

Chromium(VI) Oxidation of Alkanol Components of Sodium Dodecyl Sulfate Reverse Micelles

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Oxidation with potassium dichromate in perchloric acid medium of the alkanols 1-butanol, 1-hexanol, and 1-octanol, components of sodium dodecyl sulfate reverse micelles in alkanols, has been studied. The reaction rate is first-order with respect to Cr(VI) and depends linearly on the HClO₄ concentration in the aqueous phase, but the reaction rate decreases with the amount of alcohol in the reverse micelles. To explain the kinetic results it is necessary to consider the intermicellar exchange of the reactants, which could depend on the thickness of the layer where the surfactant and the alcohol are located.

Introduction

Reverse micelles, stable isotropic liquids in the L₂ phase of an oil/surfactant/water ternary system, strongly affect chemical reactions and enzymatic reactivity.¹ In the case of reverse micelles formed by ionic surfactants, this effect could be related to the different structure of the water located in the droplet because of the highly charged interior surface of the reverse micelle.²⁻⁷ Different chemical reactions in reverse micelles systems formed by sodium bis(2-ethylhexyl) sulfosuccinate (AOT) have been extensively studied,⁸⁻¹¹ in particular enzyme-catalyzed reactions where the enzyme is stabilized inside the water pool.¹²⁻¹⁴ Reverse micelles in alkanols have recently been used in these kinetic studies.^{15,16} The influence of reverse micelles mainly depends on the ratio $w_0 = [\text{H}_2\text{O}]/[\text{surfactant}]$,¹⁷ and although different theoretical approaches have been developed,¹⁴ results are not all well explained quantitatively.

In this paper we show the influence of SDS reverse micelles in 1-butanol, 1-hexanol, and 1-octanol on the oxidation of the corresponding alcohol with Cr(VI) in perchloric acid medium. To explain the results, it is necessary to consider the exchange of the reactants between the micelles.¹⁸⁻²⁰ This exchange is a function of the thickness of the layer where the alcohol and the surfactant are located according to our conductivity measurements.

The thickness of the layer where the surfactant and the alcohol are located was obtained from fluorescence quenching measurements using 4-(1-pyrenyl)butyric acid as probe and *N*-cetylpyridinium chloride as static quencher.

Materials and Methods

Materials. Sodium dodecyl sulfate (SDS (Sigma), 1-butanol (Merck), 1-hexanol (Sigma), 1-octanol (Merck), potassium dichromate (Sigma), perchloric acid (Merck), sodium hydroxide volumetric standard solutions (Aldrich), and the fluorescent probe 4-(1-pyrenyl)butyric acid (PBA, Aldrich) were of the highest available purity and were used without further purification. The static quencher *N*-cetylpyridinium chloride²¹ (CPyC, Merck) was recrystallized from MeOH/diethyl ether mixtures.

Potassium dichromate in perchloric acid stock solutions was prepared with a K₂CrO₄ concentration of 6 × 10⁻³ M and HClO₄ concentrations in a range 1.5-4.5 M.

The probe, PBA, is insoluble in water and soluble in organic solvents, so it was used in [NaOH] = 0.01 M in order to attach it into the micellar interface of the reverse micelles.

Methods. All the kinetic measurements were carried out at 25 ± 0.1 °C using a Hewlett-Packard 8452A diode array spectrophotometer. The reaction rates were studied by following the absorbance decrease at 350 nm corresponding to a Cr(VI) absorption maximum. Reaction mixtures have been prepared by the addition of 0.1 mL of the K₂CrO₄ stock solutions in perchloric acid to 2.9 mL of the reverse micelles solution and shaking vigorously until a transparent solution was obtained. The initial

oxidant concentration was 2 × 10⁻⁴ M, which because of the high effective H⁺ concentration in all the experiments can be considered to be in the chromic acid form.²²

Pseudo-first-order rate constants were estimated by Marquardt's algorithm from a Hewlett-Packard 9000 computer connected to the spectrophotometer. The standard deviation of the pseudo-first-order rate constants is below 0.5% in all the experiments. In these measurements the analytical concentration of the probe and the quencher are in a ranges 1 × 10⁻⁶-5 × 10⁻⁶ M and 0.001-0.01 M, respectively.

Fluorescence quenching measurements have been carried out using a Perkin-Elmer spectrofluorimeter LS-5B at 25 ± 0.1 °C. Probe excitation was performed at 340 nm, and the micellar aggregation numbers and water pool radii were determined by measuring the probe fluorescence intensity in the presence and in the absence of quencher, at the fourth peak of the emission spectra (398 nm).

