Surfactant Solubilization Behavior *via* Headspace Analysis

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Automatic headspace gas chromatography (AHGC) has been used to define the solubilization behavior of volatile organics in typical detergent surfactants. The amount of a component in the headspace at equilibrium and amount available for perception is inversely related to its solubility in the surfactant micelles. AHGC is used to determine: i) the solubilization site within the micelle for a solute; ii) the effect of the solute on the critical micelle concentration; iii) the solute partition coefficient (K); and iv) the effect of cosolvents on the critical micelle concentration. This approach offers the ability to compare solubility behavior in a complex matrix along with the advantages of direct sampling and the simultaneous analysis of many components.

KEY WORDS: Automatic headspace sampling, CMC, flavorants, gas chromatography, glycerol, partition coefficients, sorbitol, surfactants.

Headspace chromatographic methods have found applications in the monitoring of volatiles from environmental, bacterial and food sources (1,2). The effects of specific food components (*i.e.*, proteins and carbohydrates) on the release of flavorants also have been examined (3–5). For personal and household products a similar approach would be useful for studying the effects of product components, such as surfactants and humectants, on the release of flavors and fragrances. Recently, headspace analysis has been used to show the effects of product components on flavor release in dentifrice (6,7).

Surfactants can alter the intensity and character of the flavors and fragrances present in cosmetic/detergent products through differential solubility of the volatile components (8,9). It is of interest to quantitatively define these interactions between the components and the surfactants normally used in product applications. Direct headspace analysis of flavor/surfactant solutions provides a method for studying these interactions because the headspace concentration of a solute is inversely proportional to its solubility in the surfactant micelle. Recently, such methods have been used to study the solubility of hexanol in mixed ionic/nonionic micelles (10). In this study, automatic headspace gas chromatography (AHGC) was used to determine the differential solubility and localization in the micelle of two flavor compounds, menthone and cineole, in sodium lauryl sulfate (SLS) solutions. The partition coefficient and a solubilization value were determined for several flavorants in SLS, cetyltrimethylammonium bromide (CTAB) and dodecylbenzenesulfonate (DDBS) solutions. The headspace methodology is also an excellent approach for determining the critical micelle concentration (CMC) and interesting solution behaviors with cosolvents.

EXPERIMENTAL PROCEDURES

Sample preparation. Standard solutions of menthone, 1.8-cineole or menthone/1,8-cineole were prepared in Milli-Q water and added to SLS. The initial SLS concentrations for the menthone study were 1% and .75%, and these were sequentially diluted to give a series of surfactant concentrations above and below the CMC. The flavorants were at the following concentrations: menthone, 0.0003–0.009%; cineole, 0.0001%; limonene, 0.0002%; and carvone, 0.0004%. A mixture of flavor components, which included cineole, menthone, limonene, menthol, carvone and anethole, was also studied at a total concentration of 0.004% with SLS and CTAB. Solutions were also prepared with 1% SLS and increasing mole fractions (flavorant/SLS) of either 1,8-cineole (0.1–0.7) or menthone (0.2–0.5). SLS was obtained from Sigma (St. Louis, MO), CTAB from Aldrich Chemical (Milwaukee, WI) and DDBS (85% pure) from Albright and Wilson (London, England). The flavor materials were >90% pure, with the menthone sample being an 86:14 mixture of menthone/isomenthone isomers, which have the same solubility properties. The aqueous solutions (5 mL) were pipetted into the 22-mL headspace vials and sealed. Samples were run in triplicate.

Instrumental method. Sample vials were thermostatted in a Perkin-Elmer HS-100 Headspace Analyzer (Perkin-Elmer, Norwalk, CT) for 60 min at 40°C. Headspace vapors were analyzed by pressurizing the vials for two minutes followed by a timed injection (0.8 sec) of the vapors onto the gas chromatographic (GC) column. A Perkin-Elmer Sigma 2000 GC equipped with a flame ionization detector and a Supelcowax fused silica capillary column (30 M × 0.32 mm ID) were used for all analyses. The temperature program was 50°C (hold 2 min), 10°C/min to 150°C for a total run time of 12 min. Data were collected on an LCI-100 computing integrator and transferred to an IBM PC-AT with LCI-100 communications software. All components were resolved under these GC conditions and peak area deviation was <5% (<2% for menthone/cineole solubilization study). Data analysis was done with RS/1 (BBN Software) and special procedures written for chromatographic data (11).

