

Micellar Aggregation Behavior at Low Ionic Strength of Cyclic Acetal-Type Cationic Surfactants Containing the 1,3-Dioxolane Moiety

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Received: February 29, 1996; In Final Form: November 5, 1996[®]

Aggregation studies in water of several cationic acetal-type surfactants having varied hydrophobic chains, [(2-alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides (C_n -D-TAB; where $C_n = C_9H_{19}$, $C_{11}H_{23}$, $C_{13}H_{27}$), have been performed by means of dynamic light scattering in the 0.015–0.32 M NaBr concentration range over the temperature limits of 25–45 °C. The aggregation parameters (translational diffusion coefficient of micelle (D_0), hydrodynamic radius (R_h), ionization fraction (α), and aggregation number (n)) have been determined and discussed with respect to the parameters of the “classical” alkyltrimethylammonium bromides (C_n -TAB). Additionally, the effect of diastereoisomerism upon surfactant aggregation has been characterized for the *trans*- and *cis*-[(2-tridecyl-1,3-dioxolan-4-yl)methyl]trimethylammonium (C_{13} -D-TAB), (2-hydroxyethyl)dimethylammonium (C_{13} -D-HEAB), and triethylammonium (C_{13} -D-TEAB) bromides. Accordingly, the 1,3-dioxolane ring configurations and the size of the head groups do not involve noticeable diastereomeric discrimination in the self-assembling abilities. Because the studied cationic acetal-type surfactants contain a 1,3-dioxolane unit (D), they are an acid hydrolyzable type of chemodegradable surfactant, which is analogous to C_n -TAB in terms of the micellar aggregation characteristics.

Introduction

Ionic surfactants bearing an acetal-type 1,3-dioxacyclane ring, i.e., the five-membered 1,3-dioxolane or the six-membered 1,3-dioxane, have attracted much attention in the literature.^{1–3} Such chemodegradable structures (for an explanation of the term see ref 3a) are susceptible to hydrolysis in acidic media, giving rise to nonsurfactant products: a neutral, water insoluble compound and an ionic, water soluble one.^{3b} Chemical decomposition of the cyclic acetal-type amphiphiles can be useful for any number of purposes (e.g., micellar/emulsion catalysis of an organic reaction) in order to avoid unfavorable processes such as foaming and emulsification during the separation techniques.^{4,5}

Recently, we have started systematic investigations of the properties of cationic cyclic acetal-type surfactants containing a 1,3-dioxolane moiety in their structure.⁶ The incorporation of a five-membered cyclic acetal grouping between the hydrocarbon chain and the polar ammonium group of “classical” alkyltrimethylammonium bromides causes both the Krafft point and the critical micelle concentration (cmc) to decrease. The values of the standard free energy contribution of the 1,3-dioxolane ring [-D-] in the [(2-alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides (C_n -D-TAB) to micellization and adsorption at the aqueous solution–air interface ($\Delta G_{\text{mic}}^\circ$ [-D-] = -5.7 kJ/mol and $\Delta G_{\text{ads}}^\circ$ [-D-] = -21.5 kJ/mol, respectively) showed that the [-D-] moiety is approximately 1.7 times more hydrophobic than a methylene group of the alkyl chain in promoting micellization and 6.3 times more effective in promoting adsorption.⁶ It clearly indicates a higher strength of adsorption of the five-membered 1,3-dioxolane grouping at the

infinite dilution surface film rather than the tendency to micellization.

Aqueous micelles and oil-in-water microemulsions based on the C_n -D-TAB derivatives can be successfully applied as chemodegradable reaction media.⁵ They are liable to chemical degradation in both homogeneous and micellar systems, which makes them most promising components not only of micelles but especially of microemulsions. Additionally, it has been pointed out that the 1,3-dioxolane ring as a portion of C_n -D-TAB does not introduce significant changes in the catalytic ability of its micellar aggregates in relation to their hydrophobic analogues, i.e., alkyltrimethylammonium bromides.^{5a}

