Inhibition of citral degradation in an acidic aqueous environment by polyoxyethylene alkyl ether surfactants

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Citral is a flavour component widely used in food and cosmetic industries, but is chemically unstable and degrades over time in aqueous solutions due to acid-catalysed and oxidative reactions leading to loss of desirable flavour. The present study reveals the effect of non-ionic micellar solutions of Brij30 and Brij35 on the extent of solubilisation and stabilisation of citral. The rate of chemical degradation of citral in acidic aqueous solutions was found to be highest, which was subsequently reduced significantly within these studied surfactant systems, suggesting protection of citral from an acidic environment once it is incorporated into the micelles. The work concludes that polyoxyethylene alkyl ether surfactants with lower HLB value, less dense hydrophilic corona and more hydrophobic core volume are efficient in solubilising and stabilising citral against an acidic environment.

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1. Introduction

Citral (3,7-dimethyl-2,6-octadienal) an acyclic monoterpene aldehyde occurs naturally in herbs, plants and citrus fruits (Ortiz, Gonzalez-Garcia, Ponce-Monter, Castaneda-Hernandez, & Aguilar-Robles, 2010) and is composed of natural mixture of two geometric isomers geranial (trans-citral, citral A) and neral (cis-citral, citral B) in 3:2 ratio (Choi, Decker, Henson, Popplewell, & McClements, 2009). Citral is one of the most important natural flavouring compounds, which has intense lemon aroma and flavour and is widely used as an additive in food, beverages and cosmetics with high consumer acceptance (Djordjevic, Cercaci, Alamed, McClements, & Decker, 2007). Consumer demand for natural flavour ingredients and more complex and authentic aroma profiles have resulted in an increased demand for the incorporation of citral into different food and beverage products (Djordjevic, Cercaci, Alamed, McClements, & Decker, 2008). Since flavours are often used in acidified beverages, the problem with citral is that it is chemically unstable and degrades rapidly during storage at acidic pH and under oxidative stress leading to the formation of compounds that produce undesirable off-flavours, resulting in loss of product quality and a decrease in shelf life limiting its application in food and cosmetic industries (Yang, Tian, Ho, & Huang, 2011). Strategies to inhibit citral degradation, such as reduction of storage temperature, alteration of pH and the partial pressure of oxygen are not practical for many foods and beverages (Djordjevic et al., 2007). Also citral is not fully water soluble, so the formulations of citral which increase its concentration and its physical and chemical stabilities for use in foods and beverages would be a major benefit for the food industries. Since citral degradation occurs predominantly in acidic aqueous solutions, the rate of its chemical degradation can be altered appreciably by incorporating it into a colloidal dispersion such as emulsion, microemulsion or micellar solution. In earlier studies, citral has been stabilised by encapsulating it in emulsions (Djordjevic et al., 2008; Yang, Tian, Ho, & Huang, 2012; Yang et al., 2011) or micelles (Choi, Decker, Henson, Popplewell, & McClements, 2010; Rao & McClements, 2012) as encapsulation isolates citral from the reactive molecules, such as protons and free radicals present in the aqueous medium. Yang et al. (2011) studied the effects of oil-in-water nanoemulsions combined with antioxidants on the stability of citral and the results suggested that encapsulation of citral in the emulsions and the addition of appropriate antioxidants could enhance chemical stability of citral during storage. Choi et al. (2009) investigated the impact of composition of triacetin and medium chain triglycerols (MCT) on the oil–water partitioning and chemical degradation of citral and concluded that both MCT as emulsion droplets and triacetin as microemulsion droplets were able to appreciably slow its degradation rate. The problem associated with these studies is that they involve a lipid phase, which is itself prone to undergo oxidation and degradation at low pHs into products like 2-heptanone, 1-octen-3-ol and butanoic acid (Yang et al., 2011). An inverse relationship between pH and lipid oxidation has been reported in literature wherein the pro-oxidant species, which bring about the oxidation of lipids, become much more active at low pH resulting in the
development of rancid flavour (Schäfer & Buettnner, 2000; Tichivangana & Morrissey, 1985). Djordjevic et al. (2008) used whey protein isolate (WPI) and gum arabic (GA) stabilised oil-in-water emulsions to stabilise citral and showed that the rate of degradation of citral is the same in GA and WPI stabilised emulsions at pH 3. WPI was found to be more effective than GA to inhibit the oxidation of citral. However, the problem with this method is the isoelectric point associated with the proteins used for stabilisation. Depending on the pH of medium, proteins attain negative charge which promotes the oxidative reactions. Some authors employed hydrocarbon oils like octadecane (Mei et al., 2010) and hexadecane (Djordjevic et al., 2008) to stabilise citral which are not biocompatible and hence cannot be used in food industry. Choi et al. (2010) reported degradation of citral in micellar medium and concluded that citral degradation was decreased by increasing Tween 80 concentration as a result of incorporation of citral into the inner hydrophobic core of the micelle. As non-ionic surfactants are reported to be non toxic, biocompatible (Chu & Zhou, 1996), stable to pH and ionic strength of the medium (Lawrence & Rees, 2000), they have been used in a number of commercially available edible formulations approved by FDA e.g., Movicol, Miralax, etc. and for solubilisation and delivery of pharmaceuticals (Ayorinde, Gelain, Johnson, & Wan, 2000) and neutraceuticals (Brush et al., 1957).

