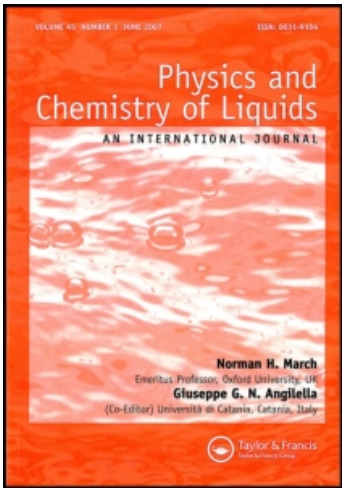

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Electrical Conductivity of Aqueous Solutions of Water-Soluble Polymerization Initiators Based on the Thioxanthone Structure

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ELECTRICAL CONDUCTIVITY OF AQUEOUS SOLUTIONS OF WATER-SOLUBLE POLYMERIZATION INITIATORS BASED ON THE THIOXANTHONE STRUCTURE

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The electrical conductivity of aqueous solutions of four chosen derivatives of 2-hydroxy-3-(9-oxo-9-H-thioxanthene-yloxy)-N,N,N-trimethyl-1-propanium chloride has been measured and analysed using the Fuoss-Justice equation. The changes of the equilibrium constants of ion-pair formation, K_A, the limiting molar conductances and the Bjerrum's parameters—q of the closest approach in ion pairs have been compared for all studied compounds and the most probable conformational structures have been suggested for them in their aqueous solutions. These results have been supplemented by the analysis of ^{1}H NMR Spectra of all four studied compounds dissolved in C_2D_5OD.

KEY WORDS: NMR spectra, thioxanthones.

Recently, several types of ketons have acquired importance as photoinitiators of unsaturated hydrocarbon polymerization[1]. The value of some ionic benzophenone and benzil compounds absorbing UV light between 200 and 350 nm has been reported in the literature for grafting of water-soluble vinylic monomers onto cellulose or wool[2]. However, in spite of their high performances, these photoinitiators are only active when irradiated at 365 nm and below in the UV range of the spectrum, therefore, their use in many technical applications which requires illumination in the blue end of the visible spectrum is impossible. In an effort to overcome these drawbacks, several groups synthesized thioxanthone derivatives, that, when used in conjunction with activators, were reported to be specially appropriate for the curing of some coating formulations between 350 and 450 nm. Like in the case of benzophenons or benzils, water-soluble thioxanthones were also developed by introducing ionic substituents in the skeleton. These compounds carry cationic solubilizing groups.

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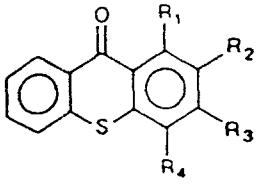


One of R_2, R_3 or R_4 is $-OCH_2C(OH)HCH_2N^+(CH_3)_3Cl^-$.

The other R substituents are independently selected as hydrogen atom or a methyl groups (Table 1). Previously other authors[3–4] compared the rates of polymerization (Rp) of acrylamide in aqueous solutions in the presence of these thioxanthones. However, the effect of substitution of methyl groups and ionic substituent was not fully explained by them. Therefore, we have decided to study four chosen water soluble thioxanthones in purpose to explain the mentioned above structural effects.

EXPERIMENTAL

All four studied thioxanthones were manufactured by International Bio-Synthetics in United Kingdom. They were crystallized twice from water and dried before being used.

All solutions were prepared gravimetrically.

Apparatus: The measurements of the conductivity were performed by means of E-315 A type bridge produced by "Mera-Tronic", Poland. A measuring cell similar to the Jones type vessel and connected with 350 cm^3 Erlenmayer flask was used. The cell was made of Pyrex glass.

Taking into account the reagents purity, equipment method of measurements and accuracy of the temperature control, the uncertainty of the measured values was less than 0.05 per cent. ^1H NMR spectra were recorded in C_2D_5OD, using a Varian 300 MHz spectrometer, with tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

The conductance data were analysed using the Fuoss-Justice equation[5] in the form:

$$\Lambda = \alpha[\Lambda_0 - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + I(\alpha c) + I_{3/2}(\alpha c)^{3/2}] \tag{1}$$

and

$$(1 - \alpha)/\alpha^2 c\gamma_{\pm}^2 = K_A \tag{2}$$

$$\gamma_{\pm} = \exp\left(-\frac{A(\alpha c)^{1/2}}{1 + Bq(\alpha c)^{1/2}}\right) \tag{3}$$

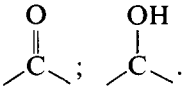
$$q = e^2/B\pi\varepsilon_0\varepsilon kT \tag{4}$$

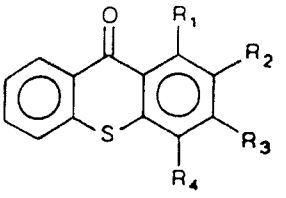
Table 1 Limiting molar conductances, Λ_0, ionic association constants, K_A and Bjerrum's characteristic distances, q for compounds (**1**, **2**, **3** and **4**).