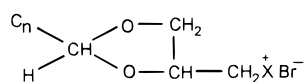
The cationic quaternary ammonium surfactants C_n -TAB form small, spherical micelles in aqueous solution up to quite high concentrations and are adequately described by geometrical arguments of micelle shape and size.⁷ Micellar parameters of aggregates formed by cationic surfactants such as shape, size, aggregation number, and diffusion coefficient can be obtained from various techniques: membrane osmometry,⁸ fluorescence probing,⁹ and quasielastic light scattering (QLS) spectroscopy.¹⁰ In particular, the QLS method has extensively been applied to study structural parameters of surfactant-based systems (e.g., micellar diffusivity,¹¹ intermicellar interactions,¹² average micelle molecular weights^{11a,13}) since this probe does not disturb the monomer–micelle equilibrium.¹⁰ Many authors have presented dynamic light scattering results of aqueous micelles formed by cationic surfactants: cetyltrimethylammonium bromide (CTAB),^{11c,d} tetradecyltrimethylammonium bromide (TTAB),^{11c,d,12b} and dodecyltrimethylammonium bromide (DTAB)^{11e} at low ionic strength, while there is no information about their acetal-type analogues.

Therefore, the main purpose of this investigation was to describe quantitatively the micellar aggregation behavior at low

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[®] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

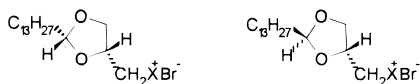
ionic strength of a series of cationic cyclic acetal-type surfactants



C _n	X	Abbreviation
C ₉ H ₁₉	NMe ₃	C ₉ -D-TAB
C ₁₁ H ₂₃	NMe ₃	C ₁₁ -D-TAB
C ₁₃ H ₂₇	NMe ₃	C ₁₃ -D-TAB
C ₁₃ H ₂₇	N(CH ₂ CH ₂ OH)Me ₂	C ₁₃ -D-HEAB
C ₁₃ H ₂₇	NEt ₃	C ₁₃ -D-TEAB

(structures given above) by means of light-scattering measurements and discuss the obtained results in relation to C_n-TAB surfactants, since variations in diffusivity, *D*, with respect to either surfactant or salt concentration in the positive slope *D* vs [surfactant] region has been well-documented for various CTAX + NaX (X = Br, Cl, OH, SO₄) systems.^{11c,d,12b-e}

Generally, the studied surfactants containing the 1,3-dioxolane ring comprise diastereoisomeric mixtures of approximately constant molar ratios of *cis* to *trans* isomers equal to 1.4.^{3b} Furthermore, to justify the assumption that the configurations of the *cis*- and *trans*-2,4-disubstituted-1,3-dioxolane surfactants with the flexible 1,3-dioxolane ring do not significantly affect the micellar aggregation, we extended our scattering studies to the pure *cis* and *trans* isomers of the selected 2-tridecyl surfactant derivatives of the structures given below.



X = NMe ₃ :	<i>cis</i> - C ₁₃ -D-TAB,	<i>trans</i> - C ₁₃ -D-TAB
X = N(CH ₂ CH ₂ OH)Me ₂ :	<i>cis</i> - C ₁₃ -D-HEAB,	<i>trans</i> - C ₁₃ -D-HEAB
X = NEt ₃ :	<i>cis</i> - C ₁₃ -D-TEAB,	<i>trans</i> - C ₁₃ -D-TEAB

This work explores in further detail the role of the 1,3-dioxolane grouping in the cationic cyclic acetal-type surfactants and their aggregation behavior in water in comparison with the classical alkyltrimethylammonium bromides.

Experimental Section

The synthesis and properties of [(2-alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides were previously described.^{3b,6} [(2-Tridecyl-1,3-dioxolan-4-yl)methyl](2-hydroxyethyl)dimethylammonium (C₁₃-D-HEAB) and [(2-tridecyl-1,3-dioxolan-4-yl)methyl]triethylammonium (C₁₃-D-TEAB) bromides were obtained by quaternization of stoichiometric amounts of 2-tridecyl-4-(bromomethyl)-1,3-dioxolane (for the preparation see ref 3b) and (2-hydroxyethyl)dimethylamine or triethylamine, respectively, in MeOH in a sealed tube at 90 °C. The surfactants obtained were purified several times by recrystallization from acetone–ethyl ether and dried under vacuum at 100 °C. (**C₁₃-D-HEAB**: yield 55%; Krafft point below 5 °C. Anal. Calcd for C₂₁H₄₄BrNO₃: C, 57.52; H, 10.12; N, 3.20. Found: C, 57.49; H, 10.13; N, 3.21. **C₁₃-D-TEAB**: yield 65%; Krafft point below 5 °C. Anal. Calcd for C₂₃H₄₈BrNO₂: C, 61.33; H, 10.67; N, 3.11. Found: C, 61.30; H, 10.69; N, 3.09.) *cis*- (*R_f* = 0.6) and *trans*-2-tridecyl-4-(bromomethyl)-1,3-dioxolanes (*R_f* = 0.7) were separated by column chromatography on silica gel (4% isopropyl ether–hexane as eluent). *cis*- and *trans*-[(2-tridecyl-1,3-dioxolan-4-yl)methyl]trimethylammonium, (2-hydroxyethyl)dimethylammonium, and triethylammonium bro-