In addition, Brij35 has even been used for stability enhancement of citral (Choi et al., 2009; Mei et al., 2010). So any serious health effect regarding the investigated surfactant system is not expected at low concentrations.

In this study, we have investigated the extent of solubilisation of citral and the rate of its degradation in aqueous polyoxyethylene alkyl ether surfactant (Brij30 and Brij35) solutions. The influence of pH, temperature, surfactant concentration and the polyoxyethylene chain length in the surfactant has been studied with the aim of identifying suitable conditions for preparing a stable micro-heterogeneous medium for citral. The experimental results of this study may be useful for designing a suitable formulation of citral required during various food, cosmetic and beverage applications.

2. Materials and methods

2.1. Materials

Citral was a Merck (India) product. Brij30 and Brij35 amphiphiles were Aldrich products. All chemicals were used as received. The chemical structures of citral and surfactants are presented in Scheme 1. The stock solutions of citral, Brij30, and Brij35 were prepared in 50 mM phosphate buffer of pH 7, 3 and 1 with triple distilled water and utilised to prepare the samples of desired concentrations.

2.2. Solubility and stability experiments

Stock nanoemulsions of 5.6 M citral were prepared in buffered surfactant solutions of Brij30 and Brij35 surfactants at various surfactant concentrations (1–5 mM) at pH 7, 3 and 1 according to method of Rao and McClements (2012). Aliquots of stock nanoemulsion were then added to the vials containing 3 ml of corresponding concentrations of Brij30 and Brij35 surfactants to give a range of final citral concentrations (4–30 mM). The 5 ml sample vials were sealed with screw caps and then were agitated for a period of 1 h on a magnetic stirrer at a temperature of (25 ± 0.5 °C) using magnetic Teflon pieces previously placed in the vials. The resulting colloidal dispersions were withdrawn periodically for turbidity measurements with a Schimadzu Spectrophotometer (model UV-1650). The turbidity of citral was determined at its λ_{max} using the formula, \( \tau = -\left(\frac{1}{I_0}\ln(I_1/I_2)\right) \), where \( \tau \) is the turbidity, \( I \) is the path length and \( I_1 \) and \( I_2 \) are the transmitted intensities with and without citral in the surfactant solutions, respectively (Staﬀord, Ploplis, & Jacobs, 1990). This method was used to monitor changes in characteristics of citral oil droplets after addition to micellar solution as well as over time.

2.3. Analysis of degradation of citral using high performance liquid chromatography (HPLC) at different pHs

The liquid chromatography system consisted of a Schimadzu LC-20A with a SPD-M20A variable-wavelength UV detector (set at 237 nm), a CBM-20A/20Alite system controller, LC-20AB pump and an injection valve with a 25 μl loop (Shimadzu, Kyoto, Japan). Separation was achieved using an Enable C18G column (250 mm x 4.6 mm, 5 μm) and a CTO-10ASvp column oven. The mobile phase used consisted of water:methanol (40:60, v/v), flowing at a rate of 0.5 ml min⁻¹. The instrument was operated at 40 °C.

