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Extraction of Piperine from *Piper Nigrum* (Black Pepper) by Aqueous Solutions of Surfactant and Surfactant + Hydrotrope Mixtures

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Abstract: The effect of combining butyl benzene sulfonate as hydrotrope with a surfactant in aqueous solutions is investigated for isolation of piperine, an alkaloid, from black pepper. The standard free energy change associated with piperine solubilization in the aqueous solutions of surfactant and hydrotrope individually and in their mixtures is determined from the solubility of piperine in these solutions. A combination of sodium dodecyl sulfate (SDS) and the hydrotrope gives increased percentage extraction of piperine as compared to the hydrotrope alone. The piperine purity recovered from aqueous solutions was higher as compared to the purity of piperine recovered using organic solvents. The piperine crystallized from aqueous solutions of surfactants and hydrotrope also showed cleaner surfaces and uniform structures with sharp edges, unlike the particles crystallized from organic solvents.

Keywords: Extraction, hydrotropes, mixed micelles, piperine, scanning electron microscopy, solubilization

INTRODUCTION

Plant products have been used in medicines, foods, perfumes, dyes, and pesticides for a along time. Their active principles serve as templates for synthetic drugs and/or provide intermediates in the production of semi-synthetic drugs (1). Although natural products are seen as potential alternatives to synthetic drugs, the technologies to recover active

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ingredients are still relying on volatile and inflammable organic solvents. For many conventional processes the loss of solvents adds significantly to the cost of the final product and thus demands newer efficient processes. Although supercritical fluid extraction has been increasingly studied, it's scale-up to treat large amounts of natural raw materials makes the process prohibitively expensive.

Piperine, an alkaloid-analog in pepper, exhibits a chemo-protective effect against procarcinogens and also possesses bacteriostatic, fungistatic, and insecticidal activities (2). It shows a protective effect against radiation in radiotherapy and is used as a bioavailability enhancer in many drug formulations (3). The newer applications of piperine underline the need for pure piperine, free from residual solvents.

In the recent past, we have reported aqueous hydrotrope solutions for extraction of water-insoluble phytochemicals from complex natural materials as an alternative to organic solvents (4–7). Hydrotropes are highly water soluble organic salts such as aromatic sulfonate salts of alkali or alkaline metals. The hydrotropic extraction is significant only above a minimum hydrotrope concentration (MHC), usually in the molar concentration range, which is a characteristic of a given hydrotrope (8). The product can be recovered by either dilution of the hydrotrope solution below its MHC or cooling down the solution. The dilution process has, however, a major disadvantage of handling large volumes of diluted aqueous solutions during the recovery step. Further, the hydrotrope solution has to be concentrated by evaporation of water which adds substantially to the energy consumption.

The extraction of piperine has been already reported by Raman and Gaikar (5) using hydrotropes such as sodium butyl benzene sulfonate and sodium butyl monoglycol sulfate from piper nigrum fruits. The mechanism of hydrotropic extraction was hypothesized by these authors in terms of the destabilization of the cellular wall structure by the hydrotrope.

In this paper we explore the synergistic effect of combining the hydrotropic effect with a surfactant for the extraction of piperine. Mixed surfactant systems are of great interest because of their superior solution properties compared to the individual molecules (9–11). Mixtures of hydrotropes with cationic and nonionic surfactants have received some attention in the recent past. The studies on cetyl trimethylammonium bromide (CTAB) + butyl benzene sulfonate (BBS) and cetylpyridinium chloride (CPC) + BBS demonstrated complex fluid behavior of these isomers with oppositely charged surfactants (12–13). The CTAB + BBS system was characterized by SANS indicating sphere-to-rod transition of CTAB micelles with the addition of small amounts ($\sim$10 mole%) of BBS with a sharp increase in the viscosity of the solution (14). Recently,

the SANS studies carried out on the mixtures of SDS + NBBS confirm the formation of mixed micelles of hydrotrope + surfactant at different concentrations (15).

The need of finding new systems for the solubilization of sparingly soluble phytochemicals, the decrease of the toxicity of some surfactants when mixed systems are used, and the fact that solubilization of polar solutes is not greatly affected by the surfactant alkyl chain length have led us to study the solubilization capabilities of mixed binary surfactant + hydrotrope solutions. It was also expected that the concentration of the hydrotrope required for solubilization can be substantially reduced because of synergistic effect of the mixed micelles.

Some authors have related the micellar solubilization in mixed micelles to an increased aggregation number (16) or the increased compactness of the micelles (17). In this report, we characterize the surfactant-hydrotrope interaction and micellar solubilization using the Regular Solution Theory (18). The same approach, commonly used for a mixed surfactant system, is adopted to characterize the surfactant-hydrotrope mixtures. The approach has certain limitations because of a somewhat rigid structure of the hydrotrope and dissimilar sizes of the hydrotrope and the surfactant. The entropy contribution could be significant in these mixtures because of the sizes differences. However, the surfactant head groups occupying the interfacial area are not significantly different in sizes and thus the RST approach was used as such. Two surfactant-hydrotrope mixed systems, namely cetyl trimethyl ammonium bromide (CTAB) + Na *n*-butyl benzene sulfonate (NBBS) and sodium dodecyl sulfate (SDS) + NBBS, are considered for the solubilization studies as well as for the extraction of piperine from pepper. The morphology of piperine crystals precipitated from aqueous solutions of surfactants and organic solvents is also investigated.

MATERIALS AND METHODS

Cetyl trimethylammonium bromide, CTAB (99%) was procured from Spectrochem Pvt. Ltd., Mumbai (India). Sodium dodecyl sulfate, SDS (99%) was obtained from SISCO Research lab, Mumbai (India) and used without any further purification. *n*-Butyl benzene, was obtained from Herdillia Chemicals Ltd., Mumbai (India). Sodium *n*-butyl benzene sulfonate (NBBS) was prepared and characterized as described in literature (19). Whole pepper berries were obtained from the local market. Other solvents used in the studies were of analytical grade.