mides were obtained in the reaction of *cis*- and *trans*-2-tridecyl-4-(bromomethyl)-1,3-dioxolanes with trimethylamine, (2-hydroxyethyl)dimethylamine, or triethylamine, respectively, in a sealed tube at 90 °C. The appropriate surfactants were purified by recrystallization from acetone–ethyl ether and dried under vacuum at 100 °C.

For the dynamic light scattering measurements, all micellar solutions were equilibrated after preparation for at least 12 h at room temperature and carefully filtered through 0.2 μm Millipore membranes directly into dustfree scattering cells. Prior to every measurement the given sample was centrifuged at 1800g for 15 min.

The light-scattering apparatus consisted of an Ar⁺ laser ILA 120 (Carl Zeiss Jena, former East Germany) operating at 488 nm with an output power of 0.8 W, a THORN EMI 9130 B03100 photomultiplier, an ALV/PM-PD preamplifier/discriminator (ALV, Germany), and a multi-tau ALV5000 digital correlator (ALV, Germany). The time correlation functions of scattered light intensity were measured at the scattering angle of 90°. The temperature of toluene which has been used as the index-matching liquid was controlled with the accuracy of 0.2 °C. After each temperature was set, the sample was left for ca. 20 min to equilibrate and stabilize the scattered light intensity. The diffusion coefficients were obtained as an average of at least five runs. Measured correlation functions were analyzed by means of the correlator's built-in software using the cumulant model.

The critical micelle concentration (cmc) of a surfactant was determined in NaBr solutions in the studied temperature range by surface tension measurements using a Krüss K 10 tensiometer equipped with a du Nuoy Pt-Ir ring. Deionized, doubly glass-distilled water was used throughout. Sets of measurements were taken at intervals until no significant change in the tension occurred. The cmc values as a function of [NaBr] and at 25, 35, and 45 °C are given in the Supporting Information (SI1).

The Krafft temperature values of the synthesized compounds were determined as follows. Five milliliters of the 2% aqueous surfactant solution was slowly cooled with constant agitation, and the temperature at which the given surfactant precipitated from the solution was recorded. The obtained temperature was similar to the midpoint of a narrow temperature range over which the solutions clarified on slow warming (at a rate of 1 °C/10 min) and with continuous vigorous shaking.

Results and Discussion

The dynamic light scattering experiments performed in the first part of this study characterize the size and micellar interactions of C_n-D-TAB aqueous micelles as a function of alkyl chain C_n (*n* = 9, 11, 13) length, surfactant concentration, and temperature under conditions of moderate ionic strength where there is assumed, as in the case of C_n-TAB systems,^{11c-e,12b} little or no spherocylindrical micellar growth. In Figure 1 the concentration dependence of *D* for C₁₃-D-TAB, C₁₁-D-TAB, and C₉-D-TAB is given at 25 °C in the [NaBr] range of 0.015–0.32 M. As shown the diffusivities form a familiar positive slope “fan” of curves which extrapolate to the *D*₀ diffusivity at the cmc (the values are given in SI1); the lower the [NaBr], the larger the slope of lines representing the dependence of the apparent diffusion coefficient on surfactant concentration. The obtained results for our systems are qualitatively similar to those found in^{11c-e,12b,c} for alkyltrimethylammonium surfactants at low salt concentrations.

