Micellization of Alkyltriphenylphosphonium Bromides in Ethylene Glycol and Diethylene Glycol + Water Mixtures: Thermodynamic and Kinetic Investigation

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Abstract The thermodynamics of micellization and other micellar properties of alkyl- $(C_{10}, C_{12}, C_{14}$ and C_{16}) triphenylphosphonium bromides in water + ethylene glycol (EG) (0 to 30% v/v) mixtures over a temperature range of 298 to 318 K and cetyltriphenylphosphonium bromide in water + diethylene glycol (DEG) mixtures (0 to 30% v/v) at 298 K have been studied conductometrically. In all cases, an increase in the percentage of co-solvent results in an increase in the cmc values. On the basis of these results, the thermodynamic parameters, the Gibbs energy (ΔG_m^o) , enthalpy (ΔH_m^o) and entropy (ΔS_m^o) of micellization have been evaluated. In addition to the conductivity measurements, kinetic experiments have also been done to determine the dependence of observed rate constant for the nucleophilic substitution reaction of *p*-nitrophenyl acetate and benzohydroxamate ions in the presence of the surfactant cetyltriphenylphosphonium bromide with a varying concentration of EG and DEG ranging from 0 to 50% v/v at pH = 7.9 and 300 K. All of the reactions followed pseudo-first-order kinetics. An increase in the surfactant concentration results in an increase in the reaction rate and for a given surfactant concentration, the rate constant decreases as the concentration of co-solvent in the mixture increases. The kinetic micellar effects have been explained by using the pseudophase model. The thermodynamic and structural changes originating from the presence of solvents control the micellar kinetic effects.

Keywords Critical micelle concentration · Solvent effect · Kinetics · Alkyltriphenylphosphonium bromide · Pseudophase model

1 Introduction

Much effort has been devoted to exploring the nature of micellization and surfactant behavior in polar organic solvents and solvent mixtures [1-8]. Changing the solvent composition

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provides an opportunity to study the role of the so-called solvophobic effect, in contrast to the hydrophobic effect in micellization [9]. The term "solvophobic interaction" has been coined to describe micellization in non-aqueous polar solvents, by analogy with hydrophobic interactions responsible for aggregation in water [10]. However, the ability of water to form unique hydrogen-bonded networks is not a necessary condition for the aggregation process. The micelles formed in non-aqueous solvents are similar in many aspects to the micelles that are formed in water, although, micelle formation is not as favored in such non-aqueous solvents for a given surfactant [11, 12]. Among the organic solvents studied so far, ethylene glycol (EG) is of particular interest as it has many characteristics similar to those of water, and therefore the study of the aggregation behavior of surfactants in water + EG mixtures provides a better understanding of the function of the liquid structure in the micellization process.

The majority of fundamental studies of the solvent effect on cationic surfactants have been made with alkyltrimethylammonium bromides and alkylpyridinium bromides [13, 14]. By comparison to these other surfactants, alkyltriphenylphosphonium bromide have not been given their due attention. The micellization behavior of binary combinations of alkyltrimethylammonium bromides has been studied by Palepu et al. [15, 16]. Recently, Palepu et al. [17] studied micellar and associated thermodynamic properties of binary mixtures of alkyltriphenylphosphonium bromides in EG + water mixtures. In the present study, we have used C₁₀-, C₁₂-, C₁₄- and C₁₆-TPB to obtain thermodynamic and structural information about water + EG and water + DEG micellar solutions. Critical micelle concentrations (cmc) and micellar ionization degrees, α , were obtained from conductivity measurements. The standard Gibbs energy, enthalpy and entropy changes for micellization, ΔG_m° , ΔH_m° and ΔS_m° , respectively, have also been determined to study the energetics of micellization reactions.

To extend our knowledge of the properties of water + ethylene glycol and water + diethylene glycol micellar solutions as reaction media, the nucleophilic substitution reaction of *p*-nitrophenyl acetate was studied in cetyltriphenylphosphonium bromide solutions. The kinetic micellar effects will be due to the micellar concentration effect. This effect depends upon the transfer of the substrate from the bulk solution to the micelle, upon the reaction mechanism, and upon the properties of the interfacial region such as local charge, polarity and water content. A study of this effect thereby gives information about the micellar pseudophase characteristics as a reaction media. Comparisons between the observed rate constants in water and in the micellar pseudophases in water + EG and water + DEG micellar solutions can be done directly, and hence provide information about the characteristics of the micellar pseudophase where the reaction occurs.