Compound	R_1	R_2	R_3	R_4	$\Lambda_0 \mid cm^2\ mol^{-1}\ ohm^{-1} \mid$	$K_A \mid dm^3 \cdot mol^{-1}$	$10^8 q \mid cm \mid$	$Rp \mid mol \cdot dm^{-3} \cdot s^{-1} \mid$
1	H	Pr	CH_3	CH_3	108.8	13.4	15.0	156
2	H	H	H	Pr	108.5	6.3	17.5	219
3	H	H	Pr	H	111.2	2.6	8.9	313
4	CH_3	Pr	CH_3	CH_3	104.0	15.21	2.8	344

Pr is $-OCH_2CH(OH)CH_2N^+(CH_3)_3$

In these equations Λ_0 is the limiting conductance, $(1-\alpha)$ is the fraction of an electrolyte acting as ion pairs, K_a is the ion association constant and $\gamma_\pm$ is mean activity coefficient of the dissociated part of an electrolyte, (the activity coefficient of the ion-pairs is assumed to be equal to unity as usual for diluted solutions). A and B are the Debye-Hückel equation (4) coefficients. The analytical form of the remaining parameters, i.e.: S, E, I, and $I_{3/2}$ is presented elsewhere[5–9]. Following the Fuoss proposal[8] the Bjerrum's characteristic distance, q (Eq. 4) was assumed as the closest approach distance. In this way, Eq. (1) become a diparametric one and it was resolved by the least squares method.[10,11] The determined Λ_0, K_A and the Bjerrum's parameter-q values are collected in Table 1.

We believe that the comparison of values of Λ_0, K_A and q (defined[5] previously) should be a source of valuable information concerning conformation of the side propoxy chain. It should also enable us to visualize the possibility of formation of internal hydrogen bonds for those compounds, which may influence the catalytic activity of the studied thioxanthones in the processes of polymerization of unsaturated hydrocarbons. As it is known[12] tetramethylammonium cation is a structure breaker in aqueous solutions. Therefore, we assume that it should appear here without the hydration layer. Similarly it is possible to conclude that the changes of the Bjerrum's parameter-q for the $+N-(CH_3)_3]^+Cl^-$ ion pair and its association constant (K_A) measured in water at 25°C should depend on the location of trimethylammonium cation (possibly close to one of the strongly hydrated centers, for example Ar–O–R;  Knowing that the catalytic activity of the studied thioxanthones is based on the effect of photochemical excitation of the free electron pair of carbonyl oxygen[3], it seems interesting to compare mentioned above parameters with the literature[3] rates of polymerization of acrylamide in water (R_p) catalyzed by the studied thioxanthones in the presence of methyldiethanolamine (MDEA). Additionally, we believe that the contingent formation of internal hydrogen bonds between hydroxy group from the side propoxy chain and the carbonyl oxygen in position 9 should influence the decrease of value of Rp. Values Λ_0, K_A, q and Rp for salts (1, 2, 3 and 4) are listed in Table 1. All compunds (**1**, **2**, **3** and **4**) can be represented by the following formula:



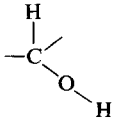
The low value of *Rp* and Λ_0 for compound (1) may be explained by assuming that in its aqueous and alcohol solutions the conformation of this molecule, where hydroxyl group from the side chain interacts with carbonyl oxygen by hydrogen bonding, is the predominant one. This assumption seems to be supported by the down-field shift, in comparison to three other studied compounds, of the doublet corresponding to hydrogen linked with carbon in position 8. The ^{1}H NMR spectra of all studied compounds were recorded in C_2D_5OD (see Table 2).

