Microemuisions as a Medium in Chemical Kinetics: The Persulfate-Iodide Reaction

María Luisa Moyá,[†] Carmen Izquierdo, and Julio Casado*

Departamento de Química física, Universidad, E-37008 Salamanca, Spain (Received: December 3, 1990; In Final Form: March 7, 1991)

Rate constants are reported for the oxidation of iodide ions by persulfate in sodium bis(2-ethylhexyl) sulfosuccinate (aerosol OT or AOT)/decane/water microemulsions. The rate law is in the form $v = k_2[I^-][S_2O_8^{2-}]$, where both concentrations are referred to the aqueous phase. The reaction rate is higher in microemulsions than when it takes place in a conventional aqueous medium. Results show that when the AOT concentration remains constant, the reaction rate decreases when increasing the molar ratio $w = [H_2O]/[AOT]$, appearing to asymptotically approach the rate in bulk water as the amount of water in the microemulsions increases. For a given w value, the reaction rate shows no dependence on the surfactant concentration.

Introduction

Microemulsions, so-called since 1959,¹ are apparently homogeneous mixtures of water and oil with large amounts of surfactants. They form spontaneously and are thermodynamically stable, the surfactants creating an extremely low interfacial tension between the oil and water, which promotes emulsification.² In many cases, the structure of microemulsions can be regarded as rather monodisperse droplets of water in oil (w/o) or oil in water (o/w).

Over the past 10 years chemists and physicists have made a concerted effort to understand the structure, dynamics, and interactions of microemulsions,^{3,4} principally because of some of their applications and specially because the microemulsion droplet can be considered as a *microreactor* where certain chemical reactions take place within the very small domain provided by the droplet. In this way, suitable control of the size of the droplet regulates the growth process for particle or polymer formation.^{5,6} On the other hand, many enzymes can be solubilized in the polar core of w/o microemulsions with the added advantage of the enzymes being dispersed in monomeric form rather than as enzyme clusters.⁴ In addition, microemulsions have recently been used to perform separations and purifications.^{7,8}

An immediate consequence of the application of microemulsions as *molecular scale reactors* is of interest in the kinetic effects associated with this possibility. The presence of the droplet can enhance or retard chemical reaction rates by large factors.⁹⁻¹⁵

Within the framework of a kinetic study of some reactions of biological interest that participate in the precursor mechanisms of certain pathological states (cf. for instance refs 16–19), it has been considered appropriate to compare the behavior of these reactions in conventional aqueous media with those observed in microemulsions. There are two fundamental reasons for this: (1) a greater approximation to the real conditions that, in a hydrophilic/lipophilic milieu, take place in vivo at the cellular level and (2) the promising future opened to physical chemistry by microemulsions within the field of food science and industry (ref 4; cf. also ref 6).

The first results of this comparative study have shown, despite the dramatic differences in behavior (and even qualitative differences), the convenience of selecting particularly suitable reactions that will allow one to discern as much as possible the effect of the actual microemulsion itself rather than other concurrent factors. Along these lines, we chose the reaction of iodide ions with peroxide sulfate (henceforth persulfate) because three conditions are fulfilled: (1) its kinetic behavior in aqueous media is well-known,²⁰⁻²⁷ (2) pH does not appreciably affect the reaction in the 2–10 range²⁸ (this is a particularly favorable aspect if we take into account the difficulty of measuring and controlling the pH in microemulsions^{29,30}), and (3) the reagents are anionic (vide infra). The present work employed AOT/decane/water microemulsions. The choice of aerosol OT or AOT (sodium bis(2-ethylhexyl) sulfosuccinate) as surfactant was based on the fact that, among other advantages, it allows the solubilization of a considerable amount of water in the bulk of different organic compounds, without having to add a fourth component; additionally, it is an anionic detergent.

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Departamento de Química física, Universidad, E-41012 Sevilla, Spain.

[•] To whom all correspondence should be addressed.



Figure 1. Plot of $\ln (k_{obs}/s^{-1})$ against $\ln ([I^-]/mol dm^{-3})$ for the $I^- + S_2O_8^{2-}$ reaction in AOT/decane/water microemulsions. The AOT concentration was 0.2 *m* and the molar ratio w = 15. T = 298 K.

Experimental Section

Materials. The surfactant AOT was from Fluka and used without further purification. Sodium iodide (Suprapur) and decane were from Merck. Sodium persulfate (p.a.) was from Carlo Erba.