2 Experimental Section

2.1 Materials

Benzohydroxamic acid was prepared by a literature method [18, 19]. *p*-Nitrophenyl acetate was obtained from SD fine chemicals. The surfactants employed in this study are decyl (C_{10} TPB), dodecyl (C_{12} TPB), tetradecyl (C_{14} TPB), and hexadecyl (C_{16} TPB) triphenylphosphonium bromides, and were obtained from Caldon Chemicals Canada (distributors for Lancaster Synthesis of England). The surfactants were purified as described earlier [15]. Freshly opened bottles of EG and DEG (Qualigens) were employed in our study. Binary solutions were prepared employing triply distilled and deionized water.

2.2 Conductivity Measurements

The conductivity experiments were performed on a CDM 83 conductivity bridge operating at 1000 Hz, with a platinum cell. The cell constant was 0.978 cm^{-1} . A conductometric titration method was employed. This method involves titrating a known volume of a surfactant solution into 10 mL of the solvent, which is contained in a thermostatted, jacketed beaker. For the pure surfactants in the presence of aqueous ethylene glycol, these titrations were carried out from 298 to 318 K at 5 K increments.

2.3 Kinetics

The reactions were investigated at 300.2 ± 0.2 K with a Varian Cary-50 spectrophotometer and a Systronics (Type-104) spectrophotometer. The reactions were followed by monitoring the decreasing concentrations of the reactant *p*-nitrophenoxide at 400 nm. All of the kinetic experiments were performed at an ionic strength of 0.1 mol·L⁻¹ (controlled with KCl). A phosphate buffer was employed to control the solution pH. All reactions were conducted under pseudo-first-order rate conditions. For all of the kinetic runs, the absorbance versus time results were fit very well to the first-order-rate equation

$$\ln(A_{\infty} - A_t) = \ln(A_{\infty} - A_0) - kt.$$
⁽¹⁾

The pseudo-first-order rate constants were determined by the method of least squares. Each experiment was repeated at least twice, and the observed rate constant was found to be reproducible within a precision of about 3% or better.

3 Results and Discussion

3.1 Micellar Properties in Aqueous Ethylene Glycol and Aqueous Diethylene Glycol Solutions

Conductivity studies were performed on the surfactants in the presence of ethylene glycol over a range of temperatures (298 to 318 K) in order to determine the dependency of the thermodynamic properties for molecular assembly on the chain length, additives, and temperature. The specific conductivity was plotted as a function of the surfactant concentration in order to determine the cmc and counter-ion binding/ionization for the surfactants at each temperature. Figure 1 shows the conductivity plot for the C_{10} TPB surfactant at 298.15 K in water, and in 5% and 10% v/v EG solutions. As indicated in this plot, the cmc value increases with increasing concentration of EG. Similar behavior was observed in all other cases. Figure 2 depicts the effect of temperature on the cmc values for C_{12} TPB in 10% EG. The cmc values as a function of the EG percent are presented in Table 1. The degree of dissociation of the micelles (α) in the mixed solvent system exhibited very little dependence on temperature, and therefore the average value of α was used for the calculation of $\Delta G_{\rm m}^{\rm o}$ at all temperatures. It was found that the cmc values of the surfactants decrease with increasing hydrocarbon chain length at any given temperature, as can be seen in Table 1. Therefore, as the chain length increases, micelles form at lower concentrations of the surfactant due to a more pronounced hydrophobic effect.

