casero, Sicilia, Rubio, & Perez-Bendito 1999). The cloud point extraction methodology used to remove metal ions from the solution consists of several basic steps. The first step is the addition of a suitable surfactant in a certain concentration, which exceeds its CMC, to an aqueous solution containing metal ions (Moghimi 2008). If the addition of a particular chelating ligand is required, it can be initially dissolved in an organic solvent or directly in water, depending on the solubility. The next step is to heat the prepared extraction solution above its cloud point. Surfactant rich phase and aqueous phase occur. The phase separation process is performed by centrifugation (Figure 3) (Sheikh, Gouda, Mostafa, & El Din 2015).

In some cases, prior to the separation process itself, it may be necessary to add a small amount of a separating agent such as salts or alcohols. The content of the
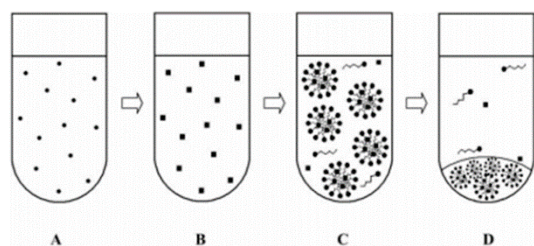
Figure 3. Cloud point extraction A - Low concentration metal ion solution; B - Metal chelates formed by the addition of a complexing reagent; C - Addition of surfactant and binding of metal chelates to the interior of the micelle; D - Phase separation after heating and centrifugation.

release agent must be a compromise between the ideal viscosity and the metal concentration (Stalikas 2002). As previously mentioned, two isotropic phases are formed during CPE. The first phase is called the surfactant rich phase and it contains the separated analyte, i.e the metal ions "trapped" inside the surfactant micelle (Yang, Jia, Yang, Li, & Liao 2017). For the most part after separation it forms a second phase called the aqueous phase. It is important to note that only the nonionic or zwitterionic surfactants that form colloidal micelles are used in CPE (Yamini, Feizi, & Moradi 2020). The following nonionic surfactants of the polyoxyethylene type are most commonly used in the CPE method:

- Triton X-100 ($T_{CPE} = 69\ °C$)

- Triton X-114 ($T_{CPE} = 25\ °C$)

- Brij 30 ($T_{CPE} = 2\ °C$)

- Brij 35 ($T_{CPE} > 100\ °C$)

- Brij 56 ($T_{CPE} = 69\ °C$)

- Brij 97 ($T_{CPE} = 72\ °C$)

- Tween 80 (nonionic surfactant based on sorbitol structures) ($T_{CPE} = 65\ °C$) (Douglas 2016)

The cloud point (T_{CPE}) depends on the surfactant used and covers a wide temperature range, as mentioned above. Nonionic surfactants generally have a lower T_{CPE} than zwitterionic surfactants (Yuan, Jiang, Cai, He, & Liu 2004). This temperature can vary depending on the surfactant concentration and dilution of the solution, especially the addition of salt. The division of the solution into two phases during CPE is primarily guided by hydrophobic interactions, i.e. Van der Waals forces, dipole-dipole, and hydrogen bonds that have separate roles and side effects (Anastas 1999). Similar effects have been observed with liquid-liquid extraction in non-polar solvents. Extraction kinetics and achieving equilibrium separation

is a fast process, from 2 to 5 minutes (Järup 2003). Performing such fast extraction, with high efficiency and a temperature of 20-25 °C, contributes to increasing the use of the CPE method (Maniasso 2001; Pramauro & Prevot 1995).

4. METAL EXTRACTION MECHANISM

Above the cloud point, the surfactant molecules act as organic solvents in the liquid-liquid extraction where the metals are distributed between the organic and aqueous phases (Ojeda & Rojas 2009). The efficiency of CPE depends on the inherent interactions of metallic species with micellar structures. The following factors must be taken into account during CPE:

a) Constant formation of metal complexes

b) Kinetics of complexation reactions

c) Phases of transfer of metal species or chelates to micellar media

It is interesting that there are distribution constants of different metal chelates related to each extracted metal species. Due to the hydrated nature of the surfactant phase, the distribution coefficients are generally lower than presented observing the conventional liquid-liquid extraction method (Abbas, Madrakian, & Siampour 2006). In this extraction the constant distributions are always independent of the nature of the metal ion. These facts indicate that the mechanism of distribution in CPE differs from that in the conventional extraction method. In addition, in CPE, the mechanism of chelate distribution differs from chelation (Farajzadeh & Fallahi 2006). Chelating reagents likely extracted due to specific interactions, such as hydrogen bonds between functional groups on chelating reagents and ether oxygen or the terminal OH- group of a nonionic surfactant and chelate, were extracted into the hydrophobic portion of the aggregated micelles (Akita & Takeuchi 1999; Tani, Kamidate, & Watanabe 1997).