The aqueous solutions of individual surfactants, hydrotropes, and surfactant-hydrotrope mixtures of different compositions were prepared

in distilled water and their surface tension was noted using a semiautomatic Fischer Surface Tensiometer by Du Nouy ring method at $30 \pm 1^{\circ}C$. The instrument was calibrated with distilled water.

The solubility experiments were carried out in a fully baffled glass reactor ($50\,cm^3$) equipped with six bladed turbine impeller (i.d. 2 cm) by suspending pure piperine in aqueous solutions of individual surfactants, hydrotrope and surfactant-hydrotrope mixtures of different concentrations. The entire assembly was kept in a constant temperature water bath during the solubility studies. The solution after equilibrating with the excess piperine for 3 hours under vigorous stirring was filtered at the same temperature and the clear filtrate obtained was diluted with methanol for analysis. The amount of piperine dissolved in the solution was estimated by UV spectrophotometer at 343 nm using the calibration curve prepared with pure piperine in methanol.

The extraction experiments were carried out in a fully baffled cylindrical vessel ($100\,cm^3$) equipped with a six bladed turbine impellar (i.d. 2 cm). The complete assembly was kept in a constant temperature water bath during experimentation. Black pepper was ground and sieved into the batches of different sizes. 5 g of ground pepper (16 mesh size) was added to $0.1\,dm^3$ solution of a known concentration of surfactant (or hydrotrope) or surfactant-hydrotrope mixtures. With increase in the solid loading, the viscosity of the suspension increases during the experiment making it difficult for sampling and filtration. If the particle size is further reduced, the solid particles absorb a significant amount of solution and form a thick paste. To avoid these problems, 5% (w/v) loading of 16 mesh size piperine powder was kept constant and the effect of other parameters on the piperine extraction was studied. The stirring rate was maintained in the range of 1000–1200 rpm so that the rate of extraction was independent of the speed of agitation. The piperine content in the samples was quantified using High Pressure Thin Layer Chromatography (HPTLC, DASAGA CD60). The samples were spotted on a TLC plate and the plate was developed using dichloromethane: ethyl acetate (9:1) mobile phase in a pre-saturated glass chamber. The well-separated spots were scanned at 343 nm and the amount of piperine extracted in the solution was determined using the calibration curve prepared with pure piperine.

To study the piperine crystals shape and size, pure piperine was dissolved in the organic solvents and aqueous solutions of CTAB, SDS, NBBS and SDS-NBBS mixtures at $90^{\circ}C$. The hot solution was then filtered and allowed to cool to room temperature of $30^{\circ}C$. The precipitated piperine crystals were examined under Scanning Electron Microscopy (Philips XL 30 SEM) after mounting the samples on specimen with carbon tabs. To avoid the charging of the samples, the

specimen was coated with a thin layer (250–300Å) of Au/Pd using sputter coater and examined at 12 KV with 45° tilt angle. The micrographs of the crystals were recorded with suitable magnification.

Continuous soxhlet extraction with MeOH was separately carried out for 60 hours to determine the piperine content of the raw material which was found to be 4% (w/w).

DETERMINATION OF MICELLAR COMPOSITION IN THE MIXED MICELLAR SYSTEM

For the calculation of the composition of the mixed micelles, Rubingh's Regular Solution Theory was used which accounts for the non-ideality of the mixtures in terms of the components' activity coefficients (18). The activity coefficients (f_1 and f_2) make the calculation of the monomer and the micelle compositions of the mixed micellar systems possible using the following set of equations.

$$\frac{(x_1^m)^2 \ln\left(\frac{\alpha_1 C_{12}^m}{x_1^m C_1^m}\right)}{(1-x_1^m)^2 \ln\left(\frac{(1-\alpha_1) C_{12}^m}{(1-x_1^m) C_2^m}\right)} = 1 \tag{1}$$

$$\beta^m = \frac{\ln\left(\frac{\alpha_1 C_{12}^m}{x_1^m C_1^m}\right)}{(1-x_1^m)^2} \tag{2}$$

$$f_1 = \exp[\beta^m (1-x_1^m)^2] \tag{3}$$

$$f_2 = \exp[\beta^m (x_1^m)^2] \tag{4}$$

$$C_m = x_1^m \ f_1 C_1^m + (1-x_1^m) f_2 C_2^m \tag{5}$$

Where, x_1^m is the mole fraction of hydrotrope in the mixed micelle, α_1 is the bulk mole fraction of hydrotrope in mixed solution, C_{12}^m is the mixed CMC of the binary systems and C_1^m and C_2^m are the MHC and CMC of pure hydrotrope and surfactant, respectively; C_m is the monomer concentration of hydrotrope + surfactant; β^m is the empirical coefficient of the regular solution activity coefficients f_1 and f_2 which gives an indication of degree of interaction between hydrotrope and surfactant in the mixed aggregates.

RESULTS AND DISCUSSION

In order to investigate the efficacy of the process, we need to know the solubility of piperine in the solutions of the individual surfactants and hydrotrope, preferably as a function of temperature and composition of mixed micelles.

Figure 1 shows the solubility of piperine in water which increases from 10 mg/dm^3 at 30°C to 140 mg/dm^3 at 90°C. Figures 2 and 3 show the solubility of piperine in aqueous solutions of CTAB, SDS, and their mixtures with NBBS at different concentrations, respectively. The CMC (or MHC) for CTAB, SDS, and NBBS is 0.9 mmol/dm^3, 8 mmol/dm^3 and 100 mmol/dm^3, respectively. For CTAB-NBBS (10:90), CTAB-NBBS (90:10), SDS-NBBS (10:90) and SDS-NBBS (90:10) mixtures, the mixed CMC is 0.28 mmol/dm^3, 0.23 mmol/dm^3, 20 mmol/dm^3, and