Preparation of the Microemulsions. Special attention was paid to the preparation of the microemulsions. Firstly, a solution of AOT in decane was prepared; then, in separate vessels, sodium iodide and sodium persulfate aqueous solutions of suitable concentrations were added to aliquot parts of the surfactant solution in decane. After these mixtures were shaken to obtain perfectly clear microemulsions, they were kept at a constant temperature for 30 min. Following this, known volumes of each microemulsion were mixed in the reaction vessel, also at a constant temperature; after the samples were shaken again, the recording of absorbance data was begun.

To verify this methodology as much as possible, the kinetic results were compared with those obtained from a different method: using a microsyringe, we added a known amount of persulfate aqueous solution to the reaction vessel containing a microemulsion with iodide, prepared as described above. After the samples were shaken to obtain perfect transparency, data collection was begun. The close agreement of the rate constant values obtained with both methods allowed us to use the former as the standard working method.

Kinetic Measurements. Kinetics were monitored spectrophotometrically by following changes in absorbance at 355 nm, the wavelength of maximum absorbance for the I_3^- ions, formed over the course of the reaction. A Shimadzu 240 spectrophotometer was employed. The reaction cuvette was kept at a constant temperature (± 0.1 °C) by a water flow from a conventional thermostat.

All runs employed a large excess of sodium iodide so that first-order kinetics were followed. Pseudo-first-order rate constants, k_{obs} , were calculated by Guggenheim's method from the absorbance data for each run, repeating all the kinetic experiments at least twice. Thus, the error in the rate constants was not above 4%.

In order to assure that determination of the rate constants by monitoring the absorbance of the I_3^- ions is not affected by a possible partitioning of I_2 from the microemulsion droplets to the continuous oil phase, absorbance was monitored in the region of the spectrum from 330 to 650 nm during the reaction. If any amount of iodine passed into the organic phase, an absorption band centered at 520 nm should be observed. For all the microemulsions studied, the only absorption band observed over the course of the reaction corresponds to the I_3^- species. On the other hand, the position and shape of the absorption band of the I_3^- ions are similar in microemulsions to those of conventional aqueous medium, showing that the determination of the pseudo-first-order rate

TABLE I: Rate Constants for the $I^- + S_2O_8^{2-}$ Reaction in AOT/Decane/Water Microemulsions of Different Composition at 298 K^a

	$10^2 k_2 / \text{mol}^{-1} \text{ s}^{-1} \text{ dm}^3$			
w = [H ₂ O]/[AOT]	$\begin{bmatrix} AOT \end{bmatrix} = 0.1 \ m$	[AOT] = 0.2 m	[AOT] = 0.4 m	
6	7.5	7.8	7.4	
8	4.3	4.5	4.3	
10	3.0	3.0	3.1	
15	1.6	1.7	1.6	
20	1.1	1.1	1.1	
25	0.9	0.9		
30	0.8	0.8	0.8	
40	0.7	0.7	0.7	

 ${}^{a}k(\text{pure water}) = 4.11 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^{3} \text{ (ref 27)}.$

TABLE II: Activation Parameters for the $I^-+S_2O_8{}^{2-}$ Reaction in AOT/Decane/Water Microemulsions of Different Composition"

	6	10	20	30	[AOT]/m
E _a # ΔH# ΔS#	49.1 ± 0.8 46.6 ± 0.8 -91 ± 5	53.6 ± 0.7 51.1 ± 0.7 -83 ± 4		58.7 ± 0.9 56.1 ± 0.9 -75 ± 7	0.1
E ₈ # ΔH# ΔS#	49.5 ± 0.6 47.0 ± 0.6 -87 ± 3		57.4 ± 0.7 54.9 ± 0.7 -79 ± 5		0.2
E₄# ∆H# ∆S#	49.5 ± 0.6 47.0 ± 0.6 -91 ± 4		57.4 ± 0.8 54.9 ± 0.8 -79 ± 6		0.4

 ${}^{a}E_{a}^{\#}$ and $\Delta H^{\#}$ in kJ mol⁻¹, $\Delta S^{\#}$ in J mol⁻¹ K⁻¹. Activation parameters corresponding to pure water: $E_{a}^{\#} = 49.5 \pm 0.3$ kJ mol⁻¹, $\Delta H^{\#} = 47.0 \pm 0.3$ kJ mol⁻¹, and $\Delta S^{\#} = -131 \pm 3$ J mol⁻¹ K⁻¹ (ref 27).

constants is unaffected by possible variations in the extinction coefficient of the ion.