The cmc values of the surfactants were found to increase in the presence of ethylene glycol, as can be seen in Table 1. Ethylene glycol is a structure breaker, breaking up the structure



Fig. 1 Plots of the specific conductivity (κ) versus [C₁₀TPB] at different volume-% of EG



Fig. 2 Plots of the specific conductivity (Specific conductivity ($\kappa/\mu \text{ s cm}^{-1}$)) versus [C₁₂TPB] at different temperatures in the presence of 10% (v/v) EG

Surfactant	Temperature (K)	CMC in aqueous media ^a (mmol·L ⁻¹)	$\begin{array}{c} \text{CMC in} \\ 5\% \ (v/v) \\ \text{ethylene} \\ \text{glycol} \\ (\text{mmol}\cdot\text{L}^{-1}) \end{array}$	$\alpha_{\rm av}$	$\begin{array}{c} \text{CMC in} \\ 10\% \ (v/v) \\ \text{ethylene} \\ \text{glycol} \\ (\text{mmol}\cdot\text{L}^{-1}) \end{array}$	α _{av}	$\begin{array}{c} \text{CMC in} \\ 30\% \ (v/v) \\ \text{ethylene} \\ \text{glycol} \\ (\text{mmol} \cdot \text{L}^{-1}) \end{array}$
C ₁₀ TPB	298	7.21	9.36	0.590	10.2	0.600	
	303		9.28		10.8		
	308		9.44		11.3		
	313		9.76		11.4		
	318		10.0		12.0		
C ₁₂ TPB	298	1.82	2.15	0.640	2.17	0.645	
	303		2.25		2.65		
	308		2.40		2.73		
	313		2.63		2.88		
	318		2.70		2.92		
C ₁₄ TPB	298	0.58	0.65	0.692	0.71	0.694	
	303		0.66		0.76		
	308		0.68		0.85		
	313		0.73		1.10		
	318		0.76		1.15		
C ₁₆ TPB	298	0.14	0.219	0.690	0.28	0.696	0.68
	303		0.220		0.30		0.75
	308		0.221		0.37		0.78
	313		0.222		0.38		0.87
	318				0.40		0.87

Table 1 Cmc and α_{av} values of the ATPBs, determined by conductivity method in the presence of ethylene glycol

^aTaken from [15]

of the water molecules around the hydrophobic chains, thus decreasing the hydrophobic effect and consequently increasing the cmc value. As the temperature increases, the resulting increase in thermal motion of the water molecules further decrease the hydrophobic effect, resulting in increasing cmc values.

Values of the cmc and counter-ion dissociation for the surfactant C₁₆TPB in 10% (v/v) DEG are given in Table 2. The values for counter-ion binding ($\beta = 1 - \alpha_{av}$) generally decrease with increasing temperature. As the temperature increases, micelles form at higher surfactant concentrations. Therefore, fewer micelles will be present at higher temperatures and fewer counter-ions will be needed to reduce the head group repulsions.

3.2 Thermodynamics of Micellization

Thermodynamic values for the micellization reaction were calculated using equations derived from the charged pseudophase separation model. In this model, micelles are considered to be a new soluble phase formed in the system at and above the cmc. The cmc can therefore be thought of as the solubility limit of the monomers.

The Gibbs energy of micellization for each surfactant in its aqueous solution, and in the presence of 5% (v/v) and 10% (v/v) ethylene glycol, was calculated with the following

Table 2 Cmc and α_{av} values ofthe C_{16} TPB determined byconductivity method in thepresence of diethylene glycol	Surfactant	factant Temperature $CMC \text{ in } 10\% (v/v)$ (K) diethylene glycol $(mmol \cdot L^{-1})$		α
	C16TPB	298 308	0.36 0.40	0.51
		318	0.46	0.68



Fig. 3 Variation of $\ln X_{cmc}$ of C_{12} TPB in 10% (v/v) ethylene glycol with temperature

equation [20, 21]:

$$\Delta G_{\rm m}^{\rm o} = (2 - \alpha) RT \ln X_{\rm cmc} \tag{2}$$

where α is the degree of dissociation, *R* is the gas constant, *T* is temperature, and X_{cmc} is the cmc value on the mole fraction scale [14]. Densities of the binary mixtures were measured using an Anton Parr DMA 5000 density meter and were used to convert the molar concentration units to the mole fraction scale.