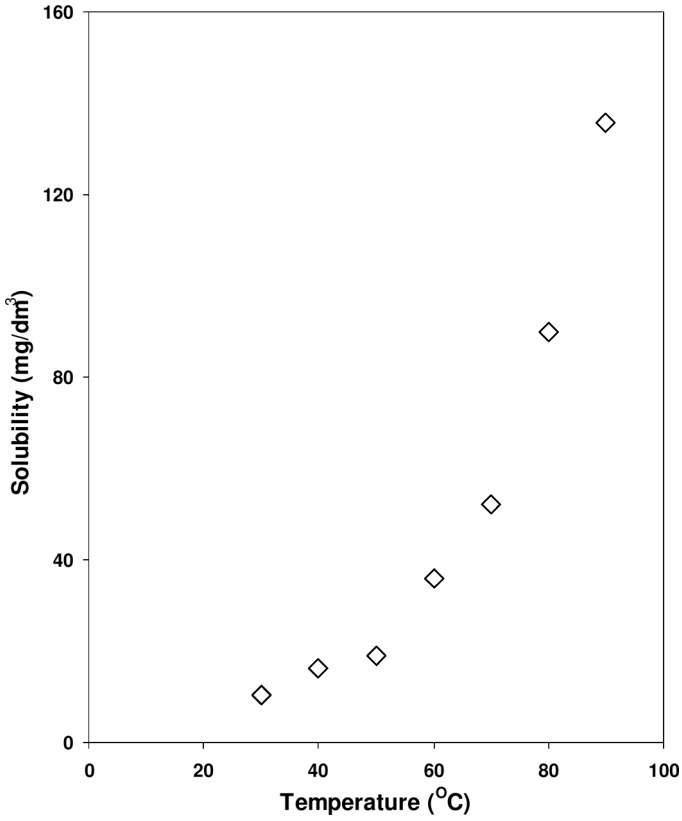


Figure 1. Solubility of piperine in water at different temperatures.

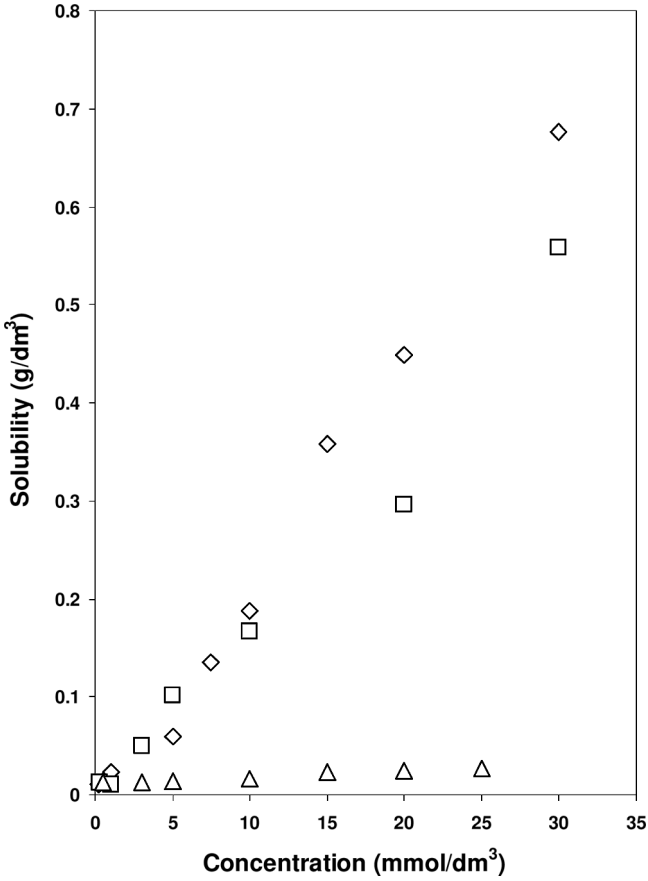


Figure 2. Solubility of piperine in CTAB-NBBS mixture at 30°C. ◇ CTAB 100%; □ CTAB 90% + NBBS 10%; △ CTAB 10% + NBBS 90%.

9 mmol/dm^3, respectively. The piperine solubility, in general, increased with the increase in concentration of the surfactant (or hydrotrope) in the solution. Below the CMC (or mixed CMC) of the solutions, the solubility of piperine was marginally higher than that in water. Beyond the CMC (or the mixed CMC), there was almost a linear increase in the piperine solubility with the surfactant concentration. Only for the CTAB-NBBS (molar ratio, 10:90) mixture, the solution became turbid after increasing the total concentration beyond 25 mmol/dm^3 where the CTAB-NBBS complex precipitates out of the solution because of its own poor solubility in water. The maximum solubility of piperine in this solution was just 25 mg/dm^3 at 30°C. CTAB alone in aqueous solution

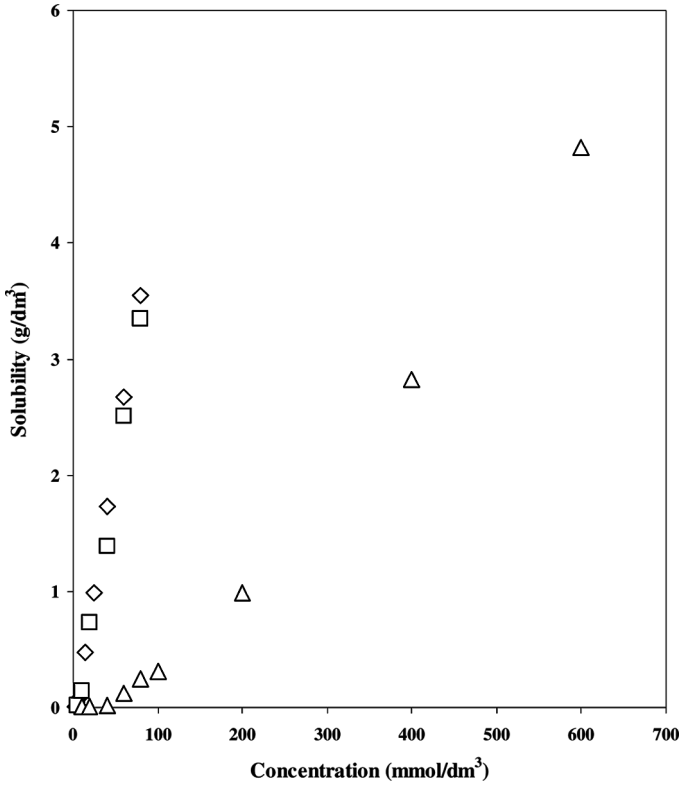


Figure 3. Solubility of piperine in SDS-NBBS mixture at 30°C. ◇ SDS 100%; □ SDS 90% + NBBS 10%; △ SDS 10% + NBBS 90%.