3. Results and discussion

3.1. Solubilisation capacity

Solubilisation is an important process in many areas of food science, such as encapsulation of lipophilic components, flavour delivery, emulsion stability, detergency, development of micelle-forming surfactants and absorption of lipophilic components within the human gastrointestinal tract (Garti, Spennath, Aserin, & Lutz, 2005). Micelles are capable of solubilising non-polar molecules into their hydrophobic interiors, thus enabling them to be dispersed into an aqueous phase in which they are normally insoluble. The aqueous solubility of citral calculated spectrophotometrically was found to be 571 mg/ml tallying well with literature value of 590 mg/ml (UN Environmental Programs, 2001) using \( ε = 2.82 \text{ L mmol}^{-1} \text{ cm}^{-1} \) determined from the calibration plot of citral in water. The solubilisation characteristic of citral in micellar solution was expressed in terms of solubilisation capacity which is a measure of maximum amount of citral that can be incorporated into a given amount of surfactant. The solubilisation capacity of surfactant solutions was determined by measuring the turbidity of system containing different citral concentrations. As shown in the prototype plot Fig.1, for lower citral concentrations the solutions appeared transparent, the turbidity of which increased slightly when citral concentration was increased. However at high-

![Scheme 1. The structures of citral and surfactants used in this study.]
er citral concentrations, a large linear increase in turbidity was observed resulting in formation of opaque solutions. Therefore, the plot of turbidity with citral concentration, showed two straight lines at relatively low and high concentrations, the point of intersection of which gives the maximum solubilisation capacity, \( C_{\text{max}} \) of a given surfactant solution towards citral. As detailed by Rao and McClements (2012), at lower concentrations of citral all the citral molecules present initially within the nanoemulsion droplets get incorporated into the micelles present in surfactant solution resulting in a slight increase in turbidity up to \( C_{\text{max}} \). However, above \( C_{\text{max}} \) the micelles that are already saturated by citral molecules do not take up the oil and hence further addition of citral keeps them in the form of nanoemulsion droplets in solution resulting in a linear increase in turbidity with increase in citral concentration. Fig. 1 also shows the effect of addition of citral nanoemulsion stock to the aqueous buffer solution without surfactant. In this case, a linear increase in turbidity with citral concentration suggests the presence of nanoemulsion droplets in water without any solubilisation effect. Therefore \( C_{\text{max}} \) observed in surfactant solutions, corresponds to an important solubilisation parameter below which micelles are capable of solubilising citral, but above which micelles are saturated with citral and hence incapable of further solubilisation.