The specific conductivities were measured at 25 ± 0.1 °C using a CRISON 525 conductimeter.

Results

Fluorescence Quenching Measurements. The theoretical

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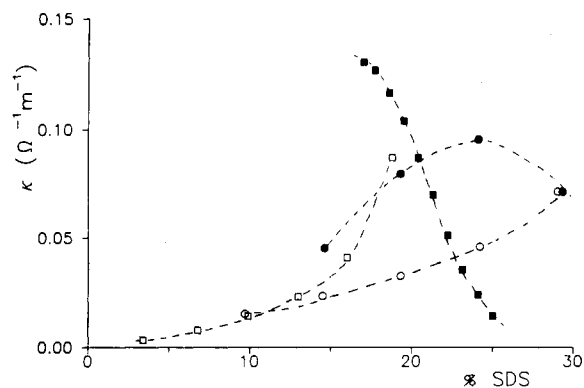


Figure 1. Specific conductivities versus the amount of surfactant for the SDS reverse micelles in 1-hexanol (O, wt % H₂O = 17.8; ●, wt % 1-HexOH = 53.2; □, H₂O/SDS molar ratio = 25.8; ■, SDS/1-HexOH molar ratio = 0.136).

treatment is based one developed by Turro and Yekta,²³ which considers both probe and quencher as solubilized into the micelles and distributed by Poisson's statistics.^{24,25} In the case of an immobile and static quencher,²¹ the ratio of fluorescence intensities in the absence (I_0) and in the presence (I) of quencher is given by

$$\ln(I_0/I) = \langle n \rangle \quad (1)$$

where $\langle n \rangle$ is the average occupation number. In the case of the reverse micelles,²⁶ where probe and quencher are solubilized in the droplet surface, the mean occupation number is given by the number of quencher molecules in the water pool ($\langle n \rangle$)

$$\langle n \rangle = \frac{[\bar{Q}]N_A}{n_{wp}} \quad (2)$$

where $[\bar{Q}]$ is the quencher concentration given in terms of liters of aqueous phase, N_A is Avogadro's number, and n_{wp} is the number of water pools per liter of aqueous phase in the micellar system. The fluorescence results using the probe/quencher system, PBA/CPyC, in the SDS reverse micelles in alkanols fit the theoretical treatment very well as reported.²⁷ From the value of n_{wp} it is possible to calculate the water pool radius and the mean micellar aggregation number by using spherical symmetry.

The micellar aggregation number and water pool radius values for the SDS reverse micelles in 1-butanol, 1-hexanol, and 1-octanol, obtained from fluorescence quencher measurements are given in Table I. Aggregation number and water pool radius are mainly determined by the amount of surfactant and water respectively, but the water pool radius varies with the $[H_2O]/[surfactant]$ and $[surfactant]/[alcohol]$ ratios as can be seen in Table I. The results obtained for the SDS reverse micelles in 1-hexanol were extensively studied in a previous publication.²⁷

Considering the reverse micellar solution as divided into spherical cells with a radius r_c , each containing a spherical water pool with radius r_{wp} , the molecules of surfactant given by the aggregation number and the corresponding amount of alcohol, the thickness of the layer where surfactant and alcohol are located is given by $r_c - r_{wp}$. It is interesting to point out that these systems are authentic microemulsions where, being part of the interface, the alcohol acts as a cosurfactant and not as a dispersant medium.²⁷

Conductivity Measurements. Specific conductivity measurements for SDS reverse micelles in 1-hexanol are given in Figure 1. The specific conductivity increases with the surfactant and the water contents in the mixture, and for the systems where an increase in surfactant is related to a decrease in the water content, the conductivity passes through a maximum value with the surfactant concentration. The same results are obtained for the SDS

