Reactions in Microemulsion Media: Schiff Bases with Targeting/Anchoring Module as Kinetic Sensors to Map the Polarity Pocket of a Microemulsion Droplet

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ABSTRACT: The hydrolysis of some tailor-made Schiff bases having flexible spacers between aldimine groups and alkoxy groups at *ortho* (*o*) or *para* (*p*) position in the benzene ring has been investigated in microemulsion media. The kinetic data of acid-catalyzed hydrolysis in anionic (sodium lauryl sulphate: NaLS) and cationic (cetyltrimethyl ammoniumbromide: CTAB) microemulsion media have been explained considering the localization of the Schiff bases at various probable pockets of the microemulsion droplet. The results are in conformity to the solubilization studies of the reported Schiff bases in microemulsions (Dash et al., Spectrochim Acta 1996, 52A, 349). The change in reactivity due to change in the spacer length and position of the alkoxy group in the Schiff bases has been rationalized on the basis of localization sites of the reaction center at different polarity pockets of the reaction media. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 458–464, 2001

INTRODUCTION

Microemulsion is an optically isotropic, transparent, and thermodynamically stable medium formed from water, oil, surfactants, and cosurfactants [1]. Owing to the varied constituents and compositions, it can solubilize a wide variety of compounds simultaneously and offer the possibility of reagent compartmentalization and of providing an interface for chemical reactions similar to the lipid–water interface found in biological systems. In particular, the use of microemulsion water droplets as a novel environment for enzyme-catalyzed reactions has attracted much interest [2]. Microemulsions contain divided domains of oil and water topologically ordered by surfactants at the internal interfaces and sometimes provide a strong barricade to separate the reactants from each other [3]. They find extensive use in selective syntheses [4,5], oxidation [6,7], hydrolysis [8–10], and photochemical [11–16] reactions, etc.

Schiff bases act as intermediates in many biological processes. Some examples of such processes are reactions involving pyridoxal enzyme [17], aldol con-

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densations [18], decarboxylation [19], transamination [20], and visual processes [21]. In an earlier work [22], we have studied the solubilization of the reported Schiff bases to map the polarity pockets of a micro-emulsion droplet.

The Schiff bases (1) reported in this article have a hydrophobic alkoxy group attached to the aromatic ring and also have a spacer with varied hydrophobicity in between the aldimine groups. The former has the capability of targeting the molecule to anchor at the interface, and the spacer group may tend to pull the anchoring polar site from the interface to a different extent into the microemulsion droplet. For the purpose, microemulsion droplets formulated from cationic surfactant (cetyltrimethyl ammoniumbromide: CTAB)—*iso*-butanol–hexane–water (CBH) and an-

ionic surfactant (sodium lauryl sulphate: NaLS)—*iso*butanol-hexane-water (ABH) were used.

EXPERIMENTAL

Materials

The synthesis of Schiff bases (1, *m-p/o-n*: *m* is the number of carbon atom in the alkyloxy chain attached to the *ortho* (*o*) or *para* (*p*) position in the benzene nucleus with respect to aldimine group, and *n* is the number of methylene groups in the spacer) and purification of surfactants and solvents were reported earlier [22]. The 16-*p/o-n* Schiff bases (1, m = 16, n = 0, 2, 4, 6 and cetyloxy group in *para* or *ortho* position) have been mostly used for various studies.

$$(p/o)$$
CH₃(CH₂)_{m = 1}O (p/o) CH₃(CH₂)_{m = 1}O $(CH=N-(CH_2)_n-N=CH$
1

Phase Diagram

Phase diagrams of the pseudoternary system [water– (surfactant–cosurfactant)–hexane] were constructed by the method reported earlier (Fig. 1) [10]. The different microenvironments in the phase diagrams were identified by the conductivity method [10].

Kinetic Measurement

The kinetic measurements were carried out spectrophotometrically using a Shimadzu model UV-



Figure 1 Phase diagram of NaLS-*iso*-butanol-hexanewater system (A) o/w region, (B) bicontinuous region, (C) w/o region [22].