Following the classical paper of Corti and Degiorgio^{12a} and subsequent papers by Bunton et al.^{11c,d,12b} we analyzed quantitatively the concentration dependence of translational diffusion

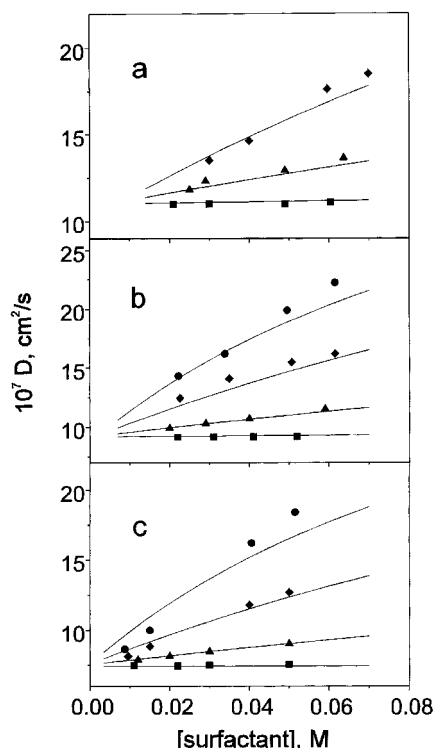


Figure 1. Translational diffusion coefficients D versus concentration of C_9 -D-TAB (a), C_{11} -D-TAB (b), and C_{13} -D-TAB (c) at various NaBr concentrations: 0.015 (●), 0.03 (◆), 0.08 (▲), and 0.32 M (■) at 25 °C. Lines are predicted values.

TABLE 1: Micellar Theoretical Interaction Parameters^a of the Surfactant + NaBr System at 25 °C

surfactant	n	α	A^b	$[\text{NaBr}]_{V=0},^c \text{ M}$
C_{13} -D-TAB	120	0.19	2.5	0.015–0.32
C_{11} -D-TAB	90	0.20	3	0.015–0.32
C_9 -D-TAB	70	0.20	3	0.03–0.32
CTAB ^d	120	0.22	15	0.05–0.10
TTAB ^d	90	0.22	7	0.15–0.20
DTAB ^e	70	0.14		0.01–0.20

^a Best-fit parameters according to directions given in SI2. ^b Hamaker coefficient in kT units. ^c This parameter denotes $[\text{NaBr}]$ which marks the boundary of the net repulsive region (i.e., where D vs $[\text{surfactant}]$ reaches zero slope). ^d Calculated using linear interaction theory (ref 11b). ^e Calculated using an approach of Stephen (ref 11d).

coefficient D of the C_n -D-TAB micelles in the studied $[\text{NaBr}]$ range (Figure 1). The procedure commonly used in such cases is based on the assumption that the interaction potential between micelles (in general, charged spheres) is given by hard sphere interaction plus the electrostatic potential (repulsive forces) and hydrophobic Van der Waals potential (attractive forces). Furthermore, one assumes that the surfactant concentrations under consideration do not exceed the value where nonlinear concentration dependence of D begins. The detailed directions to the method used are given in the Supporting Information (SI2). The values of micellar theoretical interaction parameters (i.e., micellar charge, $q = n\alpha$, where n is the aggregation number and α is the micellar ionization fraction, and the attractive Hamaker coefficient A) of the C_n -D-TAB–NaBr system at 25 °C that the experimental results best fit are summarized in Table 1 (solid lines in Figure 1). As seen, the micellar interaction data of cyclic acetal-type surfactants C_n -D-TAB correspond well to those found for C_n TAB.

For the studied C_n -D-TAB + NaBr systems, the α values lie in a narrow range: 0.19 for C_{13} -D-TAB + NaBr and 0.20 for both C_{11} -D-TAB + NaBr and C_9 -D-TAB + NaBr. The

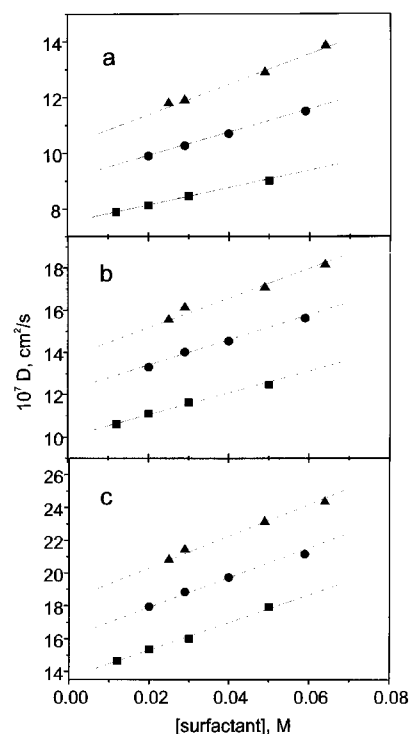


Figure 2. Translational diffusion coefficient D versus concentration of C_9 -D-TAB (▲), C_{11} -D-TAB (●), and C_{13} -D-TAB (■) at 25 (a), 35 (b), and 45 °C (c) and at a fixed 0.08 M $[\text{NaBr}]$.