The enthalpies of micellization [14] were calculated using Eq. 3:

$$\Delta H_{\rm m}^{\rm o} = -(2-\alpha)RT^2 \left(\frac{\partial \ln X \rm cmc}{\partial T}\right). \tag{3}$$

Therefore, if the dependence of the cmc values on temperature is known, a plot of $\ln X_{\rm cmc}$ versus temperature can be constructed. The slope can then be found at each temperature. These plots were found to be best fit with a second-order polynomial ($r^2 = 0.99$). A typical plot for C₁₂TPB in 10% (v/v) ethylene glycol is presented in Fig. 3. The entropies of

Surfactant	Temperature (K)	$\Delta G_{\rm m}^{\rm o}$ (kJ·mol ⁻¹)	$\Delta H_{\rm m}^{\rm o}$ (kJ·mol ⁻¹)	$\Delta S_{\rm m}^{\rm o} \\ (J \cdot {\rm K}^{-1} \cdot {\rm mol}^{-1})$
C ₁₀ TPB	298	-31.5	14.5	154
	303	-32.2	4.1	119
	308	-32.7	-7.0	83
	313	-33.0	-18.8	45
	318	-33.1	-31.4	5
C ₁₂ TPB	298	-34.6	12.3	157
	303	-35.5	3.0	127
	308	-36.0	-6.9	94
	313	-36.1	-17.5	59
	318	-36.6	-28.8	25
C ₁₄ TPB	298	-37.7	-8.0	89
	303	-38.2	-12.4	76
	308	-38.4	-16.5	63
	313	-38.8	-20.3	50
	318	-39.0	-24.8	37
C ₁₆ TPB	298	-42.2	8.7	170
	303	-42.1	4.9	155
	308	-42.3	0.8	140
	313	-42.6	-3.5	125
	318	-43.0	-8.1	110
	Surfactant C ₁₀ TPB C ₁₂ TPB C ₁₄ TPB C ₁₆ TPB	$\begin{tabular}{ c c c c } \hline Surfactant & Temperature & (K) \\ \hline C_{10}TPB & 298 & & & & & & & & & & & & & & & & & & &$	$\begin{array}{c cccccc} Surfactant & Temperature & ΔG^{o}_{m} \\ (K) & (kJ \cdot mol^{-1}) \\ \hline C_{10}TPB & 298 & -31.5 \\ 303 & -32.2 \\ 308 & -32.7 \\ 313 & -33.0 \\ 318 & -33.1 \\ \hline C_{12}TPB & 298 & -34.6 \\ 303 & -35.5 \\ 308 & -36.0 \\ 313 & -36.1 \\ 318 & -36.6 \\ \hline C_{14}TPB & 298 & -37.7 \\ 303 & -38.2 \\ 308 & -38.4 \\ 313 & -38.8 \\ 318 & -39.0 \\ \hline C_{16}TPB & 298 & -42.2 \\ 303 & -42.1 \\ 308 & -42.3 \\ 313 & -42.6 \\ 318 & -43.0 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

micellization were then calculated from Eq. 4:

$$\Delta S_{\rm m}^{\rm o} = \frac{\Delta H_{\rm m}^{\rm o} - \Delta G_{\rm m}^{\rm o}}{T} \tag{4}$$

The thermodynamics of micellization were calculated for the pure surfactants in aqueous solution as well as in the presence of 5% (v/v) and 10% (v/v) ethylene glycol. The parameter values obtained are given in Tables 3 and 4. The errors in the Gibbs energy and enthalpy values are estimated to be ± 0.5 kJ·mol⁻¹, whereas the error in the entropy values is ± 5 J·K⁻¹·mol⁻¹. It is evident that the Gibbs energies of micellization decrease as the hydrocarbon chain length increases. As previously mentioned, the Gibbs energies of micellization give a measure of the ability for micelle formation. It was found that the cmc values decrease with increasing chain length, and the Gibbs energies of micellization follow the same trend. This indicates an increased hydrophobic effect for the longer chain surfactants.

The Gibbs energies of micellization become more negative with increasing temperature in pure water, and also in the presence of co-solvents, for all of the studied surfactants. This results because the change in size of the logarithm of the cmc is more than compensated for by the *RT* term in Eq. 2.