Vis.160A spectrophotometer equipped with a waterjacketed cell compartment at 27°C. For the kinetic measurements, the microemulsions were prepared by mixing NaLS/CTAB (0.6 g), isobutanol (1.8 cm³), and different amount of hexane and water in a 25-cm3 stoppered conical flask and were kept for 30 min to attain equilibrium. Sulfuric acid of varying strength was introduced into the microemulsion to maintain the required acid concentration in the reaction medium. Then Schiff base (SB) in hexane solution ([SB] $\approx 10^{-4}$ M) was added to the microemulsion, and the whole solution was transferred to a quartz cell. The change in optical density (D_t) with time (t) at the respective analytical wavelength (for ortho series Schiff bases, 277 nm, and for para series, 320 nm) was noted. The optical density at infinite time (D_{∞}) was measured after keeping the reaction mixture for 48 h. The first-order rate constants were calculated from the plot of $\log(D_t D_{\infty}$) against time. The kinetic plots yielded a good straight line up to three half-lives (r = 0.999), and duplicate runs reproduced the pseudo-first-order rate constant within an error of $\pm 5\%$. The values of the first-order rate constants under various conditions are given in Tables I–IV.

RESULTS AND DISCUSSION

Schiff bases undergo acid-catalyzed hydrolysis to form the corresponding aldehyde and amine (Scheme I). The reported Schiff bases are insoluble in water;

Sl. No.	$[16-p-2] \times 10^4 \text{ M}$	$k \times 10^3 { m s}^{-1}$ (R)	$[16-o-2] \times 10^4 \text{ M}$	$k \times 10^3 \text{ s}^{-1} (\text{R})$
1	0.142	4.76 (0.9996)	0.235	8.44 (0.999)
2	0.212	4.61 (0.999)	0.705	8.39 (0.9997)
3	0.354	4.48 (0.9992)	1.176	8.23 (0.9997)
4	0.425	4.69 (0.999)	1.411	8.39 (0.9990)
5	0.495	4.61 (0.999)	1.646	8.44 (0.9999)
6	0.566	4.61 (0.9991)	1.881	8.23 (0.9993)
7	0.637	4.45 (0.9996)	_	

Table I First-Order Rate Constants of the Hydrolysis of 16-p/o-2 in ABH w/o Microemulsion at 27°C with Variation of Substrate Concentration; [Acid] = 0.412 N

therefore, the acid hydrolysis has been carried out in microemulsion media so as to provide the appropriate environment to the Schiff bases and the acid.



Scheme I

Spectral Characteristics

The protonated Schiff bases are found to absorb at a higher wavelength than their corresponding Schiff bases. It is noticed that the optical density value at the λ_{max} for protonated Schiff bases (SBH⁺) decreases and that at the λ_{max} value in the region of absorption of Schiff base increases with time (Figs. 2 and 3). The wavelengths of maximum absorption for the Schiff bases and the products are almost in the same region and are not easily distinguishable. The peak heights at the absorption maxima of the Schiff bases go on increasing with time, indicating the formation of the product(s) due to hydrolysis of the protonated Schiff bases. No absorption for the Schiff bases (16-*p*-6 and 16-*o*-6) or their product(s) in both the CBH and ABH mi-

croemulsions is noticed at 30 s of the reaction. Therefore, these compounds are fully protonated and the hydrolysis of the protonated form is slow. With decreasing chain length of the spacer, the λ_{max} for the Schiff base appears in both the microemulsions even at the beginning of the reaction. In acid, the Schiff bases (SB) remain in equilibrium with their protonated forms (SB + H⁺ \rightleftharpoons SBH⁺).

The appearance of the inflection point in all these curves indicates a smooth changeover of the reactants to the products. This is achieved by a one-step mechanism or through the formation of an intermediate getting converted to the products in a fast process. Because the Schiff bases and products absorb approximately at the same wavelength, the decrease in [SBH⁺] and not the increase in [product] has been used for evaluation of rate constants.

Kinetic Results

The acid concentration is always much higher than the concentration of Schiff bases and, therefore, first-order plots have been made with success (r = 0.999). The first-order rate constants are found to remain constant with change in concentration of the Schiff bases. Table I gives the values of the rate constants with the variation in the concentration of 16-p/o-2. To see if the

Table II First-Order Rate Constants of the Hydrolysis of *m-p-2* in w/o and o/w ABH Microemulsions at 27°C with Variation of Alkyl Chain

