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ORIGINAL ARTICLE

Effect of Additives on the Cloud Point of the Octylphenol Ethoxylate (30EO) Nonionic Surfactant

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Abstract The effect of different additives on the cloud point (CP) of an octylphenol ethoxylate (OPEO30) aqueous solution was investigated. The CP of OPEO30 is higher than 100 °C due to its approximately 30 oxyethylene units per molecule, which limits its use in cloud point extraction (CPE) procedures at room temperature. However, the presence of additives can promote a decrease in CP, allowing its use in CPE. Halide presence decreased the CP of OPEO30 in the following order $F^- > Cl^- > Br^-$. It was also observed that the addition of divalent anions resulted in a more pronounced salting-out effect than monovalent anions. Blends of OPEO30 and its counterpart with 7.5 units of ethylene oxide (OPEO7.5) were also investigated, and it was verified that the CP of OPEO30 decreased linearly with increasing OPEO7.5 concentration, showing that mixing surfactants is a strategy to be explored. In the presence of small amounts of alcohols that are partially soluble in aqueous solution, such as isobutanol and pentanol, cloudiness was observed at temperatures below the CP of pure OPEO30 solution.

Keywords Cloud point · Nonionic surfactants · Octylphenol ethoxylate 30EO · Electrolytes

Introduction

Nonionic surfactants represent a class of surfactants that have great potential for industrial applications including cosmetics, pharmaceuticals, ore flotation, and drilling fluids for oil recovery processes [1–4]. In analytical laboratories, nonionic surfactants have been used in cloud point extraction (CPE) procedures [1–4].

Aqueous solutions of most nonionic surfactants may become turbid when heated to a temperature known as the cloud point (CP). This is an important nonionic surfactant property. Below the CP, only a micellar solution exists with a single-phase. Above the CP, the surfactant solubility in water decreases and becomes turbid forming two phases: (1) a small volume of a surfactant-rich phase, and (2) an aqueous phase in which the surfactant concentration is approximately equal to the critical micelle concentration (CMC) [5–8].

Nonionic surfactant water solubility is due to oxyethylene units. When the carbon chain length increases and the oxyethylene chain decreases, the surfactant solubility in aqueous solution decreases. This results in a lower CP [9–11]. In addition to the presence of oxyethylene units in the surfactant molecule, the CP can be influenced by several other factors such as the concentration and presence of additives including inorganic salts and organic compounds. These additives can modify the surfactant-solvent interaction and change the CMC, the size of the micelles and the surfactant solution behavior. Thus, additives can increase (salting-in) or decrease (salting-out) the CP [1, 12–14].

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Nonionic surfactant CP has been extensively studied because of its current use in CPE, allowing various applications such as the extraction of organic contaminants and the preconcentration of metals from an aqueous environment [15–17]. In CPE, chemical species (additives) are commonly added to modify the CP. There are many studies concerning the CP of aqueous surfactant solutions, including the *tert*-octylphenol ethoxylate series, in the presence of additives that include inorganic salts, surfactants and alcohols [10].

The CP can be modified due to the breaking of the water structure by the addition of anions and some hydrophobic cations, which promotes the hydration of oxyethylene groups [11]. The occurrence of binding between cations and molecules also results in salting-in effect. The addition of anions that do not break the water structure, such as Cl^-, Br^-, SO_4^{2-}, or cations that do not complex with oxyethylene groups (Li^+, Na^+, K^+, etc.), cause a salting-out effect due to the dehydration of these groups.

Bai et al. [12] studied the effect of inorganic salt presence on the CP of a secondary alcohol ethoxylate with 7 EO groups and concluded that the various salts decreased the CP and that sodium sulfate was the most effective. Li and Chen [13] added different concentrations of sodium sulfate to the same surfactant and observed that the excess of this salt results in a very viscous surfactant-rich phase.

Delgado et al. [15] evaluated CP decreases by adding lauryl alcohol ethoxylate with 4 EO groups C12EO4 or OPEO7.5 surfactants and then extracted and pre-concentrated organic compounds from sea water. Akbaş and Batigöç [10] studied the effect of OPEO7.5 on the CP of octylphenol ethoxylate with 35 EO groups (OPEO35) and inferred that the CP decreases with increasing OPEO7.5 concentrations. Sharma and Bahadur [18] studied the effect of adding alcohols with carbon chains up to five carbons in the CP of triblock polyethylene oxide–polypropylene oxide–polyethylene oxide copolymer. They observed that in the presence of alcohols, from CH_3OH to C_4H_9OH, CPs increased while pentanol showed an opposite effect.