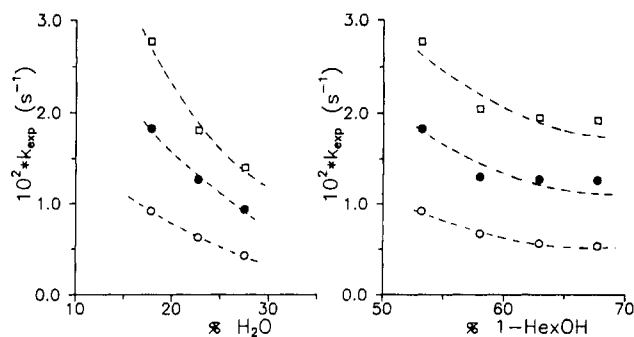


Figure 2. Variation of the pseudo-first-order rate constants for the oxidation of 1-hexanol by Cr(VI) at different HClO₄ analytical concentrations with the amount of water at a fixed ROH percentage 53.2% (A, left) and the alcohol at a fixed H₂O percentage 17.8% (B, right) in the SDS reverse micelles in 1-hexanol, (O, [HClO₄] = 0.05 M; ●, [HClO₄] = 0.10 M; □, [HClO₄] = 0.15 M).

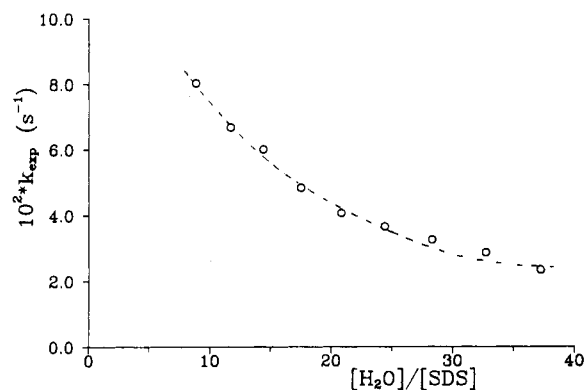


Figure 3. Variation of the pseudo-first-order rate constant for the oxidation of 1-hexanol by Cr(VI) at a fixed analytical concentration of HClO₄ 0.05 M, with the H₂O/surfactant molar ratio at a fixed SDS/1-HexOH molar ratio 0.136.

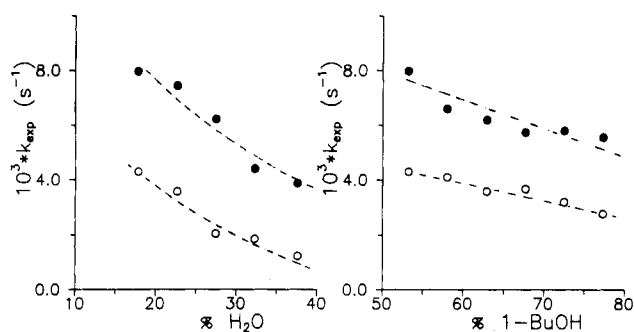


Figure 4. Variation of the pseudo-first-order rate constants for the oxidation of 1-butanol by Cr(VI) at different HClO₄ analytical concentrations with the amount of water at a fixed ROH percentage 53.2% (A, left) and the alcohol at a fixed H₂O percentage 17.8% (B, right) in the SDS reverse micelles in 1-butanol (O, [HClO₄] = 0.05 M; ●, [HClO₄] = 0.10 M).

reverse micelles in 1-butanol and 1-octanol. The specific conductivities for 1-butanol were greater than 1-hexanol, which was greater than 1-octanol, according to Table II.

Kinetic Measurements. For the oxidation of 1-hexanol in SDS reverse micelles in 1-hexanol, the pseudo-first-order rate constant decreases with the amount of water in the mixture as can be seen in Figure 2. This variation can be related to the decrease of the effective HClO₄ concentration in the aqueous phase as the amount of water increases, and in all the systems studied, the pseudo-first-order rate constant varies linearly with effective H⁺ concentration in the aqueous phase. This linear dependence can be explained by the high effective concentration of H⁺ in the water pool, so that all the Cr(VI) is in the nondissociated chromic acid form.²²

Interestingly, in the mixtures with a constant amount of water,

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TABLE I: Values of Water Pool Radii (r_{wp}), Thickness of the Layer Where Surfactant and Alcohol Are Located ($r_c - r_{wp}$), and Aggregation Number (N) of the SDS Reverse Micelles in Alkanols at Different Compositions