TABLE 2: Micellar Aggregation Parameters of [(2-Alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides (C_n -D-TAB) at a Fixed 0.08 M $[\text{NaBr}]$

compound	temp °C	$D_0,^a 10^{-7} \text{ cm}^2 \text{ s}^{-1}$	$k_D,^a \text{ M}^{-1}$	$R_h,^b \text{ Å}$
C_{13} -D-TAB	25	7.56	3.95	32.3
	35	10.1	4.79	30.9
	45	13.7	6.26	28.4
C_{11} -D-TAB	25	9.20	4.51	26.5
	35	12.4	4.72	25.2
	45	16.7	4.94	23.3
C_9 -D-TAB	25	11.0	5.10	22.4
	35	14.9	4.71	21.1
	45	19.8	4.40	19.7

^a The mean diffusion coefficient of the micelles at the cmc, D_0 , has been calculated from $D = D_0(1 + k_D([\text{surfactant}] - \text{cmc}))$ where k_D (the slope) is the interaction coefficient. The cmc values are given in the Supporting Information (SI1). ^b The apparent mean hydrodynamic radius, R_h has been obtained from the Stokes–Einstein relation ($R_h = kT/6\pi\eta D_0$, where k is the Boltzmann constant, T is the absolute temperature, and η is the shear viscosity of the solvent).

ionization fraction for CTAB + NaBr and TTAB + NaBr is slightly higher, 0.22.^{11c,d,12b} Values of A (in units of kT at 25 °C) range from 2.5 for C_{13} -D-TAB to 3 for both C_{11} -D-TAB and C_9 -D-TAB + NaBr. Also listed in Table 1 are the values of $[\text{NaBr}]_{V=0}$, which define the range of NaBr concentrations for which the interaction remains net repulsive. A larger value of $[\text{NaBr}]_{V=0}$, observed for C_n -D-TAB + NaBr in comparison to C_n TAB + NaBr, indicates that over a larger range of NaBr concentrations the micelles of C_n -D-TAB may remain substantially minimum spheres.

According to the literature data,^{11c,d,12b} dimensions of spherical micelles are temperature dependent parameters. The translational diffusion coefficients of the C_n -D-TAB aqueous micelles at a fixed 0.08 M $[\text{NaBr}]$ have been determined at 25, 35, and 45 °C (Figure 2). The values of D_0 and k_D deduced from linear least-squares fit to the data of Figure 2 appear in Table 2. The R_h values listed in the final column indicate that the increase of

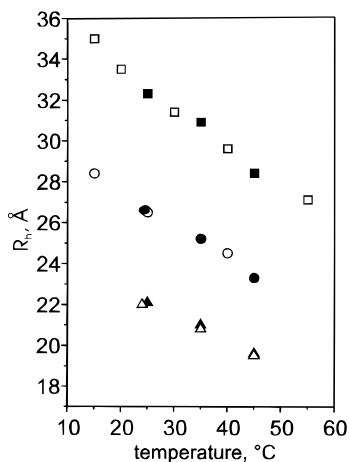


Figure 3. Plots of micellar hydrodynamic radius R_h versus temperature for C_9 -D-TAB (\blacktriangle), C_{11} -D-TAB (\bullet), C_{13} -D-TAB (\blacksquare), DTAB (\triangle), TTAB (\circ), and CTAB (\square) at a fixed 0.08 M [NaBr]. The R_h values were calculated according to footnote b of the Table 1.