RESULTS AND DISCUSSION

Critical micelle concentration. An ionic micelle has two areas of differing polarity for solubilization, the outer hydrophilic region and the hydrophobic core (12–14). Compounds with polar groups can be expected to be soluble in the hydrophilic region and, in fact, participate in micelle formation. The two solubilization areas can be demonstrated by observing the change in headspace concentration for a volatile component with increasing solution concentration at constant surfactant levels (15). This was demonstrated for menthone at 1% SLS (Fig. 1). The break in the curve is the menthone mole fraction (0.35) where solubility in the micelle hydrophilic layer is exceeded and solubility is occurring in the micellar core. For cineole a different behavior is observed. There is no break in the curve, indicating solubilization only in the micellar core (Fig. 1). At the highest concentrations an emulsion is formed. The contrasting behavior of these two compounds is similar to that reported for geraniol and ionone (hydrophilic region) *vs.* geraniol acetate and citral (micellar core) (15,16).

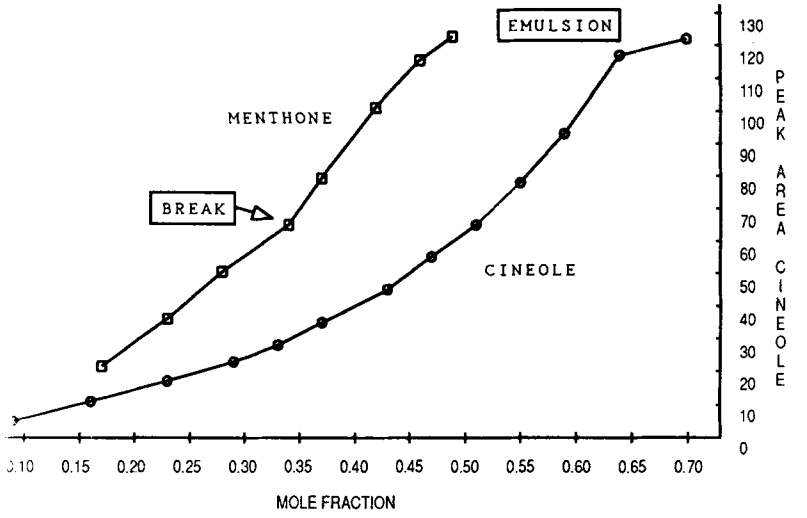

FIG. 1. Micelle solubility for menthone (—□—) and cineole (—○—).

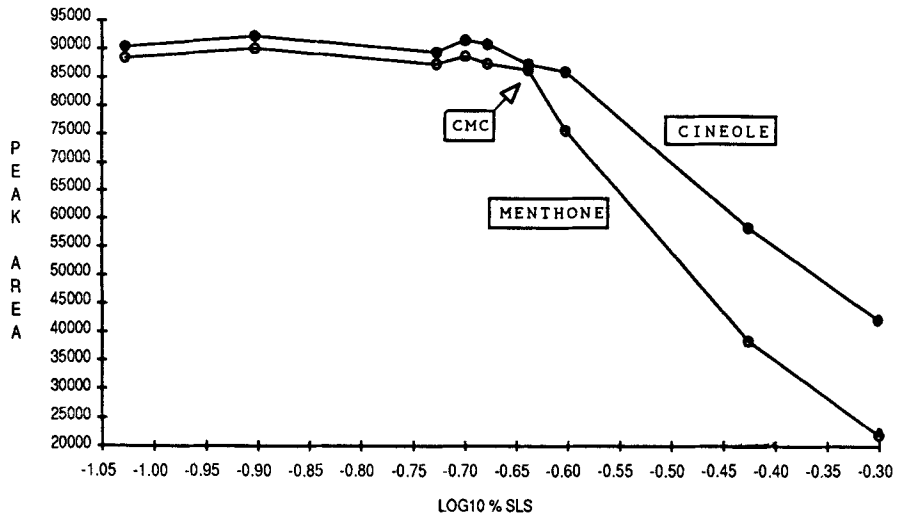

FIG. 2. Effect of surfactant level on release of cineole (— ● —) and menthone (—○—); CMC determination.