Results and Discussion

The reaction follows second-order kinetics, first order with respect to each reactant, as found in conventional aqueous solution.²⁰⁻²⁷ In this regard, Figure 1 shows the plot of $\ln (k_{obs}/s^{-1})$ against $\ln ([I^-]/mol dm^{-3})$ for a microemulsion with a surfactant concentration of 0.2 *m* and a molar ratio w = 15. The iodide molar concentration is referred to the aqueous phase. In all microemulsions used, the same behavior was found. It should be noted that this result, obtained in microemulsions, could be accounted for statistically in terms of a Poisson distribution of the reactants in the aqueous core of the droplets.¹⁴ The observed second-order rate law is also accounted for by a pseudophase model in which it is assumed that the aqueous droplets are effectively continuous on the slow time scale of this reaction.

Table I shows the values of the second-order rate constants, k_2 , for the process $I^- + S_2O_8^{2-}$ in AOT/decane/water microemulsions of different compositions, at 298 K. These rate constants were obtained by referring the reactant concentrations only to the aqueous phase and not to the entire system (AOT + decane + water); that is, we assume that the reaction takes place mainly in the aqueous core of the droplets.

Table II summarizes the kinetic activation parameters obtained from the temperature dependence of the rate constant. The temperature domain chosen for the kinetic measurements was from 285 to 303 K. In this temperature range the AOT/decane/water systems remain stable, showing perfect transparency.

From Table I three aspects can be inferred: (1) When a reaction occurs in AOT/decane/water microemulsions, its specific rate is greater than when it takes place in a conventional aqueous solution. (2) For a constant surfactant concentration, the reaction rate increases when decreasing the molar ratio $w = [H_2O]/[AOT]$, that is, when, the amount of water in the microemulsions is reduced. (3) The reaction rate does not depend on the surfactant concentration when the molar ratio $[H_2O]/[AOT]$ remains constant.

Regarding the first point, the accelerating effect could be interpreted, at a simplistic level, on the basis of electrostatic interactions. The anionic reactants would be repelled by the negatively charged heads of the AOT molecules, which would increase the local reactant concentrations and hence the reaction rate.

Table I shows that the rate constant k_2 does not depend on the surfactant concentration when w remains unchanged. In previous studies on the structure and characteristics of microemulsions, 31-35 it was found that the size of the droplets and the aggregation number of the AOT and water molecules depend only on the molar fraction w. This means that at constant w the characteristics of the microreactor droplets do not change; therefore, it is expected that neither does the rate of the process that takes place inside them. The fact that k_2 does not depend on the surfactant concentration at constant w can be considered as a kinetic argument in favor of the hypothesis that the reaction studied occurs exclusively in the aqueous core of the droplets.

From Table I it can be seen that the reaction rate increases upon decreasing w. Traditionally, reversed micelles have been viewed as spherical cavities containing an electrolyte solution; the structure and dynamics of the species in the aqueous part have been explained on the basis of phenomenological electrostatic models of the double layer formed inside the droplets.³⁷⁻³⁹ The water dipoles are strongly oriented by the ions present inside the droplet cores (which come from the surfactant), and the hydrogen-bonded network is partially broken down. As a consequence, the effective concentration of the iodide ions could be expressed as

$$[I^{-}]_{c} = n_{I^{-}} / V_{w}^{f}$$
(1)

$$V_{\rm w} = V_{\rm w}^{\rm f} + V_{\rm w}^{\rm b} \tag{2}$$

where n_{l} is the number of moles of iodide, V_{w} is the total water volume, V_{w}^{f} is the volume of *free* water, and V_{w}^{b} is the volume of bound water, that is, oriented by the ions and therefore not available to solvate the reactant species. Assuming that V_w^b is proportional to the number of moles of AOT in the microemulsion and considering that the total water volume is proportional to the number of moles of water present in the system, we can write

$$[I^{-}]_{e} = \frac{n_{I^{-}}}{V_{w}(1 - d/w)} = \frac{[I^{-}]_{aq}}{1 - d/w}$$
(3)

where d is related to the quantity of water bound in the AOT system and [I⁻]_{aq} is the iodide molar concentration in the aqueous solution before preparing the microemulsions (cf. Experimental Section).