It can be seen from Tables 3 and 4 that the enthalpies of micellization become more negative with increasing temperature for each surfactant in each solvent. However, the enthalpies calculated from Eq. 3 could differ from the values determined calorimetrically. The equation employed to determine the Gibbs energies is only applicable if the aggregation numbers are

Table 1 Thermodynamic					
parameters of the ATPBs in 10% (v/v) ethylene glycol	Surfactant	Temperature (K)	e $\Delta G_{\rm m}^{\rm o}$ (kJ·mol ⁻	$\Delta H_{\rm m}^{\rm o}$ ¹) (kJ·mol ⁻¹)	$\Delta S_{\rm m}^{\rm o}$ (J·K ⁻¹ ·mol ⁻¹)
	C10TPB	298	-29.5	9.1	129
	- 10	303	-29.8	4.0	112
		308	-30.1	-1.3	93
		313	-30.6	-7.0	75
		318	-30.9	-13.1	56
	C ₁₂ TPB	298	-31.9	-15.4	55
		303	-31.8	-17.8	46
		308	-32.2	-20.4	38
		313	-32.5	-23.2	30
		318	-33.0	-26.1	22
	C ₁₄ TPB	298	-37.4	-5.0	109
		303	-37.8	-11.5	87
		308	-38.0	-18.0	65
		313	-38.1	-24.7	43
		318	-38.2	-31.6	21
	C ₁₆ TPB	298	-39.9	11.4	172
		303	-40.2	4.8	148
		308	-40.3	-2.4	123
		313	-40.8	-10.0	98
		318	-41.3	-18.2	73
Table 5 Thermodynamic	Surfactant	0%		me	ΛC^0
parameters of the CTPBs in the presence of diethylene glycol at 298 K	Surractant	/// (v/v	i) ($(\text{mmol}\cdot\text{L}^{-1})$	$(kJ \cdot mol^{-1})$
	C ₁₆ TPB	10	().36	-40.6
		20	().49	-41.6
		30	(0.52	-42.0

large, and activities are assumed to be equal to their concentrations because the solutions are so dilute. Therefore, the obtained thermodynamic values should be viewed as approximate. However, generalizations can still be drawn from the data.

The data indicate that the micellization is favored in general by both the entropy and enthalpy terms at higher temperatures, whereas it is favored mainly by entropy at lower temperatures.

From Table 5 it can be seen that the cmc values increase with increasing volume-% of diethylene glycol. As the amount of diethylene glycol in the media increases, the structure of the water molecules around the hydrophobic chains becomes destroyed, resulting in the observed increase of the cmc. The Gibbs energies of micellization were found to become more negative with increasing concentration of diethylene glycol.

Table 6 Kinetic data for the nucleophilic substitution reaction of *p*-nitrophenyl acetate and benzohydroxa-
mate ion in the presence of water + EG micellar solutions of cetyltriphenyl-phosphonium bromide cationic
surfactants at 300 K

[C ₁₆ PPh3Br]	$k_{\rm obs} 10^3 / {\rm s}^{-1}$									
$(\text{mmol}\cdot\text{L}^{-1})$	0% (v/v) EG		10% (v/v)	EG	30% (v/v) EG		50% (v/v) EG			
	Without BHA	With BHA	Without BHA	With BHA	Without BHA	With BHA	Without BHA	With BHA		
0	0.05	9.84	0.15	6.90	0.22	3.24	0.29	0.27		
0.6	0.07	23.4	0.17	15.4	0.25	6.68	0.31	2.70		
1.0	-	35.0	-	22.1	-	9.00	-	3.40		
1.8	0.11	51.7	0.21	29.5	0.29	8.49	0.38	3.45		
2.5	-	57.5	_	36.0	_	15.0	_	3.60		
3.6	0.13	64.0	0.31	43.6	0.42	18.4	0.53	4.80		
5.5	-	73.3	_	53.0	_	23.5	_	5.50		
7.5	_	73.5	_	57.9	_	26.9	_	5.90		
9.1	0.14	74.7	0.37	58.6	0.53	27.9	0.59	6.08		

Conditions: pH 7.9, $\mu = 0.1 \text{ mol} \cdot \text{L}^{-1} \text{ KCl}$, [PNPA] = $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, [BHA] = $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, and p K_a of BHA = 8.8

3.3 Kinetic Studies in Water + Ethylene Glycol and Water + Diethylene Glycol Micellar Media

All of the kinetic reactions in the present study obeyed pseudo-first-order rate kinetics, where the concentration of the nucleophile is generally ten times greater than that of the substrate. Pseudo-first-order rate constants (k_{obs}) for the nucleophilic reaction of *p*-nitrophenyl acetate and benzohydroxamate ion (Scheme 1) in water + ethylene glycol and water + diethylene glycol micellar solutions of cetyltriphenylphosphonium bromide are summarized in Tables 6 and 7.