### 3.2. Influence of surfactant type and concentration on citral solubilisation

The influence of surfactant concentration on the solubilisation of citral in Brij30 and Brij35 micelles is shown in Fig. 1. The \( C_{\text{max}} \) of citral increased with increasing surfactant concentration, indicating the solubility enhancement of citral within the micelles of both surfactants (inset of Fig. 1). The solubility of citral increased many-fold from 3.75 mM in aqueous buffer solution to 14.19 mM in 1 mM Brij35 and 17.84 mM in 1 mM Brij30 surfactant systems. The value further increased by increasing the surfactant concentration, to about 20.67 mM in 5 mM Brij35 and 25.58 mM in 5 mM Brij30 surfactant system, respectively. The solubilisation capacity of Brij30 micelles is greater compared to Brij35 micelles, while both show solubility enhancement as compared to that in water. Citral has an appreciable availability at the interface and in the water phase due to its amphiphilic and surface active nature (Djordjevic et al., 2007). Therefore, it is envisaged that in addition to the micellar core solubilisation, citral could also get solubilised in the micellar palisade layer resulting in solubility enhancement as compared to that in water. Our finding of the locus of solubilisation (Section 3.4.) reveals that citral is indeed solubilised in both the regions of micelles being predominantly solubilised within
the core of micelles in the case of Brij30, but in the case of Brij35 micelles it is predominantly solubilised in the palisade layer. Due to the small aggregation number of Brij35 micelles (40) (Bhat, Dar, & Rather, 2008), it is expected to have large micelle concentration relative to Brij30 at a given surfactant concentration resulting in greater water–micelle interfacial area leading to appreciable palisade layer solubilisation of the citral. Moreover, the polar interactions between carbonyl group/π electrons of citral and polyoxyethylene groups of surfactants would predominate over the hydrophobic interactions between the terpenic core of citral and the non-polar tail of the surfactant due to the large number of oxyethylene groups (OE) (23) present in the headgroup of Brij35 surfactant leading to more palisade layer solubilisation. However, in case of Brij30 micelles the predominant solubilisation occurring within the micellar core is facilitated by (a) the larger volume of the micellar core (aggregation number of 101 (Bhat et al., 2008)) and (b) predominant magnitude of hydrophobic interactions between the terpenic core of citral and the non-polar tail of the surfactant because of less number of OE groups within the Brij30 surfactant head group. Since the non-polar citral (Choi et al., 2010) would have a natural tendency to get partitioned into the hydrophobic environment, therefore any micelle that facilitates its core solubilisation should act as a better solubilisation medium. In light of this discussion, since Brij30 micelles offer predominant micellar core solubilisation as compared to Brij35 micelles, the former has greater solubilisation capacity than latter. The higher turbidity of citral encapsulated within Brij30 micelles is a testimony of the larger size of these micelles encapsulating citral.

3.3. Molar solubilisation ratio (MSR) and micelle-phase/aqueous-phase partitioning of citral

The variation of maximum solubilisation capacity, $C_{\text{max}}$ with the surfactant concentration (inset of Fig. 1) shows that $C_{\text{max}}$ increases linearly with increase in surfactant concentration. Molar solubilisation ratio (MSR) (Attwood & Florence, 1983) is equivalent to increase in solubilisate concentration per unit increase in micellised surfactant concentration. It is measure of the effectiveness of a surfactant in solubilising a given solubilisate and is obtained from the slope of curve between solubilisate concentration and surfactant concentration. The MSR value of citral in Brij30 surfactant system (1.94) is more than that of in Brij35 surfactant system (1.57). The effectiveness of solubilisation can also be expressed in terms of the partition coefficient, $K_m$, of the citral between the micelle and aqueous phases and is defined as the ratio of mole fraction of the citral in the micellar phase, $X_m$, to that in the aqueous phase, $X_a$.

$$K_m = \frac{X_m}{X_a}$$ (1a)

The value of $X_m$ in terms of MSR can be written as

$$X_m = \frac{\text{MSR}}{1 + \text{MSR}}$$ (1b)

$X_a$ can be expressed as $X_a = [S_{\text{cmc}}]V_m V_m$ is the molar volume of water equal to 0.01805 L/mol at 25 °C and $S_{\text{cmc}}$ is the solubility of the solubilisate just below cmc of the surfactant which was taken equal to it aqueous solubility because solubility did not change up to the cmc of surfactants. With these expressions, $K_m$ for solubilisation becomes

$$K_m = \frac{\text{MSR}}{[S_{\text{cmc}}]V_m(1 + \text{MSR})}$$ (1c)

The $K_m$ values so obtained for Brij30 and Brij35 were $9.79 \times 10^3$ and $9.07 \times 10^3$ respectively. Since both MSR and $K_m$ values are higher in Brij30 as compared to that of Brij35, it shows that the former is better solubilising medium for citral due to the reasons mentioned in the Section 3.2.