solubilizes 690 mg/dm^3 of piperine when its concentration was increased 30 times its CMC i. e. 30 mmol/dm^3. Addition of NBBS to CTAB resulted in slight decrease in the solubility of piperine as compared to the CTAB solution alone. It has been known that CTAB forms large size compact macroassemblies in solutions when combined with oppositely charged hydrotropes with substantial micellar charge neutralization (14–20). If the electrostatic interactions are stronger between the surfactant and the hydrotrope head groups, one expects a more compact structure on mixing CTAB and NBBS with little repulsion amongst the micelle forming components. These structures would be compact enough to not allow penetration of additional neutral molecules, like piperine, into this assembly. Thus the decrease in solubility was expected with the CTAB + NBBS combination.

In case of SDS, an exactly opposite situation was expected. If highly ionic hydrotrope is co-aggregating with SDS, then the SDS micelles should show a decreased aggregation number and increased number of mixed micelles in the solutions. If the intercalation of any organic solute in the micellar structure is responsible for the solubilization in the aqueous solution, then SDS micelles should show increased solubilization of piperine in the presence of the hydrotrope. The SDS solution, in the absence of the hydrotrope, dissolves 350 mg/dm^3 of piperine at 80 mmol/dm^3 concentration which is 10 times greater than its CMC. The mixed solution of 60 mmol/dm^3 SDS and 540 mmol/dm^3 NBBS could solubilize 480 mg/dm^3 piperine, which was 480 times greater than the solubility of piperine in water. The piperine solubilized by SDS-NBBS mixture is significantly higher than that dissolved by the hydrotrope when present alone at the same concentration and 1.4 times more than that dissolved by the SDS solution but it is at the cost of 7.5 times increase in the concentration of SDS-NBBS mixture.

Table 1 shows the solubility of piperine in SDS (80 mmol/dm^3), CTAB (30 mmol/dm^3), NBBS (600 mmol/dm^3) and SDS:NBBS (10:90, total 600 mmol/dm^3) mixtures at temperatures between 30°C and 90°C. All the surfactants showed an increased piperine solubility as the temperature was increased. A 600 mmol/dm^3 NBBS solution dissolves 17.6 g/dm^3 of pure piperine at 90°C and we could almost double it by replacing just 10% NBBS by SDS.

The solubilization experiments are used to calculate the apparent mole fraction distribution coefficient (K), i.e. the ratio of the mole fraction of the solute in the micellar phase (X^M) to that in the solvent phase (X^W) and then to estimate standard Gibbs free energy change upon transferring one mole of solute from water to the micellar phase (Equation (7)). The mixed micelles are thus treated as a separate phase and the solute gets partitioned between the bulk aqueous phase and the aggregate phase (21).

$$K = \frac{X^M}{X^W} = \frac{\frac{(C^P - C^O)}{(C^P - C^O) + (C^S - C^M)}}{\frac{C^O}{(C^W + C^M + C^O)}} \tag{6}$$

$$\Delta G = -RT \ln(K) \tag{7}$$

Where C^P and C^O represent the saturation solubility of the solute in surfactant solution and water, respectively, C^S is the total concentration of the surfactant, C^M is the concentration of the surfactant in monomer form and C^W is the moles of water. In the case of single surfactant systems, C^M is replaced with the CMC of the surfactant. The surfactant (or hydrotrope) monomer concentration is not equal to the CMC (or

Table 1 . Solubility of piperine as a function of temperature

System	Total Concentration (mol/dm^3)	Solubility (g/dm^3)				
		30°C	50°C	70°C	80°C	90°C
Water		0.01 ± 0.001	0.019 ± 0.001	0.052 ± 0.004	0.09 ± 0.007	0.136 ± 0.015
SDS (X = 1.0)	0.08	3.54 ± 0.20	5.38 ± 0.27	7.14 ± 0.40	10.23 ± 0.40	14.62 ± 0.60
NBBS + SDS (9:1)	0.6	4.83 ± 0.25	6.09 ± 0.20	10.65 ± 0.37	20.54 ± 1.20	30.01 ± 1.50
CTAB (X = 1.0)	0.03	0.68 ± 0.10	1.09 ± 0.20	1.76 ± 0.20	2.57 ± 0.40	3.73 ± 0.50
NBBS (X = 1.0)	0.6	3.51 ± 0.20	4.55 ± 0.20	8.53 ± 0.50	13.13 ± 1.50	17.56 ± 1.8

MHC) in the case of mixed surfactant-hydrotrope system and it is calculated using Equations (1–5).

Table 2 lists values of K and $\triangle G$ of piperine solubilization in the surfactants and surfactant-hydrotrope mixtures. The negative sign for ΔG in all cases indicates the spontaneous transfer of piperine from aqueous bulk phase to the micellar phase. The examination of K for CTAB rich systems, however, indicates a reduction in the piperine solubility in the surfactant-hydrotrope mixture, compared to the solubilization by CTAB alone, if the total concentration of the surface active material was kept constant. Tokuoka et al. (22) had reported similar observations regarding the solubilization of synthetic perfumes by anionic-nonionic mixed surfactant systems. For the SDS rich mixture, in the presence of 10% NBBS, the reduction in the piperine's tendency to get transferred to the mixed micellar phase was negligibly small. These solubilization effects occur as a result of the interaction of the solubilizate with the individual surfactants and the interaction between the surfactants in the mixed micelles. Treiner et al. (23) have suggested that the distribution coefficient of a neutral organic solute in a mixed surfactant system follows the relationship shown in Equation (8).

$$\ln K = X_m \ln K_1 + (1 - X_m) \ln K_2 + BX_m(1 - X_m) \tag{8}$$

Where K_1 and K_2 are the apparent mole fraction distribution coefficients of a solute for the individual surfactant solutions and X_m corresponds to the micellar mole fraction of a surfactant having the value of K_1. B is an experimental parameter reflecting both the surfactant-surfactant interactions and the surfactant-solute interactions, which, within the framework of regular solution theory should be equal to the interaction parameter, β^m of the mixed system. If β^m is negative, the solubility of the solute should be less in the mixture than that predicted by the ideal mixing.

