

Review Paper

Salt-Induced Recovery of Volatile Organic Acids Using Non-ionic Surfactants [†]

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Featured Application: This research could serve as a theoretical basis for the advancement of extraction of volatile organic acids using surfactants.

Abstract: Non-ionic surfactants are considered as one of the highest useful surfactants as they are the second largest group produced by volume at about 35%. Due to their low toxicity, the demand is escalating on extensive use of these amphiphilic materials for efficient, non-energy-requiring recovery of volatile organic acids (VOA) from aqueous mixtures. This separation process is mainly due to the cloud point property of surfactants which is referred as the temperature of the system at which two phases are formed. One of the phases is micellar-rich and the other is micellar-poor. In these micelles, the surfactant molecules are oriented in a way that the hydrophilic heads shield the hydrophobic tails from the other water molecules in the system. This assembly partitions the organic compounds within the interior of the micelles which acts as the pseudo-organic phase. This work elucidates how salting-out affects the cloud point of ethoxylated non-ionic surfactants, resulting in VOA separation. Studies suggest the sensitivity of the cloud point to the presence of electrolytes, and its dependence on the parameters hydrophile-lipophile balance (HLB) and on the number of ethylene oxide (EON) units in the surfactant molecule. Electrolyte addition, in the form of salt, causes dehydration of micelles as salt is a water-structure maker. The salt changes the solvent structure by aggregation and formation of larger micelles. This translates into a lipophilic shift which reduces the cloud point and the surfactant's HLB. As the HLB decreases, the more hydrophobic the surfactant, resulting in better separation. The type of salt influences the characteristics of the inter-phase that separates the phases formed. Typically, polyvalent cations such as Al³⁺ and Ca²⁺ are more effective in decreasing the HLB than the monovalent cations (e.g., Na⁺ and K⁺) because of their higher surface charge densities. Since the surfactant's HLB is dictated by its ethylene oxide component (i.e., HLB decreases with EON), it follows that non-ionic surfactants with lower EON could achieve better separation in the presence of salt. Although the actual VOAs separation could possibly be affected by other parameters (e.g., amount of added surfactant and salts, and mass transfer rates), the response of surfactant's properties (i.e., cloud point, HLB, and EON) to salt addition could be utilized to establish an enhanced VOA extraction from aqueous systems.

Keywords: ethylene oxide number; extraction; hydrophile-lipophile balance; salting-out; short chain fatty acids

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1. Introduction

Volatile organic acids (VOAs) are short chain fatty acids with a wide range of applications in the pharmaceuticals, petrochemicals, food, cosmetics, tanning, and chemical industries. These compounds can be derived from wastewater through bacterial fermentation, typically in the form of acetic, propionic, butyric, and lactic acids each at a concentration of 2.5 to 10 g/L [1]. The processing of wastewater into a spectrum of marketable products is the concept of biorefinery. Instead of waste stream to be treated and disposed, wastewaters are used to produce precursors of high value-added products. Similar with its derivatives, the synthesis of these VOAs as platform chemicals is profitable with its current market prices of 550 USD/ton for acetic acid [2], 1600–2000 USD/ton for propionic acid [3], 1600–5000 USD/ton for butyric acid [4], and 3000 to 4000 USD/ton for lactic acid [5]. With approximately 34 billion gallons of wastewater treated daily in the United States alone [6], the recovery of these VOAs is economically attractive.

Due to the increasing demand and usage of these VOAs, there are several recovery methods that have been explored, which include absorption, adsorption, electro dialysis, reverse osmosis, nanofiltration, membrane contactor, and solvent extraction [7]. Solvent extraction is one of the most popular strategies to recover VOAs from dilute aqueous solutions because of its effectiveness. However, the downside of solvent extraction is the use of extractants (e.g., amines, C₅–C₁₂ alcohols, C₅–C₈ ketones, benzene derivatives, isoamyl acetate, di-isopropyl ether) that may be toxic or inhibitory to microorganisms if this method is to be used for in-line recovery of VOAs (i.e., extractive VOAs fermentation or in situ VOAs extraction) [8]. Hence, the use of non-ionic surfactant as extractant is recommended since generally, these surfactants are less toxic than the ionic. The absence of charge in the head of the non-ionic surfactant molecules reduces its toxicity effect on the negatively charged surface of bacterial cells [9]. In contrast, charged or ionic surfactants could interact with the charged bacterial cells making them more inhibitory to microbial growth.

This work was done to elucidate the effect of electrolyte (salt) on the recovery of VOAs using ethoxylated non-ionic surfactants. Recovery improvement was anticipated due to salting-out, which is considered a valuable mechanism to induce substances to separate out of aqueous solutions by addition of salt [10]. This happens when the water solubility of non-electrolyte substances like VOAs decreases as salt concentration increases [11]. This paper expounds how salting-out influences the behavior of surfactant-water solutions in terms of the cloud point, hydrophile-lipophile balance (HLB), and the number of ethylene oxide (EON) units. Recommendations on selection of suitable non-ionic surfactant to effectively recover VOAs from aqueous solutions were then provided based on the identified and anticipated effect of salts to the above-mentioned surfactant properties.