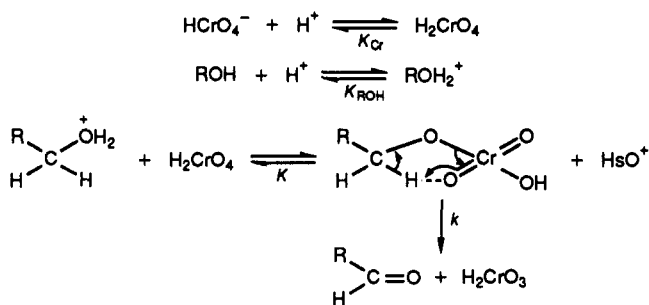
alcohol	H ₂ O, wt %	SDS, wt %	ROH, wt %	[H ₂ O]/[SDS]	[SDS]/[ROH]	r_{wp} , Å	$r_c - r_{wp}$, Å	N
butanol	40.0	15.0	45.0	42.7	0.0857	22.1	8.7	35
	27.7	10.4	68.9	42.7	0.0388	19.9	12.0	26
	14.5	5.4	80.1	42.7	0.0173	15.4	15.7	12
	7.4	2.8	89.8	42.7	0.0080	13.3	20.5	8
	3.0	1.1	95.9	42.7	0.0030	10.0	24.4	3
	35.0	20.0	45.0	28.0	0.114	20.5	9.3	43
	24.3	13.9	61.8	28.0	0.0581	18.0	12.1	29
	12.7	7.2	80.1	28.0	0.0232	15.0	16.8	17
	7.7	4.4	87.9	28.0	0.0129	13.3	20.1	12
	25.0	25.0	50.0	16.0	0.128	18.0	11.5	51
	17.3	17.3	65.4	16.0	0.0681	16.6	14.6	40
	9.0	9.0	82.0	16.0	0.0280	13.1	17.9	20
	15.0	30.0	55.0	8.0	0.140	15.6	14.7	66
	12.2	12.2	62.4	8.0	0.105	13.4	14.9	44
	hexanol	35.0	15.0	50.0	37.4	0.106	19.0	9.8
28.6		12.3	59.1	37.4	0.0735	18.2	11.9	23
21.0		9.0	70.0	37.4	0.0457	17.1	14.5	19
27.5		19.3	53.2	22.8	0.129	17.6	11.2	34
22.5		15.8	61.7	22.8	0.0909	16.8	13.3	29
19.0		13.4	67.6	22.8	0.0704	15.6	14.5	24
14.6		10.2	75.2	22.8	0.0481	15.1	16.6	21
9.9		6.9	83.2	22.8	0.0294	14.5	20.7	19
22.7		24.1	53.2	15.1	0.161	15.1	11.2	32
15.7		16.7	67.6	15.1	0.0878	14.0	14.3	25
12.0		12.8	75.2	15.1	0.0602	12.2	15.4	17
8.1		8.7	83.2	15.1	0.0370	13.3	21.4	22
5.0		5.3	89.7	15.1	0.0209	10.7	22.4	12
17.8		29.0	53.2	9.8	0.193	14.1	12.8	40
14.5		23.7	61.8	9.8	0.136	13.9	14.9	39
9.5	15.2	75.3	9.8	0.0711	11.8	17.0	23	
octanol	6.4	10.3	83.3	9.8	0.0439	11.4	21.1	20
	20.0	20.0	60.0	16.0	0.151	15.5	11.9	32
	10.4	10.4	79.2	16.0	0.0593	12.6	15.6	13
	7.0	7.0	86.0	16.0	0.0368	11.8	18.8	15

TABLE II: Specific Conductivities (κ) and Surfactant Molar Conductivities per Liter of Aqueous Phase ($\Lambda_{SDS} = \kappa/[SDS]$) for the SDS Reverse Micelles in 1-Butanol and 1-Octanol at Different Compositions

alcohol	SDS, wt %	H ₂ O, wt %	ROH, wt %	κ , $\Omega^{-1} \text{ cm}^{-1}$	Λ_{SDS} , $\Omega^{-1} \text{ m}^{-1} \text{ M}^{-1}$
butanol	29.0	17.8	53.2	0.237	0.0410
	24.1	22.7	53.2	0.322	0.0720
	19.3	27.5	53.2	0.386	0.131
	14.5	32.3	53.2	0.405	0.279
	9.6	37.6	53.2	0.336	0.551
	24.2	17.8	58.0	0.174	0.0320
	19.3	17.8	62.9	0.163	0.0356
	14.5	17.8	67.7	0.0880	0.0284
	9.7	17.8	72.5	0.0863	0.0405
	4.9	17.8	77.3	0.0588	0.0494
	19.3	17.8	62.9	0.163	0.0357
	19.3	22.7	58.0	0.246	0.0676
	19.3	32.5	48.2	0.536	0.249
	19.3	37.2	43.5	0.748	0.465
	octanol	14.4	13.5	72.1	2.64×10^{-3}
19.2		13.4	67.4	3.82×10^{-3}	1.10×10^{-3}
14.4		18.3	67.3	3.81×10^{-3}	1.58×10^{-3}
19.3		18.1	62.6	5.34×10^{-3}	1.89×10^{-3}
14.4		23.1	62.5	2.71×10^{-3}	1.37×10^{-3}
19.3		22.9	57.8	6.40×10^{-3}	2.74×10^{-3}

