Synthesis and Hydrolysis of Chemodegradable Cationic Surfactants Containing the 1,3-Dioxolane Moiety

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In acid-catalyzed reactions of long-chain aliphatic aldehydes (Ia–d where a = *n*-C_7H_{15}; b = *n*-C_9H_{19}; c = *n*-$C_{11}H_{23}$; d = *n*-$C_{13}H_{27}$), and tridecan-7-on (Ie) with 3-chloro-1,2-propane-diol, 2-alkyl- and 2,2-dihexyl-4-chloromethyl-1,3-dioxolanes (IIa–e) were obtained. They were reacted with anhydrous dimethylamine to obtain, respectively, 2-alkyl- and [(2,2-dihexyl-1,3-dioxolan-4-yl)methyl]dimethylamines (IIIa–e), which were quaternized with methyl bromide to obtain the desired ammonium bromides (IVa–e). The structure and purity of the compounds was proved by mass spectrometry and proton nuclear magnetic resonance spectroscopy. Additionally, [(2-methyl-1,3-dioxolan-4-yl)methyl] trimethylammonium bromide and [(2,2-dimethyl-1,3-dioxolan-4-yl)-methyl]trimethylammonium bromide were synthesized as nonaggregating standards. Hydrolysis reactions of the synthesized ammonium bromides were performed by 0.1 M hydrochloric acid in 1:1 (vol/vol) 1,4-dioxane–water mixtures at 50, 60 and 70°C. Rate constants of hydrolysis reactions were determined by observing carbonyl group formation at 280 nm. The hydrolytic reactivity of the studied surfactants (IVa–c,e) was determined under unaggregated conditions. Compound IVd showed decreased reactivity. The length of the 2-alkyl group has a minor effect on rate constant values. The influence of various substituents at the C-4 atom of the 2-nonyl-1,3-dioxolan-4-yl derivatives on rate constants was also investigated.

KEY WORDS: [(2-Alkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides, [(2,2-dihexyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromide, chemodegradable acetal-type cationic surfactants, kinetic and thermodynamic parameters of 1,3-dioxolane ring hydrolysis.

Chemodegradable surfactants [for explanation of the term, see Ref. (1)] have recently generated increased interest. The reason for this is their susceptibility to chemical reactions that decompose them into nonsurface-active, environmentally acceptable intermediates. Among the functional groups present in these molecules, acetal grouping is the most common. We were the first to use 2-alkyl-4-hydroxymethyl-1,3-dioxolanes as hydrophobic intermediates in the synthesis of nonionic, chemodegradable surfactants (2,3). This cyclic acetal moiety was later used in surfactant synthesis by Jaeger and Frey (4), Piasecki (5) and Takeda and co-workers (6–8).

Acetal-type surfactants can undergo hydrolysis, which splits them into aldehydes/ketones and alcohols (polyols). The mechanism and kinetics of acetal hydrolysis have been investigated in detail (9,10). However, for acetal-type surfactants that bear different polar and hydrocarbon groups, it is of interest to elucidate the impact of varying these substituents on their stability. Hydrolysis of 2-alkyl-4-hydroxymethyl-1,3-dioxolanes with short alkyl chains at the C-2 atom has been investigated by Sokołowski and Burczyk (11). Later, Piasecki (12) investigated the influence of ether-oxygen in the *β*-position with respect to the acetal grouping in 2-[2-(*ω*-hydroxyalkoxy)alkyl]-substituted 1,3-dioxolanes and 1,3-dioxanes. Recently, Jaeger *et al.* (13) investigated hydrolysis of ketal-based [(2,2-dialkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides, and Ono *et al.* (8) presented results of hydrolysis of sodium-2-[carboxylato-(alkyl)]-2-methyl-4-alkoxymethyl-1,3-dioxolanes.

In this paper, we wish to present our results of synthesis and hydrolysis investigations of chemodegradable cationic surfactants that bear the 1,3-dioxolane moiety in the hydrophobic group (Fig. 1). Thus, [(2-alkyl-1,3-dioxolan-4-yl)-methyl]trimethylammonium bromides contain, at the C-2 carbon, alkyl groups varying in hydrophobicity, including the (2,2-dihexyl-1,3-dioxolan-4-yl)-derivative (IVe) for comparison to IVb. (2-Methyl-1,3-dioxolan-4-yl)- and [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides were applied as nonaggregating standards. Additionally, some 2-nonyl-substituted hydrophobic standards—containing at the C-4 carbon various nucleophilic substituents, such as CH_2OH, CH_3, H and CH_2Cl—were employed for kinetic purposes.

