Surface Activity of Quaternary Ammonium Salts Derived from Jojoba Oil

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A number of *cis* and *trans* quatenary ammonium salts were synthesized from jojoba oil. All derivatives were found to be surface active agents, i.e., they reduced the surface tension to ~35 dynes/cm^{-1}, at very low concentrations. The relationship between the surface activity and the molecular structure is discussed.

KEY WORDS: Cationic surfactant, critical micelle concentration, jojoba, surface tension.

Jojoba oil and its derivatives are industrially promising, natural, agricultural products (1). Jojoba oil consists of long-chain wax esters rather than a mixture of triglycerides. In both natural and chemically modified states, the oil consitutes the basis of a wide range of products, ranging from cosmetics to high pressure lubricants (2). As a result of the particular properties of jojoba oil, i.e., high hydrophobicity, together with high stability, nonrancidity and nontoxicity, it has been used as the starting product in the synthesis of various quaternary ammonium and pyridinum salts to be tested as surface active agents. In this study we evaluated the surface activity of various cationic derivatives of jojoba oil.

EXPERIMENTAL PROCEDURES

Materials and methods. All the quaternary jojoba salts studied were synthesized according to procedures described previously (3,4). The formulas of these jojoba-based surfactants are presented in Tables 1 and 2.

Surface tension was measured with a Lauda tensiometer, equipped with a platinum-irridium ring. All the measurements were conducted at the air/water interface 15 min after formation of the interface. For each derivative the surface tension was measured at various dilutions, and the minimal surface tension (γ_{min}) and the critical micelle concentration (CMC) were evaluated from plots of surface tension vs log concentration. The area per adsorbed molecule at the air/water interface was calculated using the Gibbs adsorption equation for ionic surfactants.

RESULTS AND DISCUSSION

A series of surfactants was synthesized with the general formula $R_1R_2R_3R_4N^{(+)}X^{(-)}$, in which R_2, R_3 and R_4 represent various alkyl chains (Tables 1 and 2), and $X^{(-)}$ represents various ions. R_1 is either a *cis* or a *trans* monounsaturaed alkyl chain derived from jojoba oil and is composed mainly of C_{20} and C_{22} carbon atoms.

Generally, it was found that all the cationic derivatives were indeed surface active agents, i.e., they reduced the surface tension to about 35 dynes cm^{-1}, and typical γ vs log C plots were obtained, as shown in Figure 1.

The relative role of the jojobyl chain as compared to the other alkyl groups in the molecule was evaluated (Table 1). As expected, the CMC values of the various jojoba derivatives decreased with an increase in the total number of carbon atoms in the molecule, in agreement with previous studies (5). In comparison with

TABLE 1

CMC, Area Per Adsorbed Molecule (A) and the Minimal Surface Tension (γ_{min}) for Various Jojoba-Derived Surfactants

Formula[a]	CMC,M	A,Å^2	γ_{min}, dyne/cm
cis-JOJ-$N^+H_3Cl^-$	1.8×10^{-4}	82.6	32
cis-JOJ-$N^+(CH_3)_2$-$C_4H_9Cl^-$	9.4×10^{-5}	77	32
cis-JOJ-$N^+(CH_3)_2$-CH_2-C_6H_5 Cl^-	1.1×10^{-4}	76.3	35
cis-JOJ-$N^{(+)}(CH_3)_2$-$C_8H_{17}Cl^-$	6.4×10^{-5}	81.9	33

[a]*cis*-JOJ = $CH_3(CH_2)_7CH{=}CH(CH_2)_m$, m=8, 10, 12, 14.

TABLE 2

CMC, Area Per Adsorbed Molecule (A) and the Minimal Surface Tension (γ_{min}) for Various *cis* and *trans* Isomers of Quaternary Ammonium Salts.

Formula[a]	CMC (M)		A, (Å^2)		γ_{min} (dyne/cm)	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*
JOJ-$\overset{CH_3}{\underset{CH_3}{N^+}}$-$C_2H_5Br^-$	1.4×10^{-4}	2.6×10^{-3}	88.2	112.9	35	39
JOJ-N^+ ⟨⟩ $CH_3SO_3^-$	5.3×10^{-5}	2.1×10^{-4}	61.8	87.8	39	38
JOJ-$\overset{CH_3}{\underset{CH_3}{N^+}}$-$CH_3$ I^-	1×10^{-4}	1.3×10^{-2}	76.4	139.8	31	32
JOJ-$N^{(+)}H_3Cl^-$	1.8×10^{-4}	2.2×10^{-4}	82.6	93.4	32	30

[a]See Table 1.

other cationic surfactants, the CMC values of our compounds were exceptionally low, due to the very long hydrophobic jojobyl chain. It appears that the increase in the additional alkyl chains had no significant effect on γ_{min} or on the area per adsorbed molecule. This finding contradicts the situation in typical quaternary ammonium salts, in which an increase in the size of the short alkyl chains leads to an increased area per molecule (6). Since the long chain of the jojoba derivatives is composed of C_{20}-C_{22} carbon atoms, it can be assumed that this chain is coiled, and is thus very dominant in determining the area per molecule. It should be noted that coiling of the hydrophobic groups is to be expected above C_{16} (7).

The effect of the configuration—*cis* or *trans*—on the surface activity was also evaluated. As shown in Table 2, the *trans* cationic surfactants generally have higher CMC values and a larger area per molecule than the *cis* derivatives, while γ_{min} is not affected by the configuration.

From the difference in CMC and area per molecule between the *cis* and *trans* isomers, it might be concluded that the *cis* isomer is effectively more hydrophobic than the *trans* isomer. This assumption is in keeping with the difference in CMC between *cis*-oleic chain and stearyl chain for various surfactants (8). It was postulated that the *cis*-oleic chain is a folded molecule, packed into a small area, which leads to a smaller CMC than that for the stearic-acid-derived surfactant. Therefore, it might be expected that a similar folding exists in the *cis*-jojobyl chain, leading to a smaller CMC and area per molecule than the *trans*-jojobyl chain. This assumption is based on the similarity in chain structure and conformation between a saturated long chain (stearyl) and the monounsaturated jojobyl chain with a (*E*)-configuration. Dreiding models exhibit these similarities.

Since it was shown that the cationic derivatives from jojoba oil are indeed effective surface agents, a further study is now being conducted in order to evaluate their use in commercial systems.

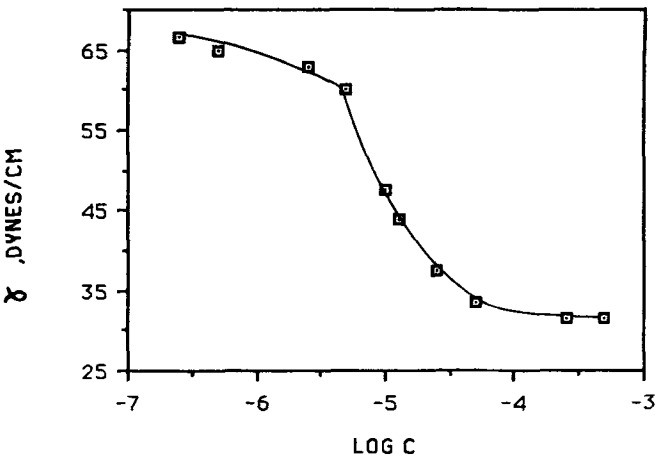

FIG. 1. Surface tension vs log concentration (w/w) of *cis* isomer of the jojoba derivative JOJ-$N^+(CH_3)_3I^-$.

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