Sl. No.		$\lambda_{ m max}$ of (SBH ⁺)	w/o ME [Acid	l] = 0.326 N	o/w ME [Acid] = 0.088 N			
	Alkyl Group		$[m-p-2] \times 10^4 \mathrm{M}$	$k \times 10^3 \mathrm{s}^{-1} \mathrm{(R)}$	$[m-p-2] \times 10^4 \mathrm{M}$	$k \times 10^3 { m s}^{-1} ({ m R})$		
1	CH ₃	321	0.507	4.18 (0.999)	0.608	7.48 (0.999)		
2	CH_8H_{17}	323	0.542	2.78 (0.998)	0.488	4.91 (0.999)		
3	$C_{12}H_{25}$	323	0.497	2.84 (0.997)	0.396	4.60 (0.999)		
4	$C_{16}H_{33}$	325	0.568	2.61 (0.999)	0.682	4.91 (0.999)		
5	C ₁₈ H ₃₇	327	0.334	2.79 (0.998)	0.425	4.72 (0.999)		

	[NaLS] M	16- <i>p</i>	- -2	16- <i>o</i> -2		
Point in Phase Diagram		$[16-p-2] \times 10^4 \text{ M}$	$k \times 10^3 \mathrm{s}^{-1} \mathrm{(R)}$	$[16-o-2] \times 10^4 \text{ M}$	$k \times 10^3 \mathrm{s}^{-1} \mathrm{(R)}$	
A ₁ (50% E)	0.531	0.71	8.06 (1.000)	1.14	17.12 (0.997)	
A ₂ (40% E)	0.417	0.71	9.02 (1.000)	1.14	15.98 (0.999)	
A ₃ (30% E)	0.313	0.71	8.06 (1.000)	1.14	16.21 (0.998)	

Table III Rate Constant of the Hydrolysis of 16-p/o-2 in o/w ME at 27°C with Variation of Surfactant (NaLS) Concentration; [Acid] = 0.089 N

hydrophobicity of the alkyl group in the substrate changes the site of the location of the Schiff bases and thereby affects the rate constants, the first-order rate constants are determined with various alkoxy groups in the Schiff bases (m-p-2). The values are found to remain unaltered (Table II) except when m = 1 (methoxy-substituted Schiff base, 1-p/o-n). The rate constant for 1-p-2 is slightly higher than all other Schiff bases. It is therefore clear that 1-p-2 is well exposed to the water surface, whereas the increasing hydrophobicity of the alkoxy group assists in anchoring the aldimine group in the decreasing polar medium in the micellar droplet. Because the boundary is not sharp but blurred, there is water penetration in the micellar medium. The rate constants remain the same for the Schiff bases with m = 8-18, which indicates a similar environment for the chromophoric group of the substrate. The similarity in behavior of these Schiff bases with varying alkoxy chain (octyloxy to octadecyloxy) has been noticed by Behera et al. [14] while carrying out the quenching behavior of the fluorescence of 1alkoxy naphthalene with varying R in w/o and o/w ABH microemulsions. Therefore, these alkoxy groups act merely as targeting groups. However, the rate-constant values are dependent on the spacer chain. These values change in the order $2 \gg 4 > 6$. The *ortho* series compounds are also found to react much faster than the corresponding *para* series compounds. The 16-p/o-2 compounds are able to trap a proton due to the topology of the protophilic groups.

In order to see the effect of surfactant concentration, the first-order rate constants have been evaluated at various [NaLS]. The rate constants are found to remain unaltered with changing [NaLS] (Table III).

It is observed that at any specific concentration of acid, the optical density of SBH⁺ is higher in ABH microemulsion than in CBH microemulsion, clearly indicating the greater extent of protonation of Schiff bases in the former. The ABH microemulsions have a negative charge at the interface and, therefore, a greater proton concentration, resulting in decrease in the pH is expected at the interface. Bissell et al. [2] have observed that the effective proton density near the surface of several anionic micelles changes over 2-3 orders of magnitude compared to the bulk. In CBH microemulsions, proton depletion is natural.

Effect of Variation of Water in ME with [H⁺] Constant

The first-order rate constants have been evaluated with varying $[H_2O]$ and constant $[H^+]$ and are presented in

Table IV Rate Constants with Variation of Water in ABH Microemulsion for the Hydrolysis of 16-p/o-n Keeping [H⁺] Constant at 27° C