Considering the effective reactant concentrations, we can write

$$v = k [I^{-}]_{e} [S_{2}O_{8}^{2-}]_{e} = k_{obs} [S_{2}O_{8}^{2-}]_{e}$$
(4)

The rate constant values in Table I, k_2 , were obtained in each case by dividing the observed pseudo-first-order rate constants by the corresponding [I⁻]_{aq}. Therefore, from eqs 3 and 4 it is possible to write

$$k_{2} = \frac{k_{\text{obs}}}{[1^{-}]_{\text{ag}}} = \frac{k_{\text{obs}}}{[1^{-}]_{e}(1 - d/w)} = \frac{k}{1 - d/w}$$
(5)

Equation 5 implies that an increase in the molar ratio w would

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Figure 2. Plot of log $(k_2/\text{mol}^{-1} \text{ s}^{-1} \text{ dm}^3)$ against log $(k_{\text{NaNO}_3}/\text{mol}^{-1} \text{ s}^{-1}$ dm³) for the $I^- + S_2O_8^{2-}$ reaction.

bring about a decrease in k_2 , as is observed in Table I.

Another alternative way to explain the trend observed (compatible with the above) is based on the consideration that, in the presence of contact of the reactants to form the activated complex, some solvent molecules would pass from the reactant solvation spheres to the aqueous droplet bulk, and consequently the overall activation process may be written as

$$A_{solv} + B_{solv} \rightarrow M^{\#}_{solv} + nH_2O$$
 (6)

In agreement with transition-state theory, the observed rate constant would be

$$k_{\rm obs} = k_0 \frac{\gamma_{\rm A} \gamma_{\rm B}}{\gamma_{\rm M} \#} \frac{1}{a_{\rm H_2O}^n} \tag{7}$$

According to this expression a decrease in water activity, $a_{H_2O_2}$ would bring about an increase in the reaction rate. Higuchi et al.³⁶ found that water activity in AOT/oil/water microemulsions decreases by decreasing the molar ratio $[H_2O]/[AOT]$. Water activity values for decane as organic phase are not available in the literature; however, if we take into account that the nature of the organic phase does not practically affect water activity, not only in a qualitative but also in a quantitative way, it seems reasonable to assume that in AOT/decane/water microemulsions water activity decreases upon decreasing the molar ratio w. These changes in water activity could also explain the increase of the rate of the process $I^- + S_2 O_8^{2-}$ when decreasing the amount of water present in the system. The changes in water activity by changing w in microemulsions are traditionally related to the interactions between water molecules and Na⁺ and SO₃⁻ ions from the AOT. The droplet cavities of the microemulsions contain a high ionic concentration which increases with decreasing w. To investigate whether the ionic concentration inside these cores plays an important role in determining the experimental trend observed when changing w, we compared our kinetic results in microemulsions with those of the process $I^- + S_2O_8^{2-}$ in conventional aqueous concentrated salt solutions. In the paper of Sánchez et al.,²⁵ an increase in the rate constant of the reaction $I^- + S_2O_8^{2-}$ upon increasing the electrolyte concentration was found for all the salts studied, within a salt concentration range from 1 to 6 mol dm⁻³. A linear correlation between log $(k/mol^{-1} s^{-1} dm^3)$ and the ionic strength of the medium was found in the above paper. To compare our kinetic data with those of Sánchez et al., we interpolated their rate constant values in conventional aqueous sodium nitrate and sodium perchlorate salt solutions on the hypothetical ionic strengths corresponding to the aqueous core of the droplets for the different microemulsions used. Assuming the fully ionization of the AOT,^{40,41} the hypothetical ionic strength ranges from 1.4 to 9.3 mol dm⁻³. Figure 2 shows the plot of log $(k/mol^{-1} s^{-1} dm^3)$ in sodium nitrate aqueous solutions against log $(k_2/\text{mol}^{-1} \text{ s}^{-1} \text{ dm}^3)$ corresponding to the different microemulsions. In this figure one observes a linear correlation between both sets of data when the ionic strength is lower than 3 mol dm⁻³, that is, when the amount of water present in the microemulsion is large $(w \ge 20)$. At low w values, a strong deviation from linear behavior is observed. Similar results are obtained upon using the kinetic data corresponding to sodium perchlorate solutions, since the main salt effects in conventional aqueous solutions are due to the salt cations. Results indicate that when the amount of water in the microemulsions is large, a decrease in the reaction rate, when wdecreases, is mainly due to a decrease in the ionic concentration inside the droplets. Because of the presence of the double layer, at low w values, other factors (which are not present in conventional aqueous solutions) play an important role in the reaction studied.