Surfactants with oxyethylene units $p > 20$ have CPs above 100 °C and therefore are rarely used in CPE. For preconcentration and separation procedures, after the extraction, a centrifugation step is generally necessary to separate the phases. During this step, the sample temperature is decreased and the turbidity is dissolved because there is only one solution phase below the CP. Thus, it is important that studies be conducted to evaluate the ability of additives to reduce the CP so that the procedure can be performed at room temperature [10, 19].

The octylphenol ethoxylate OPEO30 is a nonionic surfactant with an average of thirty oxyethylene units, described in the literature as having a CP > 100 °C [20]. Due to this characteristic, the use of OPEO30 solutions in CPE has not been reported in the literature. In general, CPE experiments are performed with surfactants with a CP below room temperature. Thus, it is necessary to use surfactants with a CP that satisfies this condition or to change the temperature with additives. In this study, the effect of various chemicals, such as salts, alcohols and a nonionic surfactant (OPEO7.5), at different concentrations, on the CP behavior of OPEO30 in aqueous solutions has been investigated.

Experimental

Materials

Nonionic surfactants used in this study were polyoxyethylated octylphenols (Triton X series from Dow). These surfactants have the chemical formula $R–C_6H_4–(OC_2H_4)p–OH$, where “R” is a branched octyl group and “*p*” is the average number of oxyethylene groups. In what follows they are abbreviated OPEOp. The surfactants OPEO7.5 and OPEO30 employed in this study were all analytical grade and were obtained from Sigma-Aldrich (St. Louis, MO, USA). The water used to prepare the sample solutions was doubly distilled and then purified with an ultra-purification system (Bedford, MA, USA). Surfactant solutions (10 %, w/v) were prepared by dissolving 10.0 g surfactant in water and diluting to the mark in a 100 mL volumetric flask.

Sodium nitrate, potassium nitrate, sodium sulfate, potassium sulfate, ammonium sulfate, sodium chloride, sodium fluoride and potassium bromide salts and isobutanol and pentanol alcohols were of analytical grade and obtained from Merck (São Paulo, Brazil).

Apparatus

CPs were obtained in a water-bath heater with an adjustable temperature (Tecnal, Piracicaba, Brazil) equipped with a digital thermometer. Temperature could be controlled within 0.1 °C.

General Procedure

The CP of the surfactant solutions was determined by visual observation of the abrupt change in the appearance of the system, which occurred during the heating of the samples solutions. For this, each aqueous surfactant solution was heated in a controlled temperature bath, and the CP was taken as the temperature at which the solution became cloudy. The determination was carried out three times in each case.

The effect of additives on the CP of OPEO30 was evaluated by adding different amounts of each chemical (salts, alcohols or OPEO7.5) to the test tube with 1.0 mL of OPEO30 solution and 10.0 mL of water. In studies with alcohol and salt additions, the concentrations were expressed in molarities. In tests involving the addition of OPEO7.5, the concentrations were expressed in w/v%. The final OPEO30 solution concentration considered in the present study was 0.9 % (w/v).

Results and Discussion

OPEO30 is described in the literature as having a CP > 100 °C [20]. Because the CP of surfactant solutions can fall below 100 °C by adding electrolytes, such as sodium nitrate, the CP of OPEO30 was determined experimentally through the addition of different amounts of sodium nitrate and extrapolating the electrolyte concentration to zero. As a result, linear relations were observed between the CP and the salt concentration as described by the following equation:

$$CP = -10.2\ C_{NaNO_3} + 113.5 \quad (r = 0.996) \qquad (1)$$

where C_{NaNO_3} is the sodium nitrate concentration in mol L^{-1}.

Using Eq. 1 and extrapolating the sodium nitrate concentration to zero, the experimental CP of the OPEO30 solution was estimated to be 113.5 °C. This result is consistent with a previous study that found a CP of 110.3 °C employing a similar extrapolation procedure [20].

Effect of the Addition of Inorganic Salts

The salts most studied for CP reduction of surfactant solutions are sodium and potassium salts [1, 8, 12]. Ions play a crucial role in surfactant solutions, and the changes in CP produced by individual ions are different. Therefore, the ability of sulfate salts (Na_2SO_4, $(NH_4)_2SO_4$ and K_2SO_4) and halogen salts (NaCl, NaF and KBr) to decrease the CP of OPEO30 was evaluated. It is worth mentioning that these effects can also be related to changes in pH promoted by the ions. The salt concentrations were evaluated from 0.2 to 2.2 mol L^{-1}, except for NaF in which concentration was as high as 0.8 mol L^{-1} due to its low solubility in aqueous solution.