3.4. Locus of solubilisation

The information about the locus of solubilisation of citral within two different micelles can be obtained by comparing $\lambda_{\text{max}}$ of citral with that in different solvents. The UV spectra of citral in a number of solvents with a variety of polarity index viz petroleum ether, diethyl ether, methanol, and water having polarity indices of 0.1, 2.8, 5.1 and 9, respectively, along with the spectra in aqueous Brij30 and Brij35 micellar solutions are given in Fig. 2. As evident from the figure, $\lambda_{\text{max}}$ of citral shows a regular bathochromic shift with increasing polarity of medium. $\lambda_{\text{max}}$ increases from 232 nm in petroleum ether to 247 nm in water through 236 nm in diethyl ether and 239 nm in methanol. Plot of $\lambda_{\text{max}}$ versus polarity index of solvent yield a straight line (inset of Fig. 2) indicating a linear increase in $\lambda_{\text{max}}$ of citral with polarity. The $\lambda_{\text{max}}$ obtained in Brij30 micellar medium was 241 nm in contrast to 244 nm in Brij35 micellar medium corresponding to polarity index of 5.8 and 7.6, respectively. This indicates that the polarity sensed by the solubilised citral is intermediate between methanol and water. It is known that the oxyethylene head groups of Brij micelles can bind water molecules which are proportional to the number of oxyethylene groups (Renwick, Hughes, Pitman, & Vité, 1976). Therefore, Brij35 micelles with 23 oxyethylene groups in the head group is comprised of a palisade layer, which would be more hydrated than the palisade layer of Brij30 micelles, where only four oxyethylene groups are present. The $\lambda_{\text{max}}$ value of citral solubilised in Brij30 micelles indicates it to be deep into the palisade layer or towards the micellar core. However $\lambda_{\text{max}}$ of citral in Brij35 micelles indicates its solubilisation in the more hydrated region, which corresponds to its palisade layer. It is also expected that the absorption band in the two surfactant systems is a superposition of two unresolved peaks, one peak corresponding to that fraction of citral solubilised in the inner hydrophobic core of micelles and the other one for the fraction of citral solubilised in the outer hydrophilic corona region of the micelle, with both regions having different polarities. For Brij30 micelles, the peak occurs more towards the non-polar region indicating more fraction of citral is solubilised within the micellar core owing to its larger micellar core volume and less dense outer hydrophilic corona, while in the case of Brij35 more appreciable amount of citral is solubilised within the outer hydrophilic corona as the peak lies further towards the polar region.

3.5. Effect of pH on stability of citral in micellar media

The absorption spectra of citral corresponding to their $C_{\text{max}}$ concentrations in aqueous buffer, pre-micellar and post-micellar con-

![Fig. 2. Absorption spectra of citral in various solvents. Inset shows variation of $\lambda_{\text{max}}$ with polarity index of solvent.](image-url)
centrations of both surfactants at pH 7, 3 and 1 are shown in Fig. 3. At pH 7, citral shows its characteristic UV spectra in all the studied systems, which indicates that it is quite stable at this pH. From the HPLC data (Fig. 4a) taken after 7 days, it is clear that citral does not degrade at this pH. From the HPLC data (Fig. 4a) taken after 7 days, it is clear that citral does not degrade at this pH. In addition to stability, the encapsulation of citral within the micelles shows remarkable solubilisation enhancement. This many-fold increase in the solubility of citral in the aqueous micellar solutions in addition to maintaining its stability may prove beneficial for the food and cosmetic industries. At pH 3, the spectra of citral in aqueous buffer and in the pre-micellar concentrations of both the surfactants show some degree of distortion as evident from Fig. 3b, which may be attributed to the degradation of citral due to its exposure to the acidic medium in these systems. It is clearly evident from the HPLC chromatogram shown in Fig. 4d that a significant amount of citral has degraded to variety of products at pH 3. In the post-micellar concentrations of surfactants, citral is solubilised within the micelles; besides the solubility enhancement of citral, the degradation is insignificant as the absorbance peak values differ feebly from those of the same solutions at pH 7. At pH 1, the UV absorption spectra of citral in aqueous buffer and in pre-micellar region of both surfactants is entirely different from its characteristic spectra indicating the complete degradation of citral owing to the strong acidic conditions prevailing in these systems. As observed in HPLC chromatogram (Fig. 4e), almost the whole of the citral degraded to different products as the peak corresponding to citral is missing. One of the main degradation end products of citral, ‘p-cymene’ has a reported λ_max of 211.5 nm (Hirayama, 1967), while others like p-menthadien-8-ol and p-menthadien-4-ol are reported to absorb strongly in the region of 214–218 nm (Baser & Buchbauer, 2009; FAO/WHO Expert Committee, 2008; Urushibara & Hirota, 1961). Furthermore, the stable aromatic degradation product of citral, ‘α-p-dimethylstyrene’, has a peak with maximum extinction coefficient at 210 nm (Das, Duportail, Richert, Klymenko, & Mély, 2012; Matyjaszewski & Sigwalt, 1987). The presence of all these degradation products at lower pH may correspond to the addition peak observed near 215 nm in Fig. 3c for aqueous and premicellar solution phases of both surfactant systems. Since the characteristic UV spectrum of citral is obtained in the post-micellar concentrations of Brij surfactants, the micellar nanostructures are thus capable of preventing the citral degradation even under strong acidic conditions of pH 1. In conclusion, the Brij surfactant micelles are capable of preventing degradation of citral at all levels of acidic pH invoking its potential prospective use in cosmetic, pharmaceutical and food industries for citral stabilisation.