Table II shows the dependence of the activation parameters of the reaction studied on the molar ratio w, at different surfactant concentrations. As was expected, these parameters do not depend on the surfactant concentration when w remains unchanged. The activation energy increases with increasing w, and the same trend is found for the enthalpy and entropy of activation. Hypothetically, one would expect that the activation parameters approach those

of bulk water at the limit of high w values; however, a substantial difference between the activation parameters corresponding to w = 30 and those in pure water (see Table II) is found. This result could be related to the microemulsions properties themselves; nevertheless, it is necessary to take into account the effect of temperature on microemulsions. In a recent paper, Bisal et al.42 have discussed the temperature effect on the structural properties of microemulsions, pointing out that the number of droplets increases upon increasing temperature; i.e., with rise in temperature the droplet radius decreases. It seems that a temperature increase reduces the interfacial tension between oil and water; the dispersion of water in oil is thus favored by increasing the number of smaller sized droplets. In this sense a fulfillment of the Arrhenius law is not expected. We have obtained good straight lines by plotting $\ln (k_2/\text{mol}^{-1} \text{ s}^{-1} \text{ dm}^3)$ against 1/T; however, the temperature range used in this study is small (from 285 to 303 K), and the structural changes due to the temperature variation are not expected to be large. Therefore, the observed fulfillment of the Arrhenius law could be apparent. A rise in temperature would produce an increase in the slope of $\ln (k_2/M^{-1} \text{ s}^{-1})$ against 1/T and hence in $E_a^{\#}$, since a decrease in droplet size produces an increase in the rate constant. At present, no possible explanation about activation parameters seems plausible.

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Phase Behavior of a System of Cationic Surfactant and Anionic Polyelectrolyte: The Effect of Salt

Kyrre Thalberg,* Björn Lindman, and Gunnar Karlström[†]

Physical Chemistry 1 and Theoretical Chemistry, Chemical Center, University of Lund, POB 124, S-221 00 Lund, Sweden (Received: December 4, 1990)

The effects of addition of simple salt (NaBr) to a system containing the anionic polysaccharide sodium hyaluronate (NaHy) and the cationic surfactant tetradecyltrimethylammonium bromide (C14TABr) are investigated. In the absence of added salt separation occurs into one dilute phase and one concentrated in both polyelectrolyte and surfactant. Addition of low concentrations of NaBr leads to a reduction of the two-phase region of the phase diagram, and at 250 mM NaBr, phase separation no longer occurs. At high NaBr concentrations (≥500 mM), phase separation also occurs, but is of a type totally different from that observed at no or low salt concentrations and involves separation into surfactant-rich and polymer-rich solutions. A new way of representing this type of systems is introduced, in which the phase diagram is shaped as a pyramid. This representation gives an illustrative and correct picture of the distribution of all ions in the system. A two-phase region corresponds to a three-dimensional body, and phase diagrams obtained at different salt concentrations correspond to different "cuts" through the body. Phase separation occuring at high salt concentrations corresponds to another body in the pyramid. Finally, the observed changes in phase behavior on addition of salt have been reproduced by a simple theoretical model based on the Flory-Huggins theory, which gives an insight into the physical origin of the phase behavior.

Introduction

The strong interaction between cationic surfactants and proteins, leading to phase separation, was discovered by Kuhn in the early 1940s.¹ It was recognized that the interaction was due to the favorable electrostatic interaction between the two species, and a number of biological polyelectrolytes were seen to display a similar behavior.² The polyanion-surfactant complexes formed could be redissolved by addition of large amounts of salt.³ This was exploited in the purification of polyelectrolytes, especially glucosaminoglycans, from biological tissue.⁴ A typical route was precipitation of the glucosaminoglycan from the biological sample with cetylpyridinium chloride, followed by redissolution at a high salt concentration and cooling until the cetylpyridinium salt precipitated out of the solution. By the same procedure, different glucosaminoglycans could be separated from each other, since

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