The main purpose of the present work was mainly to study the influence of several substituents at the C-2 and C-4 positions of the 1,3-dioxolane ring upon ring hydrolysis in homogeneous medium by a kinetic method and to determine some kinetic and thermodynamic parameters of this reaction. The results may throw some light on the stability of the surfactants under study, which is important from a practical point of view.

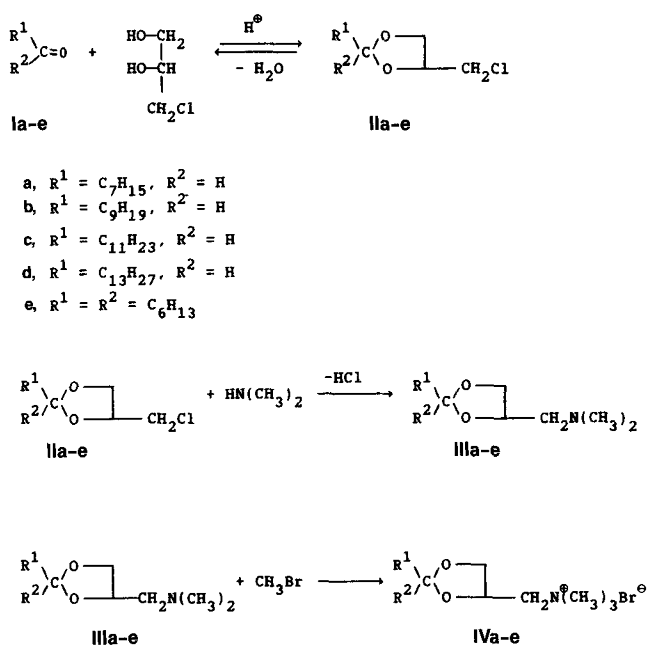

FIG. 1. Synthesis of surface-active (2-alkyl-1,3-dioxolan-4-yl)- and [(2,2-dihexyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides.

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EXPERIMENTAL PROCEDURES

Apparatus. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Tesla BS 587A apparatus (Tesla Works, Brno, Czech Republic) at 80 MHz. Tetramethylsilane (TMS) was used as an internal standard and $CDCl_3$ as a solvent.

Chromatographic analyses were carried out with a Hewlett-Packard HP-5890 Series I apparatus equipped with a mass selective detector (HP-5971A) and a computer (Hewlett-Packard, Palo Alto, CA). A glass capillary column (12 m long and 0.0002 m in diameter) containing a crosslinked methyl silicone gum was used.

Elemental analysis was performed on a Perkin-Elmer CHN Analyzer (Norwalk, CT). Melting points and boiling temperatures are uncorrected. Rates of acetal-type surfactant hydrolysis were determined in a Hewlett-Packard HP 8452A recording spectrophotometer, equipped with a thermostat.

Materials. All starting materials were of commercial grade and were usually distilled before use.

Synthesis of 2-alkyl- and 2,2-dihexyl-4-chloromethyl-1,3-dioxolanes (**IIa–e**). These compounds were synthesized according to the procedure described by Hannig and Wilhelm (14): The 0.3 mol of aliphatic aldehyde or ketone (**Ia–e**), 0.3 mol of 3-chloro-1,2-propanediol, 0.5 g *p*-toluenesulfonic acid and 250 mL of toluene were placed in a round-bottomed flask equipped with a stirrer, thermometer and Dean-Stark adapter connected to a reflux condenser. The mixture was stirred and refluxed until all reaction water was collected in the adapter. The reaction mixture was then cooled to room temperature and washed once with 100 mL sodium carbonate solution (2% by wt) and twice with 50-mL portions of water. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated *in vacuo*, and the crude product was purified by fractional distillation under reduced pressure. The characteristics of compounds **IIa–e** are presented in Table 1. Similarly, the following compounds were obtained as colorless liquids: 2-methyl-4-chloromethyl-1,3-dioxolane yield 31%, b.p. 152°C, diastereomer ratio (*trans:cis*): 1.46:1, ^1H NMR [δ: 1.1(*m*, 3H, CH_3); 2.6–4.3 (*m*, 6H)][a] and 2,2-dimethyl-4-chloromethyl-1,3-dioxolane yield 23%, b.p. 156°C, ^1H NMR [δ: 1.1(*m*, 6H, CH_3); 2.6–3.6(*m*, 5H)].