3.6. Characterisation of a few citral degradation products

HPLC has been used in the development of quantitative assays for citral (Rauber, Gutieres, & Schapoval, 2005) and its metabolites in biological matrices and pharmaceutical products (Hudaib, Bellardi, Rubies-Autonell, Fiori, & Cavrini, 2001). HPLC was used in the current study to identify the degradation products of citral at lower pH’s. The HPLC profile of citral at pH 7 shows a high resolution peak at a wavelength of 237 nm, using water:methanol (40:60, v/v) as mobile phase, given in Fig. 4a along with the HPLC profiles of two main degradation products of citral, p-methyl acetophenone (Fig. 4b) and p-cresol (Fig. 4c) used as markers in the present study. Citral at pH 7 is stable and shows an intense absorption, good selectivity and a single well resolved peak at a retention time of 3.777 min, while citral at pH 3 (Fig. 4d) and citral at pH 1 (Fig. 4e) undergoes degradation and shows a range of absorption peaks with varying retention times at the set wavelength. The HPLC profile of samples of citral at pH 3 and 1 elucidates that a
number of degradation products are formed along with p-cresol and p-methyl acetophenone, and the concentration of citral in these samples decreases as is indicated by the intensity of peaks, which corresponds to citral at retention times of 3.721 and 3.622, respectively. The presence of p-cresol and p-methyl acetophenone in these samples was identified by the comparison of the retention times with the authentic markers used, the peaks with retention times at 3.088 and 2.947 corresponds to the presence of p-methyl acetophenone while the peaks with retention time of 5.837 and 5.735 corresponds to the presence of p-cresol in the samples of citral at pH 3 and 1, respectively.

3.7. Kinetics of citral degradation

The effect of solution pH on the kinetics of chemical degradation of citral was studied spectrophotometrically over a seven
day period. The kinetics of chemical degradation of citral in aqueous solutions was studied at a citral concentration of 380 mg/ml, which is below the saturation level. However, in micellar solutions the initial concentration was below $C_{\text{max}}$ corresponding to a given surfactant concentration. The rate of citral degradation has been modelled by assuming a first-order reaction in accordance with earlier studies (Choi et al., 2009; Djordjevic et al., 2007; Yang et al., 2011):