Figure 1 shows the effect of the presence of monovalent halogenated salts at different concentrations on the CP of OPEO30. The CP decreased with increasing electrolyte molarity, and the fluoride anion provided a more pronounced effect. In the lyotropic series, it was expected that the effect on decreasing CP was in the following order: $F^- > Cl^- > Br^-$. This occurs because the ionic sizes increase along the group, consequently decreasing the formal charge density on the anion, which results in a decreased attraction on the anion and thereby decreased attraction on the water. Similar results were obtained in studies with OPEO35 [10] and its counterpart with 9.5 EO groups (OPEO9.5) [19].

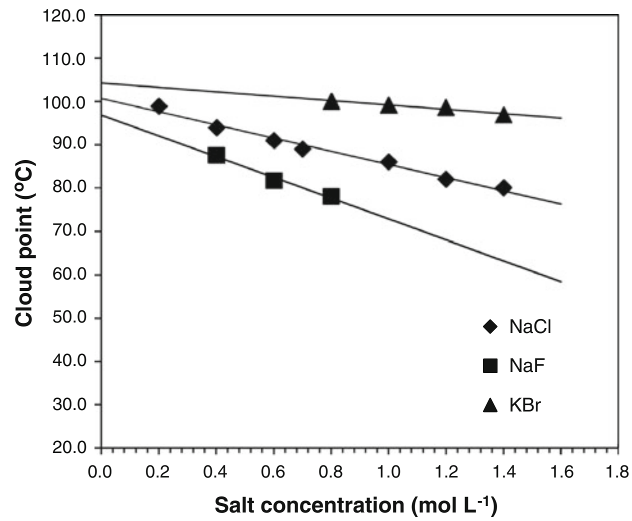

Fig. 1 Effect of halogenated monovalent salts on cloud point of OPEO30 solution (0.9 %, w/v)

A comparison of the effect of monovalent and divalent anion salts on the CP of OPEO30 was performed, and the results are shown in Fig. 2. The effect was most pronounced with divalent anion salts than monovalent anion salts. As shown in Fig. 2, with the addition of 0.8 mol L^{-1} sodium sulfate or 1.2 mol L^{-1} ammonium sulfate, the CP of the OPEO30 solution can be reduced to ambient temperature (approximately 20–25 °C). These anions promote the association between molecules, competing with hydration water of the surfactant. The overall effect of a salt on the CP of a surfactant solution depends both on its cation and anion. However, it is worth mentioning that, in general, the effects of cations are smaller compared to the effects of anions, especially with large polyatomic anions.

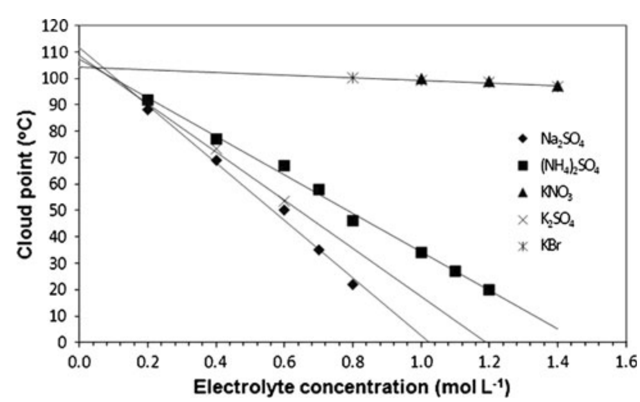

Fig. 2 Effect of different salts on the cloud point of OPEO30 solution (0.9 %, w/v)

Figure 2 also shows the effect of cations on the CP of OPEO30. The order of effectiveness on reducing CP was as follows: $Na^+ > K^+ > NH_4^+$. The same effect was observed after the addition of electrolytes to secondary alcohol ethoxylate with 7 or 9 EO groups, and C12-15 primary alcohol ethoxylate with 7 EO groups [21].

Effect of the Addition of Nonionic Surfactant OPEO7.5

In many applications, mixtures of surfactants, rather than a pure surfactant, are used to maintain the desired physical properties of the surfactant solution. Surfactant mixtures are also used to achieve desired characteristics, such as high solubilization capacity. It is expected that the CP of a mixed surfactant system will be between the CPs of the individual surfactants [9].

The CPs of binary surfactant mixtures of OPEO30 and OPEO7.5 were evaluated, keeping the OPEO30 concentration constant (0.9 %, w/v) while varying the concentration of OPEO7.5 (0.2–1.8 %, w/v).