Table 2. Partition coefficient and free energy change of transfer of piperine from bulk aqueous phase to micellar phase

System	K	ΔG (KJ/mol)
CTAB (100%)	113957	−29.33
CTAB (90%) + NBBS (10%)	88210	−28.69
CTAB (10%) + NBBS (90%)	3950	−20.86
SDS (100%)	231808	−31.12
SDS (90%) + NBBS (10%)	229507	−31.10
SDS (10%) + NBBS (90%)	44625	−26.97
NBBS (100%)	38094	−26.35

Figure 4 shows the variation of mixed CMC of CTAB-NBBS and SDS-NBBS mixtures as a function of NBBS mole fraction at 30°C. Due to the synergistic effect between the cationic surfactant and the anionic hydrotropes, the mixture of CTAB + NBBS showed CMC values much lower than the individual components. The interaction parameter, (β^m) values for CTAB-NBBS and SDS-NBBS mixed systems are -15.1 and -2.01, respectively, indicating attractive interaction not only between CTAB and NBBS but also between SDS and NBBS. Even when SDS and NBBS carry similar charges, the attractive interaction between them leads to mixed micelle formation which should be governed more by the hydrophobic effect as both have amphiphilic structures. The negative values and magnitudes of β^m for CTAB-NBBS and SDS-NBBS mixed systems support the trend observed in the apparent distribution

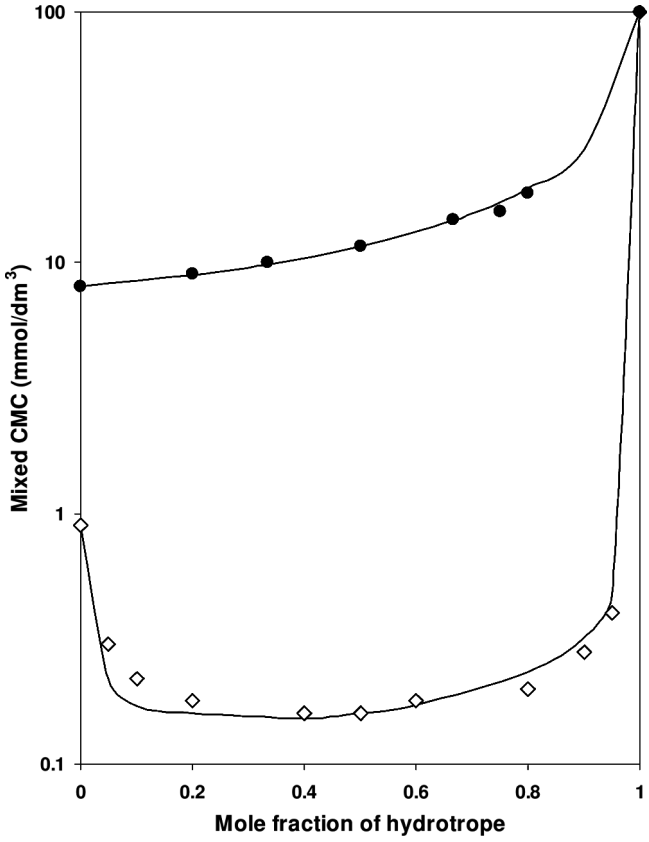


Figure 4. Mixed CMC for CTAB-NBBS and SDS-NBBS as a function of mole fraction of NBBS. ◇ CTAB + NBBS; ● SDS + NBBS.

coefficient (K) listed in Table 2. Once we have established that the surfactant + hydrotrope combination can give good piperine solubilization even at lower concentrations of the hydrotrope, we used the mixed micelles system for extraction of piperine from black pepper.

EXTRACTION OF PIPERINE FROM BLACK PEPPER

Figure 5 shows the effect of concentration SDS on piperine extraction from pepper at 30°C. There was a slight increase in the percentage extraction of piperine from 48% to 54% in 2 hours when the concentration of

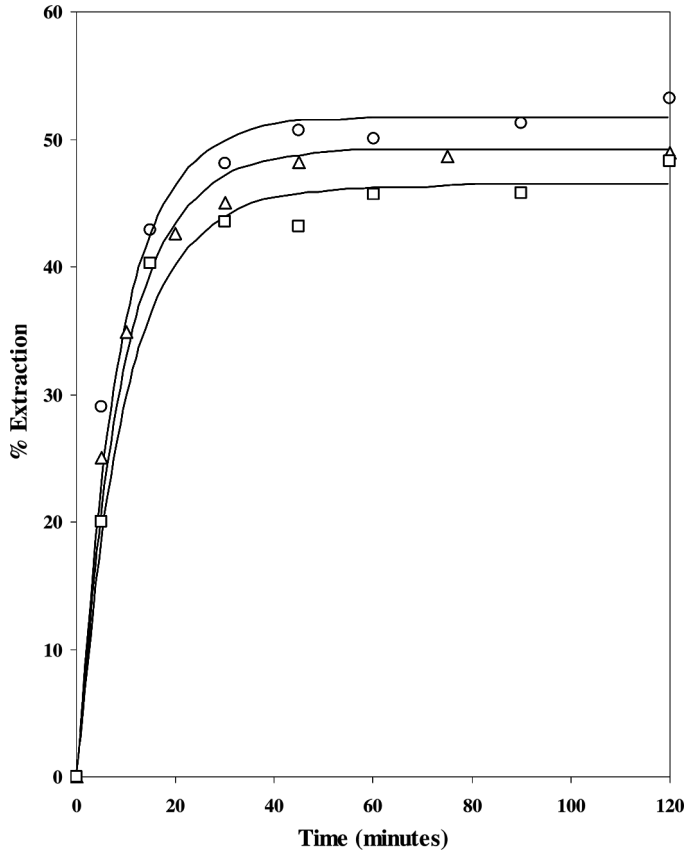


Figure 5. Effect of concentration of SDS on piperine extraction (Temperature = 30°C; Particle size = 16 Mesh). □ 0.1 mol/dm^3; D = 1.92×10^{-13} m^2/sec; △0.2 mol/dm^3; D = 2.06×10^{-13} m^2/sec; ○ 0.4 mol/dm^3; D = 2.21×10^{-13} m^2/sec.