Synthesis of 2-alkyl- and [(2,2-dihexyl-1,3-dioxolan-4-yl)methyl]dimethyl amines (**IIIa–e**). The 0.15 mol of 2-alkyl- or 2,2-dihexyl-4-chloromethyl-1,3-dioxolane (**IIa–e**), 0.75 mol anhydrous dimethylamine and 35 mL dry benzene were heated in a sealed tube at 125°C for 30 h. The precipitate was filtered off and washed twice with benzene. The organic solvent was evaporated under reduced pressure, and the residue was subjected to fractional distillation. The yield of products was in the range of 46–70 mol%. The purity and structure of the final tertiary amine was confirmed by gas–liquid chromatography (GLC) and ^1H NMR spectra (Table 2). Additionally, the following 1,3-dioxolane derivatives were obtained as colorless liquids: [(2-methyl-1,3-dioxolan-4-yl)methyl]dimethyl amine yield 59.8%, b.p. 158–162°C, ^1H NMR [δ: 1.04(*t*, 3H, CH_3); 1.98(*s*, 3H, $N(CH_3)_2$); 2.54–4.14(*m*, 6H)] and [2,2-dimethyl-1,3-dioxolan-4-yl)methyl]dimethyl amine yield 58.7%, b.p. 164–168°C, ^1H NMR [δ: 1.05(*t*, 3H, CH_3); 2.00(*s*, 6H, $N(CH_3)_2$); 2.55-3.23(*m*, 5H)].

*Synthesis of (2-alkyl-1,3-dioxolan-4-yl)- and [(2,2-dialkyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromides (***IVa–e***).* The 0.06 mol of 2-alkyl- or [(2,2-dihexyl-1,3-dioxolan-4-yl)methyl]dimethyl amine (**IIIa–e**), 18 mL dry ethyl ether and 0.4 mol methyl bromide were stirred in a round-bottomed flask at room temperature for 12 h. The reactions were followed by thin-layer chromatography. The solvent was evaporated, and the residue was recrystallized several times from acetone/ethyl ether as a white crystalline powder. The yield of products was in the range of 54–73 mol%. Their melting points are listed in Table 3. The purity and structure of the final surfactants were confirmed by elemental analyses. Similarly, (2-methyl-1,3-dioxolan-4-yl)- and [(2,2-dimethyl-1,3-dioxolan-4-yl)-methyl] trimethylammonium bromides were obtained, *i.e.*, 2-methyl-derivative, (yield 91.1%, melting point 164-166°C) and 2,2-dimethyl-derivative, yield 70.0%, melting point 195-197°C [lit.(13) m.p. 196-198°C].

TABLE 1

Characteristics of 2-Alkyl and (2,2-Dihexyl-1,3-Dioxolan-4-yl) Methyl Chlorides (IIa–e)

Compound	Diastereoisomer ratio *cis:trans*	Yield (mol%)	b.p. (°C/mm Hg)	^1H NMR[a] δ (ppm)	MS (70 eV) *m/e*
IIa	1.35:1	82.0	98–109/3.5	0.70 (*t*, 3H, CH_3); 1.0–1.4 (*m*, 12H, CH_2); 2.66–4.10 (*m*, 6H).	221 (M, 8.18%), 219 (M, 3.27), 185 (7.27), 123 (30.9), 121 (100), 111 (9.09), 93 (6.36), 75 (7.27), 69 (11.27), 57 (16.73), 55 (9.64)
IIb	1.30:1	67.1	112–114/4	0.75 (*t*, 3H, CH_3); 1.0–1.3 (*m*, 16, CH_2); 2.64–4.10 (*m*, 6H).	247 (M−1, 0.55%), 199 (0.30), 147 (0.48), 124 (1.25), 123 (29.90), 122 (4.10), 121 (100), 93 (2.80), 75 (5.65), 57 (5.09), 55 (4.13), 43 (4.38), 41 (5.92)
IIc	1.40:1	65.3	126–129/4	0.72 (*t*, 3H, CH_3); 1.0–1.35 (*m*, 20H, CH_2); 2.65–4.15 (*m*, 6H).	266 (M, 0.06), 265 (M−1, 0.22), 217 (0.27), 147 (0.51), 124 (1.28), 123 (30.1), 122 (4.12), 121 (100), 93 (2.62) 75 (5.25), 57 (5.10), 55 (4.03), 43 (4.44), 41 (5.26)
IId	1.49:1	64.6	149–154/4	0.70 (*t*, 3H, CH_3); 1.0–1.3 (*m*, 24H, CH_2); 2.76–4.20 (*m*, 6H).	304 (M, 0.04%), 303 (M−1, 0.14), 255 (0.16), 147 (0.53), 124 (1.25), 123 (30.7), 122 (4.05), 121 (100), 93 (2.10) 75 (4.01), 57 (5.08), 55 (3.93), 43 (4.69), 41 (5.00)
IIe	—	92.0	124–125/4	0.70 (*t*, 6H, CH_3); 1.0–1.4 (*m*, 20H, CH_2); 3.0–4.15 (*m*, 5H).	241 (0.72%), 207 (30.9), 205 (100), 149 (1.9), 113 (10.03), 85 (9.25), 76 (2.72), 75 (7.72), 57 (5.07), 55 (7.34), 43 (16.3), 41 (10.05)