2. Mechanism of Salting-out

The recovery of VOAs using a non-ionic surfactant proceeds through three major steps: adsorption, aggregation, and solubilization. When a surfactant is introduced in an aqueous solution of VOAs, the surfactant molecules accumulate at the surface of the solution [12]. This is termed as adsorption. The orientation of the hydrophilic head and hydrophobic tail of the surfactant molecules on the surface of the solution depends on the composition of the mixture in the bulk phase [13–16]. If the solution is too polar, the hydrophilic heads will interact with the water molecules of the solution, reducing the surface tension [17–21]. Once the surface is saturated with the surfactant, the surfactant molecules bind together and begin to form micelles. The aggregation behavior of the surfactant transforms the molecules into a dense state with the lipophilic groups (i.e., hydrophobic tails) at the interior of the micelles and the hydrophilic groups at the outside [22]. Finally, in solubilization, the lipophilic core of the micelle interacts with the hydrophobic side groups [23] of the VOAs, incorporating these acids in the aggregates of surfactant molecules.

In salt-assisted extraction, the separation of VOAs from a mixture is governed by the combination of electrostatic repulsion and enhancement of hydrophobic effect [24]. Salts in the bulk phase create a strong electric field [25], which leads to screening out of electrostatic repulsion between the surfactant hydrophilic head groups and the formation of hydration shell that makes water molecules unavailable for surfactant hydration [26]. This therefore leads to a decrease in solubility of the VOAs in the aqueous solution with increasing salt concentration. In selecting a particular salt for this application, the salt should have high solubility in water and low solubility in the surfactant. Typically used are small, multiple charged anions such as sulfates, phosphates, and carbonates [24].

3. Adjustment on the Cloud Point due to Electrolytes

Among different amphiphilic materials, non-ionic surfactants are frequently used in organics extraction due to its unique property called the cloud point. Cloud point occurs due to the decrease in affinity for water of hydrophilic heads [27]. Below the cloud point temperature is the existence of micellar solution [28] and above it is a sudden onset of turbidity in the surfactant solution [29]. This signifies that the mixture starts to phase separate. The cloudy dispersion is attributed to the dehydration of the surfactant's polyoxyethylene chain (EON) [30], hence, the formation of larger aggregates which means higher solubilization capacity to recover the VOAs.

Non-ionic surfactant exhibits optimal effectiveness if used for extraction near or below its cloud point [31]. Cloud point depression is known to occur in the presence of salt electrolytes as this property is highly affected by salinity [32]. When introduced into the aqueous solution, the salt dissociates and interacts directly with water molecules forming strong bonds, thereby increasing the enthalpy and entropy of the mixture. The surfactant affinity for the polar medium is then reduced, promoting the formation of the coacervate droplets that triggers phase separation [27].

4. Relationship between Cloud Point and HLB

Non-ionic surfactants are comprised of the hydrophobic tail and the hydrophilic headgroups with ethylene oxide units, as represented in Figure 1 [33]. The strength and size of these groups in the molecule determines the surfactant's HLB [34], which dictates how the surfactant will interact with the components in the solution. The higher the number means that the surfactant is more hydrophilic or water soluble. In particular, surfactants with HLB value less than 10 are water insoluble, while those with greater than 10 are lipid insoluble. Hence, for the recovery of VOAs, surfactants with HLB value less than 10 should be selected to form a wrapping layer that will isolate the acid molecules from the more polar components.

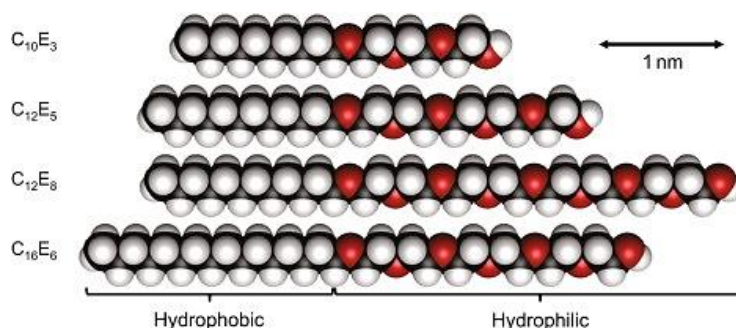


Figure 1. Molecular models of the alkyl and ethylene oxide chains of oligo(ethylene oxide) monoalkyl ether non-ionic surfactants [33].