SDS was increased from 100 mmol/dm^3 to 400 mmol/dm^3. The higher solubility of piperine, at increased surfactant concentrations, results into higher percentage extraction into the aqueous SDS solution in the given time interval. The transport of the piperine from the particle into the solution is by molecular diffusion. The experimental kinetic data were fitted in a solid-liquid extraction model reported earlier to estimate the effective diffusivity of piperine in the solid matrix of pepper (24–25). The increased concentration of SDS showed in a slightly increased effective diffusion coefficient (D) from 1.92×10^{-13} m^2/sec to 2.21×10^{-13} m^2/sec.

Figure 6 shows a comparison of efficiency of aqueous SDS solutions to extract piperine with that of organic solvents. Methanol, chloroform,

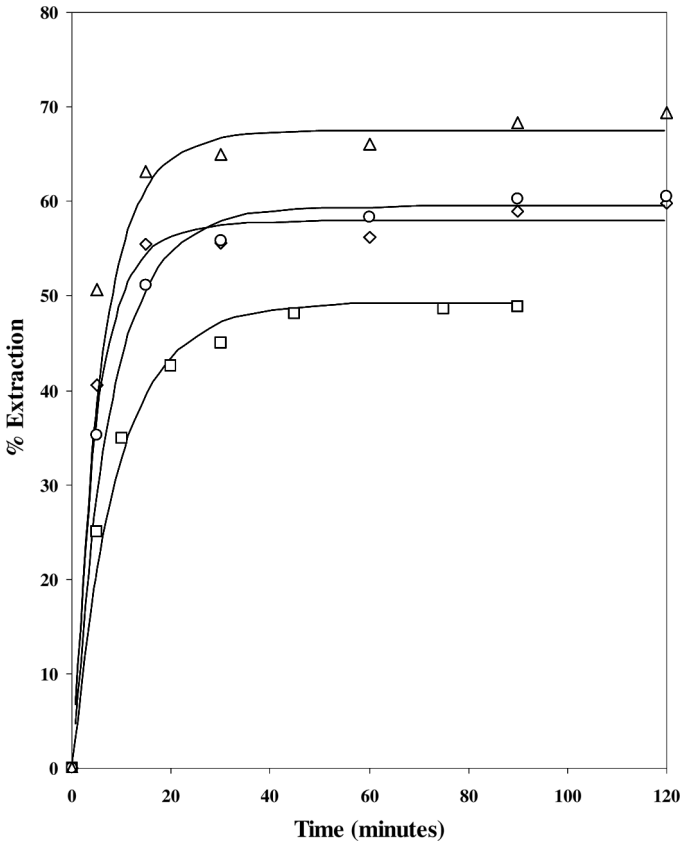


Figure 6. Effect of aqueous SDS solution and different organic solvents on piperine extraction (Temperature = 30°C; Particle size = 16 Mesh). □SDS; D = 2.06×10^{-13} m^2/sec; ○ Methanol; D = 2.49×10^{-13} m^2/sec; △ Chloroform; 3.2×10^{-13} m^2/sec; ◇ DCM; 3.91×10^{-13} m^2/sec.

and dichloromethane (DCM) showed a higher percentage of piperine extraction as compared to that using aqueous SDS solutions. The diffusion coefficient of piperine was $3.91 \times 10^{-13}\,m^2/sec$ in DCM as compared to $2.2 \times 10^{-13}\,m^2/sec$ in SDS solutions. But piperine purity extracted by aqueous SDS solutions was much higher, ($\sim$92%,) as compared to that obtained using methanol (28%), chloroform (35%), and DCM (30%), respectively (Figure 7). The extraction using organic solvents is thus non-selective as the solvents dissolve also a number of other compounds present in the pepper along with piperine. The reduced purity in the case of organic solvents can make the further processing difficult and sometimes uneconomical.

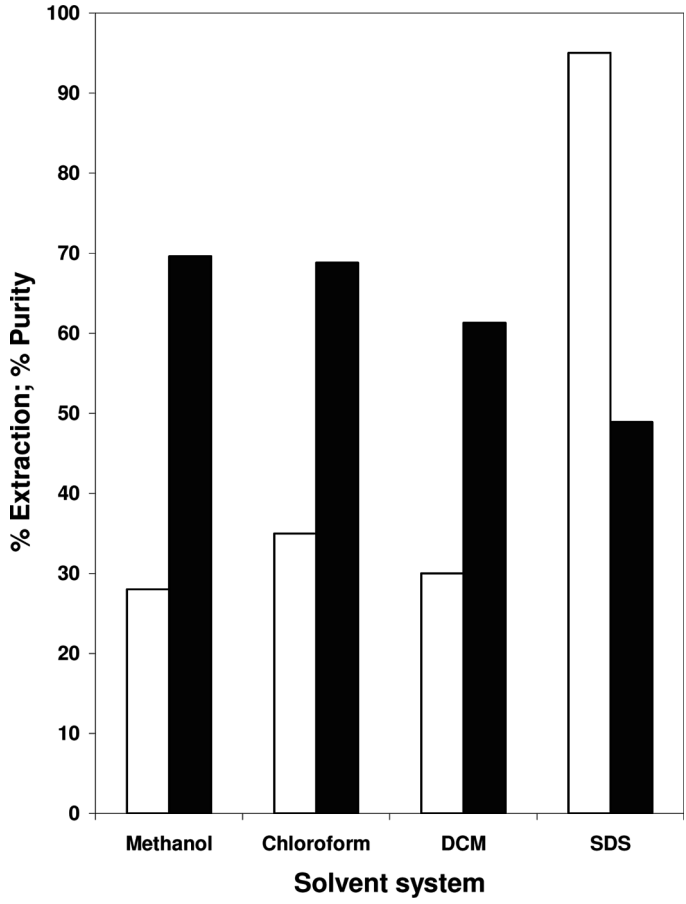


Figure 7. % Extraction and % purity of piperine in different solvents: □ % Purity; ■ % Extraction.