Another aspect related to the extraction efficiency is the ionic strength. Its increase does not significantly change the extraction efficiency, and the addition of salt makes the phase separation process easier. The degree of metal partition from aqueous solution to the surfactant-rich phase during CPE can be described by a typical distribution coefficient D:

$$D = \frac{(C_M)_s}{(C_M)_w} \tag{1}$$

where $(C_M)_s$ represents the final metal concentration in the surfactant-rich phase, and $(C_M)_w$ is its concentration in the aqueous phase after the separation process.

The extraction factor (E) is given by the following expression:

$$E = D\left(\frac{V_s}{V_w}\right) \qquad (2)$$

where V_s/V_w is the phase volume ratio, i.e. the volume of the surfactant-rich phase (V_s) divided by the volume of the aqueous phase (V_w) after the phase separation step.

The fraction of the extracted analyte p is given by the expression:

$$p = \frac{D}{D + (V_w/V_s)} \qquad (3)$$

5. ADVANTAGES AND DISADVANTAGES OF CPE

The use of micellar systems, in methods such as CPE, has attracted considerable attention in recent years mainly because it is in line with the principles of "green chemistry" (Rasoolzadeh, Hashemi, & Serenjeh 2017). Green chemistry can be defined as a set of procedures to reduce or eliminate the use or generation of toxic substances for human health and the environment (Hussain & Keçili 2020). CPE is a "green" method due to the fact that, as an extractor, it uses dilute solutions of surfactants that are less toxic than classical organic solvents used in liquid-liquid extraction. The relatively low prices of surfactants and the stability of their solutions should not be overlooked as some of the other advantages of their application (Casero et al. 1999). The small volume of surfactant-rich phase obtained by this approach allows the design of extraction strategies that are simple, inexpensive and highly efficient compared to classical extraction methods (Filik & Çekiç 2011). Another advantage of CPE over traditional extraction processes is the high preconcentration factor that can be obtained starting from small initial sample volumes (Arya, Kaimal, Chib, Sonawane, & Show 2019). Traditional extraction techniques often require an additional step of re-extracting the metal ion solution resulting in a larger final volume of the solution, so that achieving a high preconcentration factor uses a larger sample volume (Kojro & Wroczyński 2020). Therefore, CPE is a good extraction method for concentrating a wide range of metals with quantitative recovery and high preconcentration factor. This makes it possible to achieve an identical preconcentration factor to that in other techniques without the additional re-extraction step (Bezerra et al. 2005). The main limitation of CPE is the relatively low partition coefficient of several types of metals with some chelates. However, this can be circumvented by the use of highly hydrophobic ligands (Quina & Hinze 1999). Another advantage of Cloud point extraction (CPE) is the way it is performed. The CPE involves only a few manual steps and uses standard equipment and glassware that can be found in most laboratories, namely pipettes, flasks, hotplates and centrifuges (Mohd, Zain, Raoov, & Mohamad 2018). Therefore, no specialized measuring or extraction devices are required. Surfactants are quite cheap and have low flammability (Yamini & Ghambarian 2012). As already mentioned, quantitative yields are obtained in a short time and several samples can be processed at once. At the same time, there are some other limiting factors to consider (Rahnama, Eram, & Jamali 2014). The surfactants used can cause analytical interference and affect the limits of detection, especially if the analyte cannot be effectively isolated from the surfactant, depending on the analysis. The extraction efficiency decreases with increasing polarity of the solution and with extremely volatile or thermally unstable compounds (Douglas 2016).

6. CPE APPLICATION

In recent years, Cloud point extraction (CPE) has become widely utilized for separation and preconcentration of trace metals (Hagarová & Urik 2006). The metal may be in ionic form or in the form of hydrophobic chelates which are formed in certain reactions under suitable conditions. Thorough optimization of chemical and operational parameters of this method provides quantitative separation and high efficiency of preconcentration in the determination of metal ions (Bezerra et al. 2005). The use of CPE is primarily directed at metal ions and other hydrophilic compounds, however significant attention has been paid to small organic molecules. Priority is given to the removal of pollutants from water using CPE, as well as the extraction from solid and biological samples (Pocurull, Fontanals, Calull, & Aguilar 2020). In addition to metal ions, this includes phthalates, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzodioxins and dibenzofurans, chlorophenol and organochlorine pesticides (Kachangoon, Vichapong, Burakham, Santaladchaiyakit, & Srijaranai 2018). CPE applications in drug-related studies are of interest. Some of the extracted drugs are benzodiazepines, lorazepam, alprazolam, followed by preconcentration of β-lactam antibiotics as well as countless studies to determine the active compounds in Chinese herbs (Douglas 2016).

7. CONCLUSION

The cloud point extraction methodology offers a simple, fast, inexpensive process and, unlike other preconcentration techniques, does not pollute the environment. All of the above contributes to the popularization of research and application of the CPE method as an alternative to conventional extraction methods.

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