[a]Chemical shifts downfield from trimethylsilane. Abbreviations: ^1H NMR, proton nuclear magnetic resonance; MS, mass spectra.

TABLE 2

Characteristics of (2-Alkyl-1,3-Dioxolan-4-yl) and [(2,2-Dihexyl-1,3-Diolxsolan-4-yl) Methyl] Dimethyl Amines (IIIa–e)[a]

Compound	Yield (mol%)	b.p. (°C/mm Hg)	^{1}H NMR δ (ppm)
IIIa	68.0	106–110/4	0.85 (*t*, 3H, CH_3); 1.1 (*m*, 12H, CH_2); 1.82 [*s*, 6H, $N(CH_3)_2$]; 2.58–4.10 (*m*, 6H)
IIIb	69.8	119–122/4	0.61 (*t*, 3H, CH_3); 0.93 (*m*, 16H, CH_2); 1.73 [*s*, 6H, $N(CH_3)_2$]; 2.58–4.10 (*m*, 6H)
IIIc	52.8	137–140/4	0.66 (*t*, 3H, CH_3); 0.99 (*m*, 20H, CH_2); 1.80 [*s*, 6H, $N(CH_3)_2$]; 2.60–4.15 (*m*, 6H)
IIId	46.2	158–161/4	0.88 (*t*, 3H, CH_3); 1.26 (*m*, 24H, CH_2); 2.28 [*s*, 6H, $N(CH_3)_2$]; 2.72–4.40 (*m*, 6H)
IIIe	65.7	156–159/4	0.68 (*t*, 6H, CH_3); 0.98 (*m*, 20H, CH_2); 1.80 (*s*, 6H, $N(CH_3)_2$]; 2.60–3.60 (*m*, 5H)

[a]See Table 1 for abbreviations.

TABLE 3

Characteristics of (2-Alkyl-1,3-Dioxolan-4-yl)- and [(2,2-Dihexyl-1,3-Diolxolan-4-yl) Methyl]trimethylammonium Bromides (IVa–e)

Compound	Yield (mol%)	m.p. (°C)	Molecular formula	Molecular analysis found (calcd.) % C	H	N	Br
IVa	54.4	paste	$C_{14}H_{30}O_2N$ Br	51.7 (51.9)	9.4 (9.3)	4.2 (4.3)	24.5 (24.7)
IVb	65.4	110–112	$C_{16}H_{34}O_2N$ Br	54.4 (54.5)	9.8 (9.7)	3.9 (4.0)	22.6 (22.7)
IVc	71.6	139–141	$C_{18}H_{38}O_2N$ Br	56.6 (56.8)	10.1 (10.0)	3.7 (3.7)	21.0 (21.1)
IVd	73.3	166–167	$C_{20}H_{42}O_2N$ Br	58.7 (58.8)	10.5 (10.3)	3.35 (3.4)	19.4 (19.6)
IVe	70.0	143–147	$C_{19}H_{40}O_2N$ Br	58.0 (57.9)	10.4 (10.2)	3.5 (3.6)	20.15 (20.3)

Synthesis of 2-nonyl-1,3-dioxolane and 2-nonyl-4-methyl-1,3-dioxolane. The 1,3-dioxolane derivatives were obtained according to procedures described earlier (15): The 2-nonyl-1,3-dioxolane and 2-nonyl-4-methyl-1,3-dioxolane were obtained from decyl aldehyde and ethylene glycol/1,2-propanediol with yields of 93.3 and 96.7%, respectively.