TABLE III: Second-Order Rate Constants ($k_{exp}/[H^+]$) and Third-Order Rate Constants ($k_{exp}/[H^+][ROH]$) for the Oxidation of 1-Octanol in the SDS Reverse Micelles in 1-Octanol at Different Compositions

H ₂ O, wt %	SDS, wt %	OcOH, wt %	[H ₂ O]/[SDS]	[SDS]/[OcOH]	$10^2 k_{exp}/[H^+]$, $\text{M}^{-1} \text{ s}^{-1}$	$10^3 k_{exp}/[H^+][ROH]$, $\text{M}^{-2} \text{ s}^{-1}$
18.1	19.3	62.6	15.2	0.139	2.55	6.32
18.3	14.4	67.3	20.4	0.0967	3.10	6.77
22.9	19.3	57.8	19.0	0.151	2.62	6.60
13.4	19.2	67.4	11.2	0.129	2.42	8.12
13.5	14.4	72.1	15.0	0.0902	2.16	4.81

SCHEME I

the pseudo-first-order rate constants decrease with the increase in the amount of alcohol (Figure 2). Pseudo-first-order rate constants decrease with the water content at a constant surfactant/alcohol molar ratio (Figure 3), but they do not significantly vary at a constant water/surfactant molar ratio.

The same kind of results are obtained for the oxidation of 1-butanol (Figure 4) and 1-octanol (Table III) in the SDS reverse micelles. Few results have been obtained for the oxidation of 1-octanol because of the reduced size of the reverse micelles region L₂, in the phase diagram.

Second-order rate constants, $k_{exp}/[H^+]$, show a linear dependence with surfactant/alcohol molar ratio (Figure 5) for the SDS reverse micelles in 1-hexanol and 1-butanol, independently of the composition of the mixture.

Discussion

To explain the kinetic results, it is necessary to consider the reaction mechanism for the oxidation of alcohols in the aqueous phase by Cr(VI) in perchloric acid medium.^{22,28} The reaction mechanism is given in Scheme I. The reaction passes through chromic ester formation from chromic acid and the protonated alcohol. By neglecting the chromic ester and the protonated

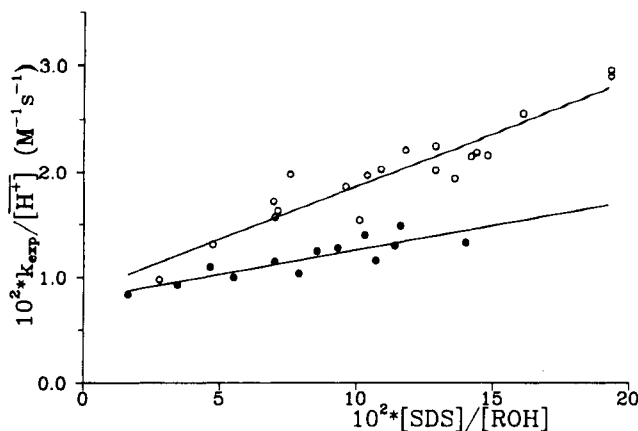


Figure 5. Second-order rate constants, $k_{\text{exp}}/[\text{H}^+]$ ($[\text{H}^+]$ concentration per liter of aqueous phase) for the oxidation of alkanols by Cr(VI) in SDS reverse micelles in alkanols versus the surfactant/alcohol molar ratio (O, oxidation of 1-hexanol; ●, oxidation of 1-butanol).

alcohol concentrations as compared with the total alcohol concentration, a pseudo-first-order rate constant is deduced as

$$k_{\text{exp}} = \frac{k'K_{\text{Cr}}[\text{H}^+]^2[\text{ROH}]}{1 + K_{\text{Cr}}[\text{H}^+]} \quad (3)$$

where k' is the product of the constants

$$k' = kKK_{\text{ROH}} \quad (4)$$

This rate equation fits our kinetic results obtained in the aqueous phase for the oxidation of 1-butanol, 1-hexanol, and 1-octanol.²⁸ This mechanism also explains the results obtained for the oxidation of these alcohols in SDS aqueous solutions by considering alcohol distribution between aqueous and micellar phases, with the reaction in the micellar phase occurring between the protonated alcohol in the micellar phase and the chromic acid in the aqueous phase across the micellar boundary.²⁸