The effect of added electrolytes on the cloud point of non-ionic surfactants has been the subject of many studies and most of this research determined that the HLB value changes with the cloud point [35–38]. In a study by Arkhipov et al. [39], the equation

representing the change in cloud point of a neonol surfactant, upon addition of NaCl (Equation (1)), has the same form with the equation for its effective HLB (Equation (2)). This clearly shows the dependence of HLB on the cloud point. In both equations, the cloud points and the HLBs decrease with the addition of salt exponentially. The notations t_{cp} and t_{cp}^0 represent the cloud point of the aqueous solutions, C is the salt concentration, N and N_0 refer to the HLB numbers in the presence and absence of salt, and k is the slope coefficient that dictates the boundary conditions for cloud point and HLB based on C , respectively. Due to the processes of dehydration of the non-ionic surfactant molecules and competing action of electrolyte ions, the micelle size increases with decreasing number of aggregates and the value of the cloud point decreases along with the HLB [39].

$$t_{cp} = t_{cp}^0 \exp(-kC) \quad (1)$$

$$N = N_0 \exp(-kC) \quad (2)$$

5. Response of Hydrophilic Units to Kosmotropicity

Kosmotropicity refers to the efficiency of most common ions as promoters of salting-out and it follows the decreasing orders of the Hofmeister series [40,41]. For anions, the hierarchy is $\text{OH}^- > \text{SO}_4^{2-}, \text{CO}_3^{2-} > \text{ClO}_4^- > \text{BrO}_3^- > \text{Cl}^- > \text{H}_3\text{CCOO}^- > \text{IO}_3^-, \text{IO}_4^- > \text{Br}^-, \text{I}^- > \text{SCN}^- > \text{NO}_3^-$, while for cations, the hierarchy is $\text{Na}^+ > \text{K}^+ > \text{Li}^+ > \text{Ba}^{2+} > \text{Rb}^+ > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mg}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+} > \text{Cs}^+ > \text{Mn}^{2+} > \text{Al}^{3+} > \text{Fe}^{3+}, \text{Cr}^{3+} > \text{NH}_4^+ > \text{H}^+$. A more kosmotropic ion promotes enhanced degree of hydrogen bonding with water molecules in a solution. On the other hand, the ions which diminish the water molecule structure by disrupting the hydrogen bonding pattern are termed as chaotropic ions [42]. The order of interaction of these types of ions is not always in accordance with the Hofmeister series as it varies depending on the nature of the system.

The variation in the salting-out ability of the ions depends on the competition between the hydrogen bonding of ion-surfactant's hydrophilic group, ion-water, ion-ion, water-water and water-surfactant's hydrophilic group. In a molecular dynamic simulation study on the effects of addition of monovalent salt to polyethylene oxide surfactant solutions, the interaction was initiated with the ion binding with water as a single entity [43]. At the air-ion solution interface, the phase is negatively charged [44] because of the strong adsorption tendencies of the anions than the cations [45–47]. Within the solution, the anions dominate the cations in terms of salting power in majority of the cases [48–50]. After dissociation of salts, short-ranged interactions among various species take place favoring most of the hydrogen bonding interactions. The hydration of the hydrophilic groups in the form of ethylene oxide units in ethoxylated surfactants is then highly influenced by the charge density of ions [43]. With increasing salt concentration, the cloud point decreases with HLB [45]. Since higher surface charge density ions are much more effective at decreasing the surfactant's cloud point and HLB, this therefore means that polyvalent cations have higher salting power than the monovalent cations [51].

Since salts bring about the dehydration of the hydrophilic moiety of the surfactant causing the enhancement of micelle formation, the ethylene oxide number (EON) should also be considered in selection of non-ionic surfactant for the recovery of VOAs. The EON dictates the hydrophilicity of the surfactant while the propylene oxide content is typically used to measure the hydrophobicity [52]. The HLB is directly proportional with the EON. When the EON value is high, the solubility of the surfactant in the aqueous solution increases [53] which is not ideal since the aim is to dehydrate the surfactant entities to attain the separation of VOAs.

In some cases, manufacturers of surfactants do not provide the EON value. Since EON increases with critical micelle concentration (CMC) [54], CMC can also be used as a guide in selecting the suitable surfactant for VOAs recovery. CMC is a parameter that defines the surfactant concentration at the onset of micelle formation [55]. With a lower

value of CMC, the faster is the formation of bilayer, and the larger the hydrophilic head group parameter and the hydrophilic area per molecule of the non-ionic surfactant [54].

6. Conclusions and Recommendations on Selection of Non-ionic Surfactant

In selecting the suitable non-ionic surfactant in recovery of VOAs, the nature of the surfactant and the type of organic acid to be recovered should be considered. Since the mechanisms involved in the separation of VOAs from other components of an aqueous mixture include the dehydration of micelles and the hydration of the hydrophilic groups, the target acid to be separated should be less polar compared with the other components. This favors the binding of the hydrophobic tails of the micelles with the acid's hydrophobic chain. With the aim of increasing the solubilization capacity of the surfactant which corresponds to more acid molecules being entrapped by the micelles, the HLB value should be low. This is because the solubilization capacity is larger for a surfactant with longer alkyl chain or if the surfactant is lipophilic. The HLB is directly proportional with the CMC and EON. However, between the CMC and EON, it is more straightforward to use the CMC in selecting the suitable non-ionic surfactant since it specifies the amount of surfactant required to reach the maximum surface tension reduction. Hence, the lower the value of the CMC, the less amount of surfactant is required to effectively recover the VOAs. Aside from the HLB and CMC, the cloud point temperature of the surfactant should be checked to ensure occurrence of two-phase partitioning and optimal effect of using the surfactant. The recovery of the VOAs can still be enhanced by salting-out wherein the selection of appropriate salt type can be based initially on the anions and the charged density of ions.

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