For (**1**): ^{1}H NMR (300 MHz, C_2D_5OD) δ (p.p.m.)8.45(d.J = 9.6 Hz)—$1H_8$. Simultaneously, we believe that the $+N(CH_3)_3]^+$ group should occupy space close to these two strongly hydrated centers. This results in the formation of the hydration layer around the trimethylammonium cation and is visualized by the high value of the Bjerum's parameter q (the distance of the closest approach in the ion pair). However, such location of this group (far from the thioxanthone skeleton) enables an easy access to it by the chloride anion. This leads to the relatively high value of K_A (13.4 $dm^3 \cdot mol^-$). In case of analogous solutions of the compound (**2**) the hypothetical conformational structure with weak hydrogen bond between the hydroxyl group from the side chain and sulphur from the thioxanthone skeleton has been assumed and the $+N(CH_3)_3]^+$ group according to this structure should be situated close to them. This results in the formation of the hydration layer around the trimethylammonium cation, analogously as it has been observed for (**1**), and is visualized by the high value of q ($17.5 \cdot 10^{-8} \cdot$ cm). Simultaneously the analysis of the model of the studied molecule, arranged according to this conformation, shows that the $+N(CH_3)_3]^+$ group is situated closer to the thioxanthone skeleton than it has been observed for (**1**), which results in decrease of K_A for (**2**) (see Table 1).

In case of the compound (**3**), we would like to suggest the possibility of formation of the internal hydrogen bond between the hydroxy group from the side chain and oxygen bonded to carbon, from the thioxanthone seleton, in position 3. This assumption seems to be supported by the down-field shift, in comparison to other compounds, of doublet coresponding to two hydrogens linked with carbon in position 1'. For (**3**): ^{1}H NMR (300 MHz, C_2D_5OD)δ(p.p.m.)4.28(d.J = 8 Hz)—$2H_{1'}$. Additionally the relatively high value of Rp for (**3**) confirms that the electron structure at carbonyl oxygen is not interrupted as it was observed for (**1**) and (**2**). This compact arrangement of the side chain results in a high value of limiting conductance (Λ_0 = 111.2 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$) and a law value of association constant (K_A = 2.6 $dm^3 \cdot mol^{-1}$). Finally, a lower value of the parameter q ($8.9 \cdot 10^{-8}$ cm) for (**3**), in comparison to (**1**) and (**2**), indicates a weaker influence of hydrogen bonded groups on solvation layer around the trimethylammonium cation.

The lowest value of the limiting conductance (Λ_0) for compound (**4**), in comparison to remaining three studied thioxanthones, indicates that the radius of this molecule

Table 2 Proton NMR Spectral data compounds (**1**, **2**, **3** and **4**). Spectra were recorded in C_2D_5OD, using Me_4Si as an internal standard.

Compound	CH_3	CH_3	CH_3	CH_2		CH_2	3 CH_3	$H_{aromatic}$
(**1**)	2.3(s)	2.3(s)	—	4.075 (d.J = 6.6 Hz)	4.52(m)	3.55 (d.J = 6 Hz)	3.24(s)	$1H_8$-8.45(d.J = 9.6 Hz) $1H_1$-8.00(b.s.) 1H-7.45(m) 2H-7.65(m)
(**2**)	—	—	—	4.18 (d.J = 6 Hz)	4.60(m)	3.63 (d.J = 6 Hz)	3.25(s)	$1H_8$-8.35(d.J = 8 Hz) $1H_1$-7.95(b.s.) 2H-7.62(m) 1H-7.42(m) 2H-7.20(m)
(**3**)	—	—	—	4.28 (d.J = 6 Hz)	4.58(m)	3.65 (d.J = 6 Hz)	3.25(s)	$1H_8$-8.20(d.J = 8 Hz) $1H_1$-7.90(b.s.) 2H-7.60(m) 1H-7.40(m) 2H-7.30(m)
(**4**)	2.3(s)	2.3(s)	2.6(s)	3.70 (d.J = 6 Hz)	4.55(m)	3.60 (d.J = 6 Hz)	3.25(s)	$1H_8$-8.20(d.J = 8 Hz) $1H_1$-7.45(m) 2H-7.60(m)

in aqueous solutions is the greatest. This growth of the size of the studied cation seems to be caused by the presence of methyl groups in positions 1, 3 and 4 and by the linear shape of the propoxy side chain. We assume that the absence of internal hydrogen bonds within the molecule of (**4**) is confirmed by a high value of Rp and by a high up-field shift of a doublet corresponding to two hydrogens linked with carbon in position 1′. For (**4**): ^{1}H NMR (300 MHz, C_2D_5OD)δ(p.p.m.)3.70(d.J = 6 Hz) $- 2H_{1'}$. Also a relatively high value of K_A and a small value of q seem to result from a remote location of the $\dashv N(CH_3)_3]^+$ group from strongly hydrated centers in the studied molecule.

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