CPs <100 °C were not observed when the concentration of OPEO7.5 was <0.4 %. As shown in Fig. 3, from OPEO7.5 concentrations >0.5 % (w/v), CP values decrease linearly with increases in the OPEO7.5 concentration as described by the following equation:

$$\mathrm{CP} = -23.0\,\mathrm{C}_{\mathrm{OPEO7.5}} + 102.2 \quad (r = 0.995) \qquad (2)$$

where $\mathrm{C}_{\mathrm{OPEO7.5}}$ is the OPEO7.5 concentration in %, w/v.

According to Akbaş and Batigöç [10], this effect is due to increased micelle concentration, which results in a greater micelle-micelle interaction, facilitating phase separation. Wang et al. [22] evaluated the effect of adding octylphenol ethoxylate series surfactants (OPEO7.5, OPEO9.5) to OPEO4.5 CP and concluded that the OPEO4.5/OPEO9.5 mixture resulted in a higher CP than the OPEO4.5/OPEO7.5 mixture.

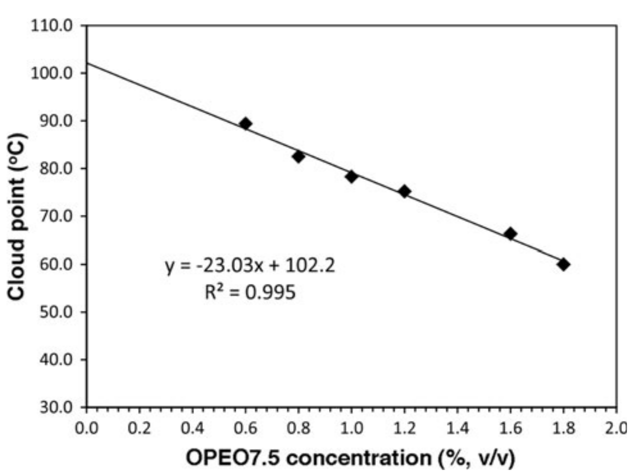

Fig. 3 Cloud point of OPEO30 solution (0.9 %, w/v) in the presence of OPEO7.5

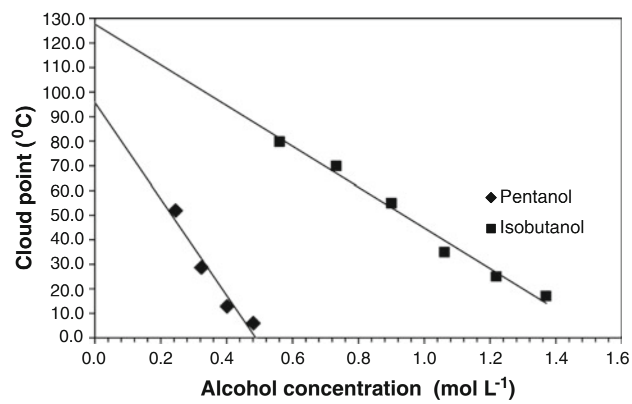

Fig. 4 Cloud point of OPEO30 solution (0.9 %, w/v) in the presence of isobutanol and pentanol

Effect of Alcohols

Long chain alcohols are partially soluble in water. Thus, these molecules can be solubilized in the micelles and absorbed into the micelle-water interface leading to the growth of the micelle and reduced surfactant CP [11]. Studies in the literature show that the short chain alcohols with a relatively high solubility in an aqueous solution increases whereas the long-chain alcohols solubilization into surfactant micelles decreases the CP of a nonionic surfactant micelle aqueous solution [2, 11, 18, 21].

In the present study, various concentrations of isobutanol and pentanol were added to an aqueous solution of OPEO30. When isobutanol was at concentrations <0.6 mol L^{-1}, no turbidity was observed at temperatures <100 °C. As shown in Fig. 4, although the addition of both alcohols promotes the reduction of OPEO30 CP, pentanol decreased it more than isobutanol. The presence of organic additives, which are infinitely water soluble, increases the free energy of the surfactant in the micelle or in the separated surfactant-rich phase [23]. Similar results were obtained when alcohols with carbon chains greater than four carbons, decreased the CP of aqueous solutions of silicone surfactants [21].

Conclusions

In cloud point extraction, the CP is a critical factor and the use of surfactants that are cloudy at room temperature are necessary. The CP of OPEO30 is higher than 100 °C, which limits its use in CPE procedures at room temperature. However, it was observed that the addition of salts, alcohols with carbon chains greater than three carbons, or OPEO7.5 decreases the CP of OPEO30 aqueous solution.

In most cases, a linear relationship between CP and additive concentration was found. In this way, the use of additives may be an effective strategy that can facilitate the use of OPEO30 in CPE procedures.

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