Because of this solubility difference, menthone and cineole represent suitable compounds to probe surfactant solubilization. The effect of SLS on the solubilization of menthone is shown in Figure 2. As the surfactant concentration increases, the headspace level remains constant until the CMC is exceeded. The CMC can be determined from the headspace data by examining the intersection between the linear portion of the curve (<CMC) and the exponential curve (>CMC). For menthone at low concentrations (<0.0009%), the value for the peak area of menthone at 0.23% was significantly different from the 0.25% value. This corresponds to the 8 mM CMC value reported for SLS at 25°C but less than the 0.25% for 40°C (16). Concentrations of solubilizates greater than 0.01 mole fraction can cause a lowering of the CMC values (12). Table 1 shows the effect of the solution concentration of menthone on the CMC where values >0.007 mole fraction begin to reduce the CMC.

TABLE 1

Effect of Concentration of Solute on CMC

CMC	% Menthone	Mole fraction menthone/SLS
.23	.0003	.002
.23	.0009	.007
.22	.003	.02
.21	.009	.07

For the less polar molecule, cineole, the break is not as sharp and occurs at 0.25% SLS, which matches the value reported from surface tension data. These differences indicate that solubility of cineole occurs after formation of the micelle, whereas menthone participates in micelle formation (Fig. 2).

Partition coefficient. The thermodynamic partition

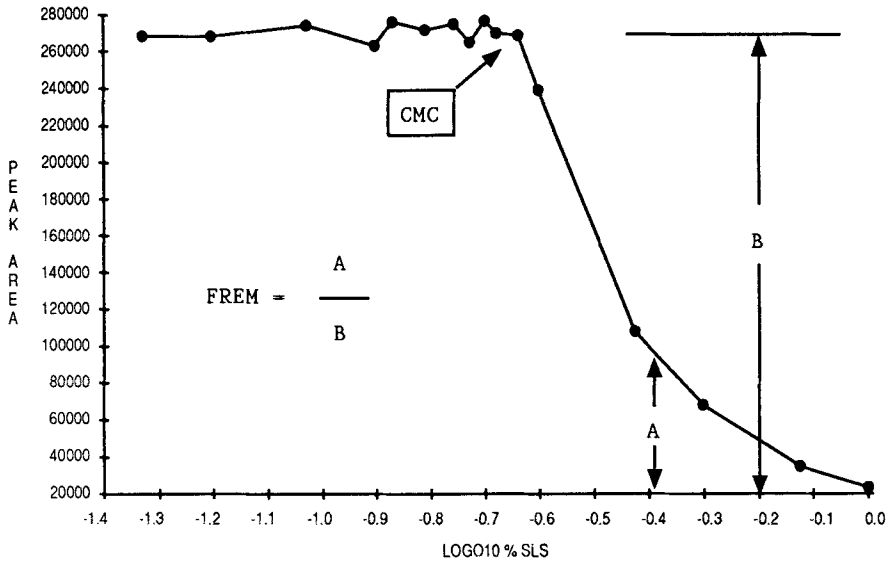

FIG. 3. Determination of fraction remaining (FREM) in headspace for menthone in SLS.

coefficient (K_{mw}) of a compound between the aqueous solution and the micelle can be determined from a comparison of the headspace concentration below the CMC and at a given surfactant concentration. The headspace data provide both the CMC of the surfactant and the fraction remaining in the headspace (FREM) for a specific component, *e.g.*, menthone, at a given surfactant concentration (Fig. 3). From these data the mole fraction of the component in the micelle can be calculated. K_{mw} is a ratio of these two values (17). The equation for the calculation of K_{mw} is shown below, where C_s equals surfactant concentration; C_{cmc}, critical micelle concentration; and FREM, ratio of peak areas in presence and absence of surfactant. The ratio of [1-FREM]/FREM is substituted for the component mole fractions in the equation:

$$K_{mw} = [1\text{-FREM}] \times 10^3/ [\text{FREM}] \times 18 \times [C_s - C_{CMC}]$$

The validity of this approach was verified by determining the K_{mw} values for pentanol, hexanol and heptanol at 40°C and comparing them against the reported values (40°C) (18). The values were 1.01 *vs.* 0.67, 1.94 *vs.* 1.60, and 6.05 *vs.* 3.94 (all $\times 10^3$), respectively.