From the solubility studies, it is amply clear that the increased temperature leads to much higher and selective solubilization of piperine in the surfactants or surfactant + hydrotrope mixtures. Also, at elevated temperatures, the increased hydrolysis of cellulose biomatrix can result in the rupture of the matrix and facilitate faster transfer of piperine from the cells into the surfactant solutions. Figure 8 shows the effect of temperature on the rate of piperine extraction with 0.2 mol/dm^3 aqueous SDS solution in the range 30°C to 90°C. The percentage extraction of piperine substantially increased at higher temperatures. At 90°C, 98% piperine could be extracted in the solution within 70 minutes and the effective diffusion coefficient of piperine was estimated to be 2.82×10^{-13} m^2/sec.

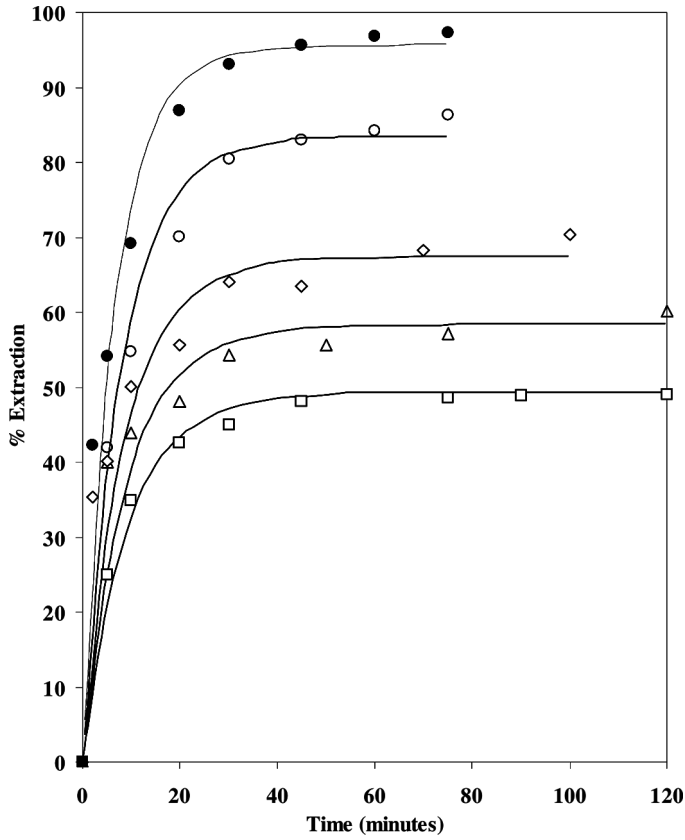


Figure 8. Effect of temperature on piperine extraction (SDS concentration = 0.2 mol/dm^3; Particle size = 16 Mesh). □ 30°C; D = 2.06×10^{-13} m^2/sec; △ 50°C; D = 2.11×10^{-13} m^2/sec; □ 70°C; D = 2.19×10^{-13} m^2/sec; ○ 80°C; D = 2.31×10^{-13} m^2/sec; ● 90°C; D = 2.82×10^{-13} m^2/sec.

Figure 9 compares the extraction of piperine from pepper using surfactant and surfactant-hydrotrope mixtures. At 30°C, 0.2 mol/dm^3 SDS as well as CTAB showed 50% piperine extraction while the SDS + NBBS (90:10) mixture could extract 45% piperine, in 90 minutes. NBBS alone showed somewhat lower extraction (30%) of piperine from the raw material under the similar conditions. The higher solubility as well as the greater extent of permeabilization of the cell structure by SDS and CTAB can be responsible for the increased extraction of piperine. The aqueous solutions of CTAB and SDS also showed slightly higher effective diffusion coefficients of piperine, i.e. 3.06×10^{-13} m^2/sec and 2.06×10^{-13} m^2/sec, respectively.

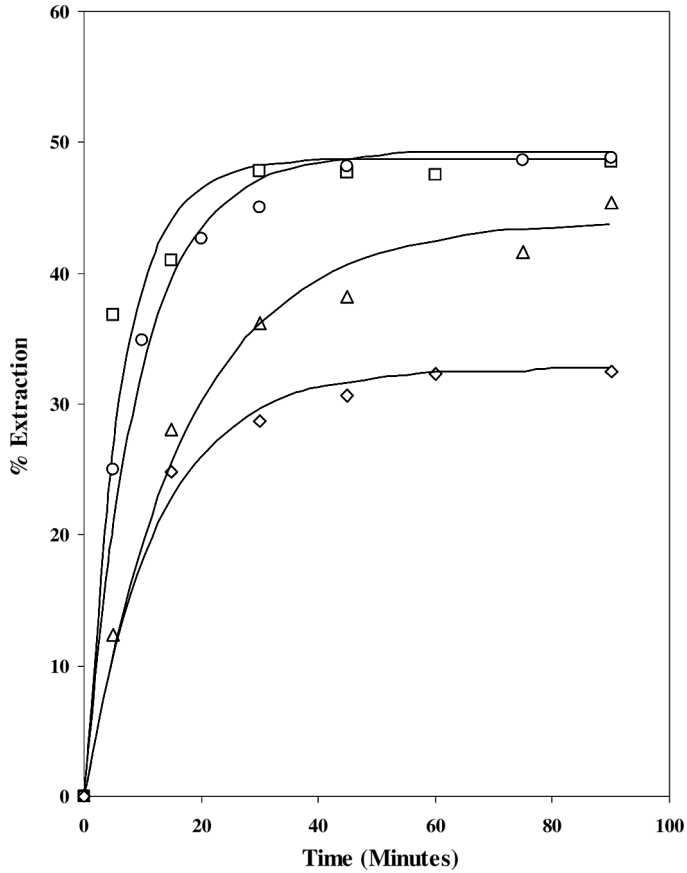


Figure 9. Effect of type of surfactants, hydrotrope and surfactant-hydrotrope mixture on piperine extraction (Temperature = 30°C; Concentration = 0.2 mol/dm^3; Particle size = 16 Mesh): □ CTAB; △ SDS + NBBS; ○ SDS; ◇ NBBS.