The observed rate constants (k_{obs}) increase with increasing surfactant concentration, and then gradually level off. This dependence of the observed rate constant can be explained by considering that an increase in surfactant concentration results in further incorporation of the substrate, i.e., *p*-nitrophenyl acetate, into the micelles where the benzohydroxamate ion concentration is higher than that in the bulk phase (because cationic micelles bind anionic nuceophiles). For a given surfactant concentration, the observed rate constant decreases as the concentration of EG and DEG in the solvent mixture increases. These variations in k_{obs} upon changing the concentrations of EG and DEG should reflect thermodynamically the structural changes produced in the micellar solutions by the presence of different amounts of the organic solvent. The decrease of rate constants resulting from addition of an organic solvent to water can be explained by taking into account the fact that its presence diminishes

[C ₁₆ PPh3Br]	$k_{\rm obs} 10^3 / {\rm s}^{-1}$								
$(\text{mmol}\cdot L^{-1})$	0% (v/v) DEG		10% (v/v)	DEG	30% (v/v) DEG		50% (v/v) DEG		
	Without BHA	With BHA	Without BHA	With BHA	Without BHA	With BHA	Without BHA	With BHA	
0	0.05	9.84	0.11	7.53	0.16	3.88	0.21	2.56	
0.6	0.07	23.4	0.14	18.2	0.18	7.05	0.26	2.97	
1.0	_	35.0	_	23.1	_	8.60	_	3.51	
1.8	0.11	51.7	0.18	31.6	0.24	9.05	0.31	3.7	
2.5	_	57.5	_	38.8	_	16.1	_	4.32	
3.6	0.13	64.0	0.26	44.7	0.32	19.2	0.48	4.93	
5.5	_	73.3	_	54.4	-	23.6	_	5.60	
7.5	_	73.5	_	58.1	_	26.6	_	6.51	
9.1	0.14	74.7	0.32	59.3	0.4	28.0	0.52	6.75	

Table 7 Kinetic data for the nucleophilic substitution reaction of p-nitrophenyl acetate and benzohydroxa-
mate ion in the presence of water + DEG micellar solutions of cetyltriphenyl-phosphonium bromide cationic
surfactants at 300 K

Conditions: pH 7.9, $\mu = 0.1 \text{ mol} \cdot \text{L}^{-1} \text{ KCl}$, [PNPA] = $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, [BHA] = $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, and pK_a of BHA = 8.8



benzohydroxamate ion

Scheme 1 Nucleophilic substitution reaction of PNPA and BHA in presence of surfactant

the water content and decreases the polarity of the reaction medium. A decrease in polarity results in a large destabilization of the polar transition state, with respect to the initial state, thus retarding the reaction.







3.4 The Pseudophase Model

Reactivity occurring in association colloids has been thoroughly studied during the past several decades [22–25]. It is widely accepted that the rate enhancements observed in these aggregated systems are largely the result of increases in concentration of reactants in the interfacial volumes where the reactions occur [24–27]. Quantitative treatments of reactivity in association colloids frequently are based on the pseudophase model [26–28]. One of the basic assumptions of this model is that the aggregate constitutes a pseudophase, separated from the bulk solution where it is dispersed, so that reagents partition between the bulk phase and the aggregate pseudophase. Thus, bimolecular nucleophilic reactions can be described as illustrated in Scheme 2.

In Scheme 2, subscripts "bulk" and "m" indicate the aqueous and water + EG and micellar pseudophase, respectively, and D_n represents the micellized surfactant. That is, $[D_n] = [D_T]$ - cmc, where $[D_T]$ is the stoichiometric surfactant concentration and cmc is the measured critical micelle concentration obtained under the experimental conditions (i.e., in varying amounts of EG and DEG in the solvent mixtures; the cmc is the minimum surfactant concentration required to observe any kinetic effect). Scheme 2 considers the distribution of PNPA between the aqueous bulk phase (aqueous and water + EG) and micellar pseudophase, K_m^{PNPA} . The distribution of the benzohydroxamate ion, BHA, between both pseudophases is considered through the distribution constant K_m^{BHA} . The different reactivities in the bulk and micellar pseudophases have been taken into account through the corresponding second-order rate constants k_2^{bulk} and k_2^{m} . The values of k_2^{bulk} were obtained by studying the reaction in the absence of surfactants.