In the case of SDS reverse micelles in alkanols at the high H^+ concentration in the water pool, where Cr(VI) is located, all the Cr(VI) is in the chromic acid form,²² H_2CrO_4 , so that the rate equation reduces to a pseudo-first-order reaction with a rate constant given by

$$k_{\text{exp}} = k'[\overline{\text{H}^+}][\overline{\text{ROH}}] \quad (5)$$

where $[\overline{\text{H}^+}]$ corresponds to the H^+ effective concentration in the micellar interface, $[\overline{\text{ROH}}]$ corresponds to the alcohol concentration in the volume element where the reaction is supposed to occur, and k' is the rate constant written in terms of this volume element.

Taking into account that for both ions H^+ and Na^+ there is no difference between the specific interactions with the surfactant head group,²⁹ the ratio H^+/Na^+ in the micellar interface is related to the ratio of the effective concentration of these ions in the aqueous phase. According to this and to our experimental conditions, all the H^+ can be considered located in the micellar interface. The same results have been obtained for the AOT reverse micelles in heptane.³⁰

In a first approach we tried to explain these results taking into account the molecules of the alcohol located in the water droplet surface by considering the aggregation number and the hydrated surfactant head-group area, but it was not possible to adjust the kinetic results in this manner. Therefore, we calculated the alcohol concentration in the volume of the layer given by $r_c - r_{\text{wp}}$. This alcohol concentration is nearly the same in all the mixtures and thus does not explain the kinetic variation either.

Taking into account that these kinetic results correspond to a reaction where the reactants are located in the separated hydrophilic and hydrophobic parts of the reverse micellar system,

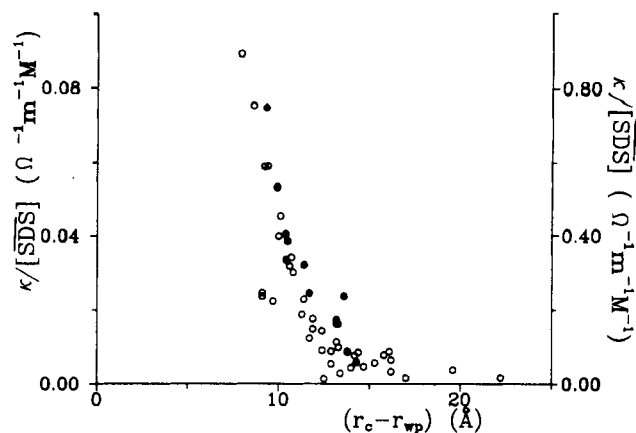


Figure 6. Molar surfactant conductivities ($\Lambda_{\text{SDS}} = \kappa/[\text{SDS}]$) versus the thickness of the layer where surfactant and alcohol are located, $r_c - r_{\text{wp}}$ (O, SDS reverse micelles in hexanol, ordinate axis on the left; ●, SDS reverse micelles in butanol, ordinate axis on the right).

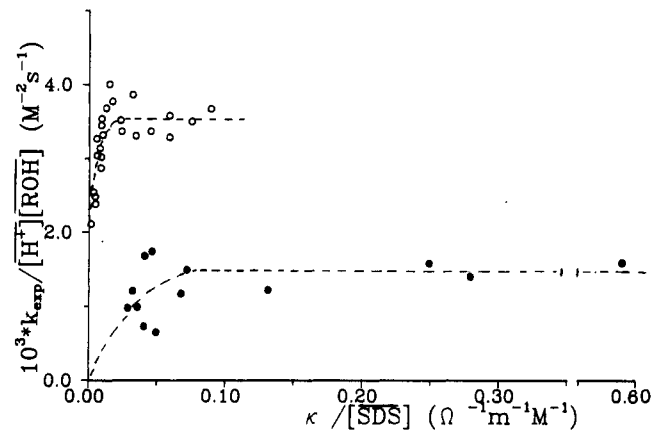


Figure 7. Third-order rate constants ($k_{\text{exp}}/[\text{H}^+][\text{ROH}]$) for the oxidation of alkanols in SDS reverse micelles in alkanols versus the surfactant molar conductivity (Λ_{SDS}) (O, SDS reverse micelles in 1-hexanol; ●, SDS reverse micelles in 1-butanol).

it should be necessary to consider the intermicellar reactant exchange.¹⁸⁻²⁰ This intermicellar reactant exchange could be related with surfactant molar conductivity.