the extrapolated diffusion coefficient is caused not only by the decrease of solvent viscosity and the increase of aggregate mobility in solution with increasing temperature but also by the decrease of aggregate dimensions. It is also significant that, for C_n -D-TAB ($C_n = C_9H_{19}$, $C_{11}H_{23}$, $C_{13}H_{27}$) at fixed temperature and ionic strength, the lines representing the micellar apparent diffusion coefficients are almost parallel to one another, indicating that the nature and strength of intermicellar interactions are similar for all homologues studied. Such a behavior has not been observed for alkyltrimethylammonium homologues.^{11d,e} The magnitude of the diffusivity intercept D_0 for the studied C_n -D-TAB surfactants increases with descending hydrophobic chain length (with increasing cmc). The parameter k_D , a measure of the intermicellar interactions under the studied conditions, shows little variation with the alkyl chain length, but increases strongly with increasing temperature. The relationship of micellar hydrodynamic radius R_h vs temperature for C_n -D-TAB and C_n TAB at a fixed 0.08 M [NaBr] is presented in Figure 3. Accordingly, a mild micellar growth can be observed, as measured by the mean R_h upon the temperature decrease. The presented R_h (temperature) curves introduce another confirming evidence for the size similarities between the C_{13} -D-TAB and CTAB, C_{11} -D-TAB and TTAB, as well as C_9 -D-TAB and DTAB micelles. Comparing DTAB at 24 °C, TTAB and CTAB at 25 °C, Briggs et al.^{12b} observed a uniform increase in the hydrodynamic radius of 3.16 Å per pair of additional methylene groups. In the present studies, the differences in R_h between micelles of C_9 -D-TAB, C_{11} -D-TAB, and C_{13} -D-TAB are 4.1 and 5.8 Å (see Table 2), respectively. The behavior observed for the 1,3-dioxolane surfactants may be associated, as in the case of C_n TAB surfactants,^{12b} with possible changes of micellar shape with the C_n length change.

Thus far, the equilibrium mixture of *cis*- and *trans*- C_n -D-TAB (*cis/trans* = 1.4) has been applied in the aggregation studies. In the following section we characterize the dependence of aggregate behavior upon the surfactant stereochemistry. It has been found for symmetrical 1,3-dioxolanes¹⁴ that the five-membered 1,3-dioxolane ring exists in the planar envelope configuration. The free energy differences ΔG^0 (*trans* \leftrightarrow *cis*) obtained for the diastereoisomeric *cis*- and *trans*-2,4-disubstituted-1,3-dioxolanes are relatively small—the energies themselves are slightly higher for the *trans* isomers than those for the *cis* ones independent of the bulk of the substituent at the C-2 atom of the 1,3-dioxolane ring. Burczyk et al.¹⁵ first described surface activities of pure *cis*- and *trans*-2-alkyl-4-

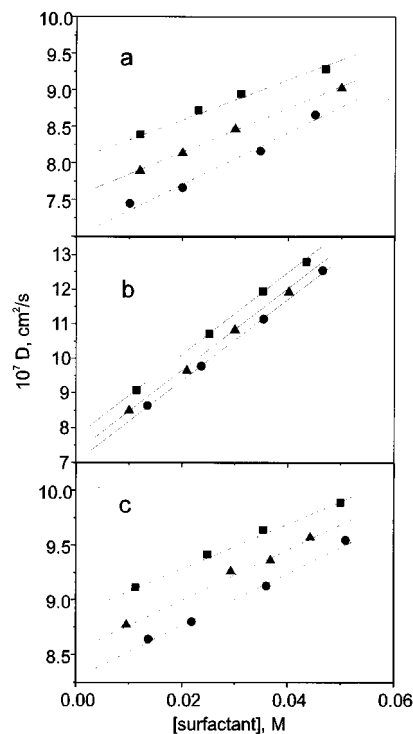


Figure 4. Translational diffusion coefficient D versus concentration of *cis* isomer (\blacksquare), *trans* isomer (\bullet), and *cis/trans* mixture, molar ratio 1.4 (\blacktriangle) of C_{13} -D-TAB (a), C_{13} -D-HEAD (b), and C_{13} -D-TEAB (c) at a fixed 0.08 M [NaBr] and at 25 °C.

TABLE 3: Micellar Aggregation Parameters of Pure *cis*- and *trans*-[(2-Tridecyl-1,3-dioxolan-4-yl)methyl]trialkylammonium Bromides and Their Diastereomeric Mixtures at a Fixed 0.08 M [NaBr] at 25 °C

compound	cmc, 10^{-4} M	SE, ^a kcal mol ⁻¹	R_h , Å	D_0 , 10^{-7} cm ² s ⁻¹	k_D , M ⁻¹
<i>cis</i> - C_{13} -D-TAB	1.13	13.8	30.0	8.14	3.11
<i>trans</i> - C_{13} -D-TAB	0.75	14.5	34.5	7.09	4.81
C_{13} -D-TAB	0.96		32.3	7.56	3.94
<i>cis</i> - C_{13} -D-HEAB	0.95	13.9	31.5	7.76	14.9
<i>trans</i> - C_{13} -D-HEAB	0.81	14.6	34.7	7.03	16.8
C_{13} -D-HEAB	0.87		33.4	7.32	15.7
<i>cis</i> - C_{13} -D-TEAB	0.76	14.1	27.5	8.88	2.01
<i>trans</i> - C_{13} -D-TEAB	0.65	15.2	29.5	8.28	2.78
C_{13} -D-TEAB	0.70		28.5	8.56	2.64