K_{mw} can differ significantly when compared at low concentrations of surfactant and at saturation of the surfactant micelles with the solute (19). In studies in which cyclohexane was the solute, an approximate 10% increase in the solubilization constant in SLS occurred with a two-fold increase in mole fraction of solute (20).

In the current studies, the partition coefficient represents a limiting value at low mole fractions of solute/surfactant. K_{mw} for menthone at 0.5% SLS showed small changes across menthone concentrations (14.2 $\times 10^3$ at 0.07 mole fraction and 17.8 $\times 10^3$ at 0.001) and was unchanged across 0.5–2.0% SLS concentrations. A value of 14.0 $\times 10^3$ was obtained for menthone in the presence of several other fragrance components at a total fragrance level of 0.005% and 1% SLS.

K_{mw} values for a cationic surfactant, CTAB, and another anionic surfactant, DDBS, were shown to differ from SLS for some components; however, the rank order for components varying in polarity was the same (Table 2). For simple alcohols, the octanol/water partition coefficient (log P) and the K_{mw} values are highly correlated (21). A cationic system did show a correlation with log P values for single examples of simple ketones, alcohols, esters and amines (21). Values for ethers and halocarbons did not fit the same correlation. However, since log P increases with hydrophobic character, while K_{mw} values are actually higher for compounds with polar substituents because of the nature of the micelle (K{menthone}>K{limonene}), a similar correlation would not be expected across all classes of compounds, as suggested in a recent report (22). Log P values are not generally available for fragrance/flavor compounds and the calculated values from structural parameters do not take into account the stereochemical features found in these molecules. Calculated log P values and the micellar partition coefficient (K_{mw}) for several flavorants are shown in Table 2 (23).

TABLE 2

Micellar Partition Coefficients (Values $\times 10^{-3}$)

Flavorant	SLS	DDBS	CTAB	LOG P[a]
Limonene	5.8	3.0	5.0	4.5
Cineole	5.8	3.5	5.0	2.8
Carvone	11.4	5.8	5.4	2.1
Menthone	15.0	9.5	9.9	2.8
Menthol	23.5	16.2	21.3	3.3
Anethole	23.6	19.3	35.7	3.3

[a]Calculated.

Though K_{mw} allows a comparison of solubility across surfactants, the fraction remaining of a flavorant in the headspace provides more descriptive information for detergent systems. A plot of 1/FREM *vs.* % surfactant for concentrations above the CMC gives a linear relation-

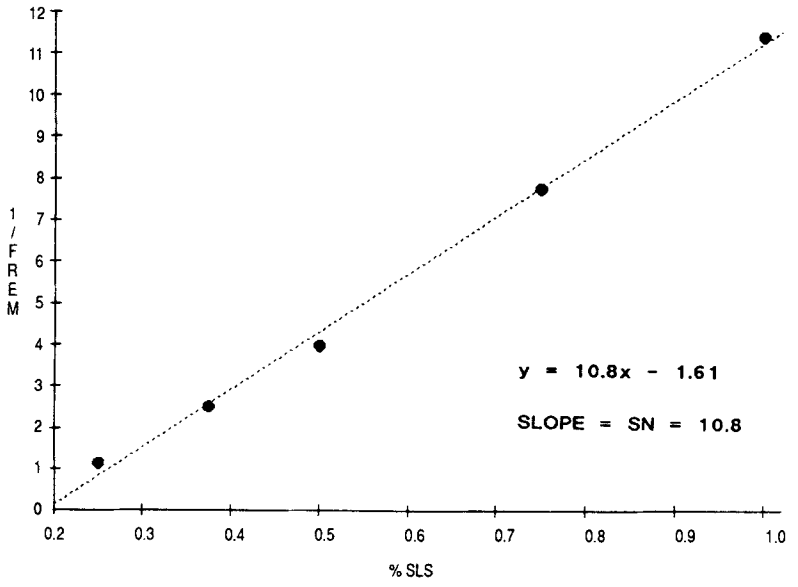

FIG. 4. Determination of solubility number for menthone in SLS derived from the plot of 1/FREM *vs.* the surfactant concentration in percentages.