Schiff Base			$k \times 10^4 { m s}^{-1}$ at Various Mole Fraction of Water in ABH Microemulsion						on		
	0.12	0.16	0.20	0.26	0.34	0.36	0.40	0.44	0.50	0.56	0.60
16- <i>p</i> -2	26.14	29.91	31.62	41.31	42.43	42.77	42.91	43.12	45.53	51.50	59.62
16- <i>p</i> -4	0.72	0.99	1.25	1.48	1.71	1.66	1.74	1.95	1.85	3.00	3.75
16- <i>p</i> -6	0.65	0.74	0.62	0.98	1.05	1.17	1.25	1.30	1.39	1.47	1.63
16-0-0	25.2	23.3	20.21	15.25	14.26	14.07	14.41	15.99	19.72	23.98	26.83
16-0-2	61.32	66.50	71.25	78.05	80.65	87.50	90.32	90.50	93.40	115.2	120.6
16-0-4	1.92	2.32	2.72	3.25	3.43	3.46	3.42	3.56	3.95	5.92	6.75
16-0-6	1.25	1.54	1.76	2.02	2.64	2.73	3.10	3.33	3.43	3.51	3.62



Figure 2 Successive scans during the hydrolysis of 16-*pn* (n = 2, 3, 4, and 6) in the presence of sulfuric acid in ABH w/o microemulsion at 27°C; direction of arrow is with



Figure 3 Successive scans during the hydrolysis of 16-*o*-n (n = 0, 2, 4, and 6) in the presence of sulfuric acid in ABH w/o microemulsion at 27°C; direction of arrow is with time.

Table IV. The plots of k vs. $n_{\rm H_2O}$ consist of three regions (Fig. 4). The rate constants initially increase with increasing $n_{\rm H_2O}$ for all compounds except for 16o-0 (where it decreases), then levels off with a subsequent sharp rise (which is not observed for 16-p-6

time.

and 16-*o*-6). This behavior reveals the existence of three zones of microemulsions, that is, w/o ME, bicontinuous zone, and o/w ME, which are interconvertible by addition or removal of water (Fig. 1).

w/o Microemulsion
$$\xrightarrow{+H_2O}_{-H_2O}$$
 Bicontinuous $\xrightarrow{+H_2O}_{-H_2O}$ o/w Microemulsion



Figure 4 Plots of $k \times 10^4$ s⁻¹ vs. mole fraction of water for 16-*o*-*n* and 16-*p*-*n* compounds (a: 16-*o*-0; b: 16-*p*-*n*; and c: 16-*o*-*n*).

The polarity and the nucleophilicity of water present at the interface changes with the nature of the zone.

The sharp increase in the rate constants in the water-rich region is attributed to a greater exposure of the reaction site to the nucleophilic water. The 16-o-0 Schiff base does not show a bathochromic shift in acid medium. The compound also does not undergo hydrolysis in the absence of acid. The nature of the plot of k vs. $n_{H_{2O}}$ for the compound indicates that the hydrophilic moiety is in the bulk water pool, in which it undergoes protonation slowly followed by fast hydrolysis of the protonated form. The initial decrease in the rate constant with increasing $n_{H_{2O}}$ in the w/o ME may be due to dilution of acid, whereas the steep increase in the rate constant in o/w ME may be ascribed to increasing availability of nucleophilic water for attack at the protonated aldimine linkage.

It is observed from Table IV that the reactivity of the Schiff bases is of the order 16-p/o-6 < 16-p/o-4

< 16-p/o-2 at all concentrations of water. This may be attributed to the localization site of the Schiff bases. With increasing length of spacer, the hydrophobicity of Schiff bases increases, and, hence, the exposure of the substrate to the water core becomes less. The solubilization study of the Schiff bases also substantiates this proposition [22]. Kevan et al. [23] have carried out photoinduced electron transfer (PET) from (alkoxvphenyl) biphenyl porphyrins (CnOPTPP) to the interface water of anionic aerosol dioctyl AOT and CTAB/alcohol-reversed micelle at 77 K. The photolvsis is found to depend on three factors, namely, (1) Cn alkyl chain length, (2) the interface charge, and (3) the kind of cosurfactant alcohol. Because of increasing hydrophobic interaction between the surfactant alkyl chain length and the alkyl chain of CnOPTPP, the distance between the porphyrin moiety and interface water (D_2O) is supposed to increase. The decrease in the photo-yield confirms this proposition. In the present study, the change of alkyl chain length is not found to influence the rate constant.

CONCLUSION

The model of the microemulsion presented earlier [22] explains satisfactorily the behavior of Schiff bases towards acid-catalyzed hydrolysis. The Schiff bases behave as sensors to study the following:

- 1. The presence of a targeting hydrophobic chain is responsible for anchoring the molecule at the interface.
- 2. A hydrophobic spacer pulls the reaction site away from the interface.
- 3. The extent of the hydrophilic unit protruding into the water is determined by the hydrophobicity of the spacer and not of the targeting chain.

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