Kinetic measurements. Hydrolyses of the 1,3-dioxolane derivatives by 0.1 M HCl were carried out in 1,4-dioxane–water (1:1) mixtures at 50, 60 and 70°C. The reaction rates were followed by observing carbonyl group formation at 280 nm: The 20 μL of 1 M solution of the studied compound in methanol was transferred to a 1.0-cm quartz cell placed in the thermostated cell compartment of the spectrophotometer after addition of 2 mL of 0.1 M HCl in 1,4-dioxane-H_2O. Addition of 1,3-dioxolane derivative marks the zero time of reaction. The absorbance (A) at λ 280 and 350 nm was measured as a function of time (t) against a blank similarly prepared without HCl. From the absorbance time curves, the initial slope (dA/dt), initial rates, rate constants and thermodynamic activation parameters were calculated by a standard method (16).

RESULTS AND DISCUSSION

The structure of the products was corroborated by mass spectrum (MS) and ^{1}H NMR spectra. The chloromethyl derivatives gave a common characteristic fragmentation pattern through α-cleavages to the ring. The molecular ion peak is not present. The parent ion peak usually is due to $C_4H_7O_2Cl^+$ (*m/z* 121, 123). Some common ions that are considered to arise because of ring cleavage are at *m/z* 77, 75 ($C_3H_4Cl^+$), 57 ($C_3H_5O^+$), 55 ($C_4H_7^+$), 43 ($C_2H_3O^+$), 41 ($C_3H_5^+$). GLC analysis revealed that, as expected, the acetal-type surfactants were mixtures of diastereoisomers. The chromatograms of compounds **IIa–d** indicate the presence of two substances with different retention times. In each of the four acetals, **IIa–d**, which differ in the 2-alkyl length, the one with the longer retention time occurs in excess. The ratio of the *trans/cis* isomers exceeds the 1.3:1 ratio. The chemical composition of the products was confirmed by the ^{1}H NMR spectra. Quaternization of compounds **IIIa–e** was performed in nearly quantitative yields. No attempt was made to separate the diastereoisomeric acetal precursors of **IVa–d**.

Generally, the derivatives of 1,3-dioxolanes undergo hydrolysis in aqueous acidic solutions, which is an opposite process to the formation of the acetals and ketals from the respective aldehydes or ketones and 1,2-diols presented elsewhere (9). According to the literature, the specific acid hydrolyses of the 1,3-dioxolanes proceed with a rate-determining step involving cleavage of the protonated acetal or ketal grouping (16,17). The surfactants under consideration, along with the assumed standards, appear to be useful for studies of the ring substituent preferences *vs.* surfactant stability.

The rate constants of hydrolysis of all studied compounds containing the 1,3- dioxolane moiety, determined in 0.1 M hydrochloric acid at three temperatures (50, 60

TABLE 4

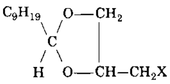
Rate Constants and Thermodynamic Parameters for Hydrolysis[a] of [(2-Alkyl-1,3-Dioxolan-4-yl)- and (2,2-Dihexyl-1,3-Dioxolan-4-yl) Methyl]trimethylammonium Bromides (IVa–e)

			k_ψ 10^4 (1/s)					
Compound	R^1	R^2	50	60	70	E_α (kJ/mol)	ΔH_α^b (kJ/mol)	$-\Delta S_\alpha^b$ (J/mol K)
IVa	n-C_7H_{15}	H	0.234	0.658	1.740	92	90	72
IVb	n-C_9H_{19}	H	0.355	0.956	2.284	86	83	73
IVc	n-$C_{11}H_{23}$	H	0.400	1.018	2.470	84	81	69
IVd[c]	n-$C_{13}H_{27}$	H	0.275	0.734	1.901	91	88	59
IVe	n-C_6H_{13}	n-C_6H_{13}	1.684	3.321	8.100	81	78	76
	CH_3	H	0.297	1.146	2.557	102	99	25
	CH_3	CH_3	4.160	11.74	28.16	97	95	17

[a] [HCl] = 0.1 M, 1:1 (vol/vol) 1,4-dioxane–water.
[b] Values calculated for the temperature of 50°C.
[c] Performed above critical micelle concentration.