From the specific conductivity results it is possible to calculate the molar conductivity of the surfactant, $\Lambda_{\text{SDS}} = \kappa/[\text{SDS}]$, where $[\text{SDS}]$ is the effective surfactant concentration per liter of aqueous phase, and it is interesting to emphasize that this value depends on the thickness of the layer where surfactant and alcohol are located ($r_c = r_{\text{wp}}$) and Λ_{SDS} decreases as $r_c - r_{\text{wp}}$ increases. Figure 6 shows that values of these molar conductivities follow the same variation in all the reverse micellar systems studied. The conductivity mechanism for these reverse micellar systems is not well established, and it probably depends on micellar collisions with intermicellar ion exchange,³¹ which according to these results increase with the decrease in $r_c - r_{\text{wp}}$ and the rise in r_{wp} (Figure 6).

Values of third-order rate constants, $k_{\text{exp}}/[\overline{\text{H}^+}][\overline{\text{ROH}}]$ are plotted versus molar conductivity in Figure 7, and it is interesting to note that the rate constant increases linearly with surfactant molar conductivity reaching a plateau at high molar conductivity (k_{max}), when the intermicellar reactants exchange is supposed to be large enough. Only a few of the results obtained at low alcohol contents in SDS reverse micelles in 1-hexanol, very close to the stability limit of the isotropic reverse micelles region L_2 , in the phase diagram, do not follow this variation.

Values for k_{max} are $1.6 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$, $3.5 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$, and $7.0 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ for 1-butanol, 1-hexanol, and 1-octanol, re-

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spectively, and it is interesting to notice this variation of k_{\max} can be related with the dielectric constant effect on this reaction given by

$$\ln k = a + b(1/\epsilon) \quad (6)$$

with $b = 35$, obtained in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ mixtures.²⁸

The third-order rate constants for the reaction in aqueous phase is nearly the same for all the alcohols studied,²⁸ $k = 0.045 \text{ M}^{-2} \text{ s}^{-1}$, and k_{\max} values follow expression 6 with the same slope, $b = 35$, by considering the dielectric constant of the volume element

where the reaction occurs, the correspondent alkanol dielectric constant.

From these results it can be concluded that rate constants for this reaction, where the reactants are located in the separated parts of the reverse micellar systems, increases with molar surfactant conductivity that account for intramicellar reactants exchange and could also be related with water channels formation.

Registry No. SDS, 151-21-3; $\text{H}_2\text{Cr}_2\text{O}_7$, 7778-50-9; BuOH, 71-36-3; $\text{HO}(\text{CH}_2)_3\text{CH}_3$, 111-27-3; $\text{HO}(\text{CH}_2)_7\text{CH}_3$, 111-87-5; H_2O , 7732-18-5.

Relaxation Dynamics, Vibrational Spectra, and Solvent Donor Number Effects for Na^+ Interacting with Acyclic Polyethers