ship (significance >.99), independent of surfactant concentration, whose slope can be used to compare solubilization behavior of solutes (Fig. 4). Table 3 also shows these differential solubility numbers (DSN) for several volatile flavorants. Where a single surfactant is involved, the K_{mw} is directly related to the DSN through the molecular weight. However, in detergent systems the active ingredients usually involve a mixture of surfactants, and here the DSN values make a comparison of solubility behaviors possible. The values for solubilization capacity and partition coefficient for several fragrance materials in SLS have recently been reported (24). The solubilization values were calculated as the slope of a plot of the maximum additive concentration (amount of solute added to SLS solution to give an emulsion) *vs.* the molar concentration of SLS.

Effect of cosolvent. Two humectants, glycerol and sorbitol, which have opposite effects on flavor release and on the CMC of SLS, were also examined. A solution of flavorant, SLS and sorbitol (28%) gives a CMC of 0.12% by surface tension measurements and a CMC of 0.17% by headspace values for menthone. For glycerol, the CMC is increased (0.28% for 29% solution and 0.23% for 15% solution *vs.* 0.2% for no humectant) as measured by headspace values for menthone.

These results show the difference between the formation of micelles as measured by techniques that require micelles, *i.e.,* headspace or fluorescence, and techniques that measure the maximum surface absorption, such as surface tension (9). In most cases similar directional effects occur for both approaches. However, with glycerol, the decrease in surface tension is correlated to an increase in the CMC. The basis for the differing effects of the two humectants on the CMC is related to the manner in which they modify the initial interaction between the surfactant and water. Glycerol, like urea, is a water structure breaker that increases the originial entropy of the original solution and decreases the entropy change on micellization (9,25,26). This inhibits micelle formation and requires

TABLE 3

Solubility Numbers for Different Surfactants

Flavorant	SLS	DDBS	CTAB
Limonene	3.4	2.1	—
Cineole	4.3	2.0	2.5
Carvone	9.8	3.0	2.8
Menthone	10.8	4.8	5.3
Menthol	20.1	8.7	10.1
Anethole	25.9	12.2	27.4

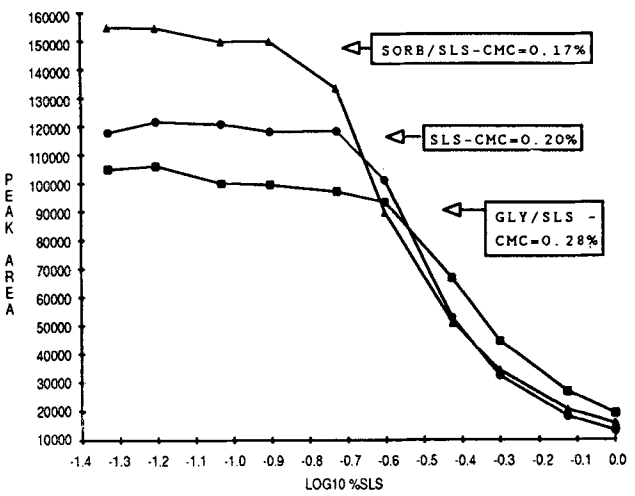

FIG. 5. Comparison of effects of glycerol and sorbitol on release of menthone from an SLS solution. Glycerol (29%; —■—), sorbitol (28%; —△—), SLS alone (—●—).

higher concentration of surfactant for micellization to occur. At 60% glycerol the curve flattens out. Other solvents that increase the CMC of some surfactants are dioxane, ethanol and ethylene glycol (26–28). Water structure formers, such as xylose and sorbitol, lead to a net increase in entropy, favoring micellization, and give a lowering of the CMC.

Sorbitol has been reported to decrease the CMC of a nonionic surfactant as determined by the fluorescence technique (28). Glycerol and polyethyleneglycol increase the CMC of SLS while simple alcohols of longer carbon chain than ethanol reduce the CMC (17,29). Figure 5 shows the combined effects of initial solubilization (below the CMC, where glycerol>sorbitol) and micellization (CMC sorbitol<glycerol) with these humectants on menthone release from solution. The two humectants show similar solubilization capacity at >1% SLS.

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