TABLE 5

Rate Constants and Thermodynamic Parameters for the Hydrolysis[a] of (2-Nonyl-1,3-Dioxolan-4-yl)-Derivatives as Hydrophobic Standards:



	k_ψ 10^4 (1/s)					
X	50	60	70°C	E_α (kJ/mol)	ΔH_α^b (kJ/mol)	$-\Delta S_\alpha^b$ (J/mol K)
CH_2OH[c]	738.0		7056.0			
H	30.0	66.7	161.5	86	83	37
CH_3	25.9	58.5	130.2	82	79	49
CH_2Cl	0.85	2.56	4.51	85	82	68

[a] [HCl] = 0.1, 1:1 (vol/vol) 1,4-dioxane–water.
[b] Values calculated for the temperatue of 50°C.
[c] Approximated according to Reference 11.

and 70°C) in 1:1 (vol/vol) 1,4-dioxane–water mixtures, are collected in Tables 4 and 5. The observed pseudo-first-order rate constant, k_ψ, introduces a weighted average of rate constants for *trans/cis* diastereoisomers in the case of acetal-type derivatives. According to recent literature findings (13), the hydrolytic reactivities of aggregated ketal-based chemodegradable surfactants are much smaller than those of unaggregated forms, which suggests that the microenvironmental effects of surfactant-organized structures cause electrostatic depletion of hydronium ion and lower polarity of the Stern-layer reaction volume. The hydrolytic reactivity of the studied chemodegradable surfactants (**IVa–e**) represents the unaggregated system except for surfactant **IVd**, for which a reduced reactivity is observed. The critical micelle concentration values of 2-undecyl, 2,2-dihexyl and 2-tridecyl-substituted surfactants in 1,4- dioxane–water solutions, determined at 70°C by a conductivity method, were 0.0021, 0.0023 and 0.0005 M, respectively.

The rates of hydrolysis for a series of dioxolane ring-containing acetal type surfactants do not vary much with the length of the 2-alkyl group (Table 4), which is in accord with the kinetic findings observed for shorter-than-C_6H_{13} alkyl groups at C-2 of the 1,3-dioxolane ring (11,18–20). The stability of all acetal-type surfactants in relation to the assumed standard, *i.e.*, [(2-methyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromide, is similar. The hydrolytic reactivity of the ketal-type surfactant **IVe** and the corresponding standard [(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]trimethylammonium bromide are substantially higher than that of the surfactant **IVb**.

Additionally, we attempted to compare the stabilities of the synthesized surfactants **IVa–e** with the stability of the selected hydrophobic standards, namely 1,3-dioxolane derivatives containing the 2-nonyl substituent at the C-2 atom and other than $CH_2N(CH_3)_3Br$ substituents at the C-4 carbon of the dioxolane ring (Table 5). Generally, the hydrophobic standards hydrolyze at least two orders of magnitude faster than all examined ammonium salts. The hydroxy methyl group in position 4 of the dioxolane ring of the 2-nonyl derivatives, compared to the hydrogen atom, causes the most significant decrease of the ring stability and, on the other hand, the 4-methyltrimethylammonium group stabilizes the 1,3-dioxolane ring to the highest extent among the studied acetals. This electron-withdrawing cationic group may easily create the electron deficit inside the dioxolane ring and form a partial positive charge, further protecting it against both protonation of the ring at the O-1 and O-3 atoms and consequently against rapid cleavage of the protonated acetal or ketal grouping.

Tables 4 and 5 give the least-square values of the parameters of the Arrhenius equation for the studied hydronium ion-catalyzed hydrolyses. The Arrhenius equation was satisfactorily obeyed in all cases. The activation energy values are similar for all the examined compounds, with no substituent preferences at C-2, as well as at C-4. This means that the chemodegradability mechanism of the 1,3-dioxolane ring does not depend on the kind and position of the ring substituents. The activation entropies decrease both with the alkyl chain size at C-2 and with the bulk of the C-4 substituents, which is reflected by the increased transition-state packing of the studied hydrolyses.

The obtained kinetic findings for the chemodegradability of the studied systems indicate that the synthesized quaternary ammonium bromides containing the 1,3-dioxolane grouping, **IVa–e**, may constitute a surfactant class of technical and economic importance. They can be satisfactorily applied in synthetic organic chemistry as components and convenient stabilizing agents of environmentally acceptable reaction media as micelles and microemulsions.

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