^a Strain energies (SE) comprise the energies corresponding to the deformations that are calculated in the course of the energy minimization.¹⁶

(hydroxymethyl)-1,3-dioxolanes as determined by either the efficiency of surface tension reduction or the standard free enthalpy of adsorption; they are not very different. Accordingly, both diastereoisomers with substituents at C-2 and C-4 carbon atoms occupy almost the same surface area, indicating small conformational differences. Furthermore, Jaeger et al.^{2c} have recently proved that there are no detectable differences in the energetics of compression for monolayer films cast from either *cis*- or *trans*-[(2-heptadecyl-2-methyl-1,3-dioxolan-4-yl)methyl]-trimethylammonium bromides. The monolayer characteristics of *cis* and *trans* isomers were identical, but slightly different than that of a 50:50 mixture of the two.

The diffusion coefficient dependence upon the surfactant concentration of pure *cis* and *trans* isomers of the selected surfactants (C_{13} -D-TAB, C_{13} -D-HEAB, and C_{13} -D-TEAB), as well as their diastereoisomeric mixtures (*cis/trans* = 1.4), is shown in Figure 4, while the micellar aggregation parameters are summarized in Table 3. Included values of the surfactant strain energy (SE)¹⁶ that describe the strain present in rings are

not very different within the selected *trans/cis* forms of surfactants, and only a small diastereoisomeric differentiation is introduced by the bulk of the head group substituent. As shown the aggregation behavior is slightly altered for the sets of pure diastereoisomers respective to the C₁₃-D-TAB, C₁₃-D-HEAB, and C₁₃-D-TEAB derivatives. The extrapolated diffusion coefficients found for the *cis* and *trans* isomers of C₁₃-D-TAB, C₁₃-D-HEAB, and C₁₃-D-TEAB differ approximately 15, 10, and 7%, respectively.

Evidently, both diastereoisomers of each surfactant series in the micellar state take up conformations in which there is little compression involving the tridecyl substituent, and furthermore the very flexible 1,3-dioxolane ring adjusts itself to the steric requirements of the methyltrialkylammonium head group. Thus, as the substituents around the quaternary nitrogen atom at the C-4 atom become larger, the differences between *cis* and *trans* isomers seem to disappear in respect to their micellar aggregation behavior.

Acknowledgment. This work was supported by grants of the Chemistry Department, Technical University of Wrocław, Poland.