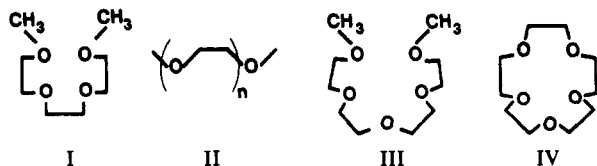
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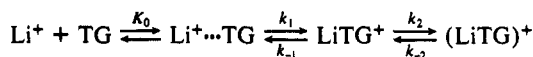
Ultrasonic relaxation spectra of Na^+ salts and tetraglyme (TeG) at molar ratio $R = [\text{TeG}]/[\text{NaX}] = 1$ in the solvent acetonitrile ($\epsilon_{25} = 36.0$, donor number $\text{DN} = 14$) can be interpreted in terms of two Debye relaxation processes. Existence of three molecular configurations participating in the two relaxation processes is supported by infrared spectra in the 800–900 cm^{-1} wavenumber region. The tetraglyme spectral envelope splits into three Gaussian–Lorentzian bands. However, for Na^+ + poly(ethylene oxides) (PEO) of average molar mass $\bar{M} = 400, 1000, \text{ and } 2000$ and $R = [(\text{CH}_2\text{CH}_2\text{O})_n]/[\text{NaX}] = 1$ (with $\text{X} = \text{ClO}_4^-$ or BPh_4^-) the slower relaxation of the two observed processes shifts to lower frequencies than those observed for the Na^+ + TeG systems in acetonitrile. Dimethylformamide (DMF), which is almost isodielectric with acetonitrile, but with a much larger DN, when used as the solvent for Na^+ + TeG at $R = 1$, yields an ultrasonic relaxation spectrum interpretable by a single relaxation process, which is comparable to the faster relaxation of the same sample system in acetonitrile. The same is true for Na^+ + PEO with average molar mass ranging from 400 to 2000 and with $R = 1$ at 25 °C. However, the reverse rate constant for the formation of the Na^+ PEO contact pair in DMF is smaller than the corresponding rate constant for the dissociation of Na^+TeG . The infrared spectra in the 800–900- cm^{-1} region of Na^+ + TeG in DMF show no evidence of an alteration of the polyether band, suggesting that no significant inclusive species (Na^+TeG), with Na^+ embedded in the TeG, is formed in DMF. Ultrasonic relaxation spectra of Na^+ interacting with cyclic 15C5 in DMF at 25 °C are also reported. The ultrasonic relaxation spectral envelope can be interpreted by the sum of two Debye relaxation processes at variance with the case of Na^+ + TeG in DMF. The existence of an inclusive complex ($\text{Na}^+15\text{C5}$) in DMF is suggested, despite the large solvent donor number. This reflects a greater affinity of the macrocycle 15C5 than of the acyclic TeG for the Na^+ cation. Thus the solvent and the ligand configuration (and at times the anion) compete for the first coordination sphere positions of a given cation.

Introduction

Recently, we reported¹ relaxation kinetic data for Li^+ + triglyme (TG) (see I below) and Li^+ + poly(ethylene oxide) PEO (see II below) at molar ratio $[(\text{CH}_2\text{CH}_2\text{O})_n]/[\text{Li}^+] = 1$ in acetonitrile at 25 °C. The ultrasonic spectra were interpreted by two Debye relaxation processes. With the polymeric system II tailored to mimic the possible coordination of the monomeric triglyme I plus



Li^+ system at ratio $[\text{TG}]/[\text{Li}^+] = 1$ it was found that the rate constants of formation and dissociation (according to the Eigen–Winkler² scheme)



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(2) Eigen, M.; Winkler, R. In *Neurosciences: Second Study Program*; Schmitt, F. O., Ed.; Rockefeller University Press: New York, 1970; pp 685–96.

$k_1, k_{-1}, k_2,$ and k_{-2} , were indistinguishable for the TG and PEO systems. This suggested¹ that the ultrasonic spectra reflect the local forward and reverse processes of each single polyether $(\text{CH}_2\text{CH}_2\text{O})_n + \text{Li}^+$ moiety. It was thus of interest to extend the above study to another alkali cation such as Na^+ because of the parallels to be drawn in terms of solvation and because of the wider biological interest of Na^+ compared to Li^+ .

We chose the longer tetraglyme III denoted TeG and PEO of various average molar masses \bar{M} but with a ratio $[(\text{CH}_2\text{CH}_2\text{O})_n]/[\text{Na}^+] = 1$ instead of $[(\text{CH}_2\text{CH}_2\text{O})_4]/[\text{Na}^+] = 1$ to facilitate comparisons with the crown ether 15C5 (IV) instead of 12C4. This was done to optimize cavity size and coordinating ability for complexation of Na^+ . This definition of R implies a coordination number of 5 for Na^+ and of 4 for Li^+ . The solvent acetonitrile ($\epsilon_{25} = 36.0$, $\text{DN} = 14$)³ was used as before for Li^+ , but dimethylformamide ($\epsilon_{25} = 36.71$, $\text{DN} = 26.6$) was also used in order to explore the role of solvent in the mechanism of complexation of Na^+ by the polyethers. Solvent does have a major effect, DMF being able to prevent formation of the inclusive wrapped species $(\text{NaTeG})^+$ in contrast to the ineffectiveness of acetonitrile. This contrasts with the behavior of the macrocyclic ligand 15C5, which is able to form inclusive complexes $(\text{Na}15\text{C5})^+$ with Na^+ in DMF, reflecting its greater affinity for

(3) Gutmann, V. *Coordination Chemistry in Non-Aqueous Solutions*; Springer-Verlag, Vienna, Austria, 1968.