CRYSTAL STRUCTURE IN AQUEOUS SOLUTIONS OF SURFACE ACTIVE MATERIAL AND ORGANIC SOLVENTS

The micrographs of the piperine crystals from aqueous solutions and organic solvents are shown in Fig. 10 (a–f). There was significant difference in the surface characteristics of the crystals obtained from the both these aqueous solutions. The crystals obtained from either ethanol or chloroform were irregular in shape. Most importantly, there was appreciable irregular surface growth on these crystals. There are

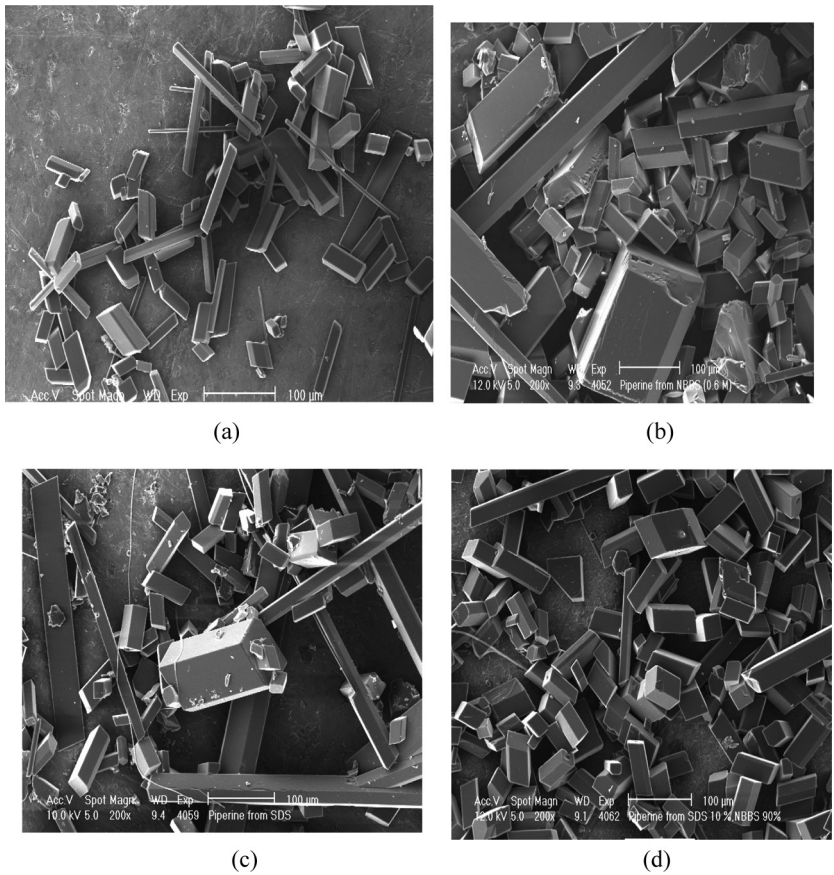
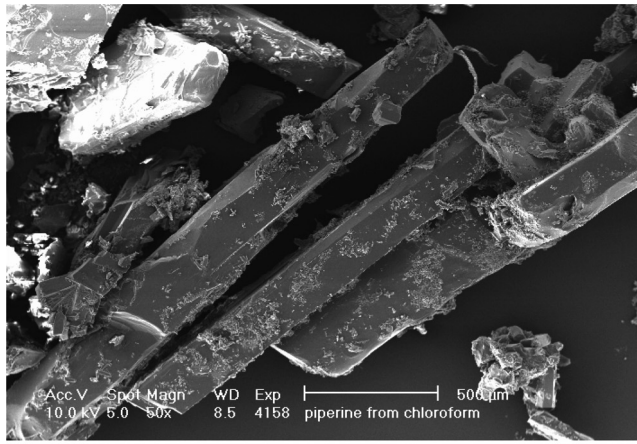


Figure 10. Morphology of piperine crystals from (a) 0.2 M CTAB solution (b) 0.6 M NBBS solution (c) 0.2 M SDS solution (d) 0.2 M SDS-NBBS mixture (e) chloroform (f) ethanol.



(e)

(f)

Figure 10. (Continued).

two different approaches to clarify the effect of solvent-surface interactions. Calculations based on ''surface roughening'' considerations predict that favorable interactions between the solute and the solvent on specific faces will lead to reduced interfacial tension, causing a transition from a smooth to a rough interface and a concomitant faster surface growth (26). Alternatively it has been proposed that preferential adsorption of solvent molecules at specific faces will inhibit growth of those faces as the removal of the bound solvent molecule poses an additional energy barrier for continued growth (27).

The crystals obtained from aqueous solutions of surfactants, hydrotropes, or their mixtures were uniform, having sharp edges and without any stepwise incomplete growth on the surface. The handling of the crystals obtained from aqueous solutions is easy as compared to those obtained from organic solvents. The crystals obtained from CTAB and SDS solutions were comparatively thinner and longer whereas those obtained from NBBS and SDS + NBBS solutions were bulky and smaller in length.

CONCLUSION

Beyond CMC (or mixed CMC), there was almost a linear increase in piperine solubility with the concentration of the surface active material. The negative sign for ΔG indicates spontaneous transfer of piperine from aqueous bulk phase to the micellar phase.

There was increase in the % extraction as well as effective diffusion coefficient of piperine as the concentration or the temperature of the aqueous SDS solution was increased. The organic solvents, showed a greater % of piperine extraction as compared to that using the aqueous SDS solution. But these solvents were highly non-selective and dissolved a number of other compounds along with the piperine. The purity of piperine was more in the aqueous SDS solution based extraction. The crystals obtained from aqueous solutions of surfactants, hydrotropes, or their mixtures were uniform, having sharp edges and without any growth on the crystal surfaces as compared to highly irregular crystals obtained from methanol and chloroform.

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