$$C(t) = C_0 \exp(-kt)$$

where $C_0$ is the initial citral concentration, $C(t)$ is the citral concentration remaining at time $t$, and $k$ is the degradation rate constant. A few prototype plots showing variation of $\ln(C_t/C_0)$ versus time at different pH values in aqueous and 1 mM Brij30 and 1 mM Brij35 micellar solutions are shown in Fig. 5. The values of $k$ in aqueous and micellar solutions of Brij30 and Brij35 at different pH values were determined by carrying out a linear regression on plots of $\ln(C_t/C_0)$ versus $t$ and are plotted in Fig. 6a as a function of surfactant concentration at various pH values. The data in Fig. 5 shows that there is little change in citral concentration over the period of 7 days at pH 7, even in aqueous solution, which is in conformity with the results of HPLC. In addition the degradation rate constant of citral is very low in aqueous Brij30 and Brij35 micellar media at pH 7, which does not vary much with concentration of surfactant (Fig. 6a). $k$ showed values of 0.0138, 0.116 and 0.255 day$^{-1}$ in aqueous solutions at pH 7, 3 and 1 respectively indicating the rate of degradation to be highest at acidic pH values. In aqueous micellar media, $k$ was very low at all pH values as compared to that in pure aqueous solutions with a maximum at pH 1. This shows that the surfactant micelles were capable of decreasing $k$ due to partitioning of citral molecules into the micelles isolating them from the acid present in aqueous environment and hence retarding the degradation rate. In addition, the increase in surfactant concentration leads to further decrease in value of $k$ due to increase in micellar concentration and hence the partitioning of citral within the micelles (Fig. 6a). Fig. 6a indicates that Brij30 micelles are more capable of stabilising citral from chemical degradation than Brij35 micelles and relatively stable microemulsions of citral were formed within Brij30 micelles. As described in earlier section due to the large core volume and lower Laplace pressure inside the Brij30 micelles, citral is mainly solubilised within the micellar core and hence proves to be a better solubilisation medium both in terms of solubility enhancement and protection from chemical deterioration of citral. For Brij35, an appreciable amount of citral is solubilised in the palisade layer, where it is in direct contact with reactive pro-oxidative species and is hence prone to undergoing degradation, explaining the relatively lower potency of Brij35 micelles to protect citral from degradation.

Though the formulations of citral with Brij surfactants showed excellent physical stability in the temperature range of 25–40°C, the rate of degradation, however, increased with increase in temperature. The variation of $k$ with temperature in 3 mM Brij30, 3 mM Brij35 and aqueous solution at pH 1 is given in Fig. 6b. The increase in rate of degradation with temperature is more in the case of aqueous solution than in the micellar solutions, indicating that the temperature effect on the increase in degradation rate is considerably suppressed by the presence of micelles. The comparative account of variation of rate of degradation of citral with temperatures solubilised within different surfactant micelles shows that in Brij35 micelles, where citral is preferentially solubilised in

Fig. 5. Variation of $\ln(C_t/C_0)$ with time ($t$) at pH 7, 3 and 1 for (a) buffer solution, (b) 1 mM and Brij30 surfactant solution and (c) 1 mM Brij35 surfactant solution. Regression coefficients of linear fits were greater than 0.98 for all studied systems.
the palisade layer/interfacial layer, the effect is more pronounced as compared to that in Brij30 micelles, wherein citral is preferentially solubilised in the micellar core. This points to the easy access of pro-oxidant species to interfacially solubilised citral molecules in Brij35 micelles leading to significant increase in the probability of encounters between two reactants with temperature. These results suggest that a surfactant system with a lower HLB value, less dense hydrophilic corona and more hydrophobic core volume is efficient in solubilising and stabilising citral.

4. Conclusions

In summary, this study reports the solubilisation and stabilisation of citral by micelles of polyoxyethylene alkylether based non-ionic surfactants. The solubilisation capacity strongly depends on concentration and number of oxyethylene groups present in the head group of surfactant. The locus of solubilisation of citral is mainly towards the non-polar region of Brij30 while in case of Brij35 more appreciable amount of citral is solubilised within the outer corona indicating the significant effect of number of oxyethylene groups per head group of surfactant in citral encapsulation. The encapsulation of citral results in increased chemical stability of citral in acidic pH range where aqueous solutions without micelles are incapable of stabilising the citral. Brij30 proves to be a better solubilising as well as stabilising medium for citral as compared to Brij35 micellar medium at all acidic pH’s. This study concludes that Brij surfactants with a lower HLB value, less dense hydrophilic corona and more hydrophobic core volume are efficient in solubilising and stabilising citral against an acidic environment.

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References


![Fig. 6. Variation of Degradation constant (k) with; (a) concentrations of Brij30 and Brij35 surfactant at pH 7, 3 and 1 at 25 °C and (b) temperature (in °C) for 3 mM Brij30, 3 mM Brij35 and aqueous solution at pH 1.](image-url)