The concentration of hydroxamate in the micellar pseudophase has been defined as the local molar concentration within the micelle pseudophase: $[HA]_T = [HA]_m/D_n \overline{V}$, where \overline{V} is the molar volume in dm³·mol⁻¹ of the reaction region and $[D_n]\overline{V}$ denotes the fractional volume of the micelle in which the reaction occurs. We assume that \overline{V} is equal to the partial molar volume of the interfacial reaction region in the micellar pseudophase. Micellar binding of both substrates, PNPA and the benzohydroxamate ion, is governed by hydrophobic interactions, and the equilibrium constants K_m^{PNPA} and K_m^{BHA} are expressed by referring these concentrations to the total volume of the micelle. The observed rate constant, k_{obs} , based on Scheme 2 and the above considerations, is given by the following equation:

$$k_{\rm obs} = \frac{k_2^{\rm bulk} + \frac{k_2^{\rm m}}{\nabla} K_{\rm m}^{\rm PNPA} K_{\rm m}^{\rm BHA}[D_n]}{(1 + K_{\rm m}^{\rm PNPA}[D_n])(1 + K_{\rm m}^{\rm BHA}[D_n])} [\text{BHA}]_T.$$
(5)

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Fig. 4 Simulated rate-surfactant profiles for the reaction of *p*-nitrophenyl acetate and benzohydroxamate ion in the presence of C₁₆TPB in water + EG mixtures (*lines* are predicted values with model, $\bigcirc -0\%$, $\bigcirc -10\%$, $\bigcirc -30\%$, $\blacksquare -50\%$)



Fig. 5 Simulated rate-surfactant profiles for the reaction of *p*-nitrophenyl acetate and benzohydroxamate ion in the presence of C_{16} TPB in water + DEG mixtures (*lines* are predicted values with model, $\bigcirc -0\%$, $\bigcirc -10\%$, $\bigcirc -30\%$, $\blacksquare -50\%$)

	0% (v/v)	10% (v/v)		30% (v/v)		50% (v/v)	
		EG	DEG	EG	DEG	EG	DEG
$k_2^{\rm W}/({\rm M}^{-1}{\rm s}^{-1})$	91.9	61.6	70.3	28.9	36.2	20.1	23.9
$K_{\rm m}^{\rm PNPA}/({\rm M}^{-1})$	440	90	150	95	120	90	110
$K_{\rm m}^{\rm HA}/({\rm M}^{-1})$	28.1	60	32.3	20	8.7	10	7.4
$k_2^{\rm m}/({\rm M}^{-1}{\rm s}^{-1})$	5.0	4.1	5.2	4.0	7.8	1.6	1.9

Table 8 Kinetic parameters obtained by applying pseudophase model for the nucleophilic reaction of PNPA with benzohydroxamate ions in the presence of C_{16} TPB cationic micelles

When the data in Tables 6 and 7 are fitted with Eq. 5, Figs. 4 and 5 are obtained. The agreement between the experimental data and the fitted model is good. This indicates that the pseudophase model is valid.

The results presented in Table 8 allow us to study the influence of the nature of the micelles on the reaction of PNPA with varying concentrations of ethylene glycol and diethylene glycol. The micellar binding constants of PNPA and BHA in the C₁₆TPB micelle provide conclusive information on the reactivity patterns. This association constant of PNPA is obtained by fitting experimental data in micellar systems with the value of $K_m^{PNPA} = 440 \text{ L} \cdot \text{mol}^{-1}$ for C₁₆TPB micellar systems obtained in the absence of EG and DEG. The values of the distribution constants of BHA decrease with increasing concentrations of EG and DEG in the reaction medium. Taking into account these micellar parameters, the changes in the polarity of the interfacial region and aggregation number of the micelles are the key factors for the decrease in k_{obs} values observed in the presence of these solvents.

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