Supporting Information Available: Values for cmc as a function of [NaBr] and temperature (SI1) and calculation of the Hamaker coefficient (*A*) and the micellar ionization fraction (α) (SI2) (6 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) Yamamura, S.; Nakamura, M.; Takeda, T. *J. Am. Oil Chem. Soc.* **1989**, *66*, 1165. (b) Ono, D.; Masuyama, A.; Nakatsuji, Y.; Okahara, M.; Yamamura, S.; Takeda, T. *J. Am. Oil Chem. Soc.* **1993**, *70*, 29.
- (2) (a) Jaeger, D. A.; Frey, M. R. *J. Org. Chem.* **1982**, *47*, 311. (b) Jaeger, D. A.; Jamrozik, J.; Golich, T. G.; Wegrzyn Clennan, M.; Mohebalian, J. *J. Am. Chem. Soc.* **1989**, *111*, 3001. (c) Jaeger, D. A.; Mohebalian, J.; Rose, P. L. *Langmuir* **1990**, *6*, 547.
- (3) (a) Sokołowski, A.; Piasecki, A.; Burczyk, B. *J. Am. Oil Chem. Soc.* **1992**, *69*, 633. (b) Wilk, K. A.; Bieniecki, A.; Burczyk, B.; Sokołowski, A. *J. Am. Oil Chem. Soc.* **1994**, *71*, 81.
- (4) (a) Martin, C. A.; Golich, T. G.; Jaeger, D. A. *J. Colloid Interface Sci.* **1984**, *99*, 561. (b) Jaeger, D. A.; Chou, P. K.; Bolikal, D.; Ok, D.; Kim, K. Y.; Huff, J. B.; Yi, E.; Porter, N. A. *J. Am. Chem. Soc.* **1988**, *110*, 5123.
- (5) (a) Wilk, K. A.; Bieniecki, A.; Matuszewska, B. *J. Phys. Org. Chem.* **1994**, *7*, 64. (b) Bieniecki, A.; Wilk, K. A. *J. Phys. Org. Chem.* **1995**, *8*, 71. (c) Bieniecki, A.; Matuszewska, B.; Wilk, K. A. *Pol. J. Chem.* **1995**, *69*, 1174.
- (6) Sokołowski, A.; Bieniecki, A.; Wilk, K. A.; Burczyk, B. *Colloids Surf.* **1995**, *98*, 73.
- (7) (a) Lianos, P.; Zana, R. *J. Colloid Interface Sci.* **1981**, *84*, 100. (b) van Os, N. M.; Haak, J. R.; Rupert, L. A. M. *Physico-chemical Properties of Selected Anionic, Cationic and Nonionic Surfactants*; Elsevier Science Publishers: Amsterdam, 1991. (c) Buckingham, S. A.; Garvey, C. J.; Warr, G. G. *J. Phys. Chem.* **1993**, *97*, 10236.
- (8) Attwood, D.; Elworthy, P. H.; Kayne, S. B. *J. Phys. Chem.* **1970**, *74*, 35.
- (9) (a) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951. (b) Malliaris, A.; Lang, J.; Zana, R. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 10929. (c) Warr, G. G.; Grieser, F.; Evans, D. F. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1829. (d) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675. (e) von Wandruszka, R. *Crit. Rev. Anal. Chem.* **1992**, *23*, 187.
- (10) (a) Chu, B. *Laser Light Scattering*; Academic Press: New York, 1974. (b) Berne, B. J.; Pecora, R. *Dynamic Light Scattering with Application to Chemistry, Biology and Physics*; Wiley: New York, 1976. (c) Pecora, R. *Dynamic Light Scattering, Applications of Photon Correlation Spectroscopy*; Plenum Press: New York, 1985.
- (11) (a) Corti, M.; Degiorgio, V. *Chem. Phys. Lett.* **1978**, *53*, 237. (b) Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1976**, *80*, 1075. (c) Nicoli, D. F.; Dorshow, R. B.; Bunton, C. A. *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1984; Vol. 1, p 455. (d) Dorshow, R. B.; Bunton, C. A.; Nicoli, D. F. *J. Phys. Chem.* **1983**, *87*, 1409. (e) Rohde, A.; Sackmann, E. *J. Phys. Chem.* **1980**, *84*, 1598.
- (12) (a) Corti, M.; Degiorgio, V. *J. Phys. Chem.* **1981**, *85*, 711. (b) Dorshow, R. B.; Briggs, J.; Bunton, C. A.; Nicoli, D. F. *J. Phys. Chem.* **1982**, *86*, 2388. (c) Athanassakis, V.; Moffatt, J. R.; Bunton, C. A.; Savelli, G.; Nicoli, D. F. *Chem. Phys. Lett.* **1985**, *115*, 467. (d) Biresaw, G.; McKenzie, D.; Bunton, C. A.; Nicoli, D. F. *J. Phys. Chem.* **1985**, *89*, 5144. (e) Ortega, F.; Bacaloglu, R.; McKenzie, D. C.; Bunton, C. A.; Nicoli, D. F. *J. Phys. Chem.* **1990**, *94*, 501.
- (13) Kratochvil, J. P. *J. Colloid Interface Sci.* **1980**, *75*, 271.
- (14) (a) Willy, W. E.; Binch, G.; Eliel, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 5392. (b) Pihleja, W. E. *Suom. Kemistil. B.* **1970**, *43*, 143. (c) Altona, C.; Bugs, H. R.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 973.
- (15) Burczyk, B.; Piasecki, A.; Weclawski, L. *J. Phys. Chem.* **1985**, *89*, 1030.
- (16) (a) Burket, U.; Allinger, N. L. *Molecular Mechanics*, ACS Monograph 177; American Chemical Society: Washington, DC, 1982. (b) All calculations of the strain energy (SE) were performed with HyperChem version 4.0. Geometry optimization was performed using the MM+ force field with the energy convergence criterion 0.01 kcal/mol, and then semiempirical calculations were carried out using the AM3 method.