

# Effects of salts and mixed aqueous-acetonitrile solvent on the rate of alkaline hydrolysis of 4-nitrophthalimide in the presence of cationic micelles

M. Niyaz Khan\*, Rodhiah Musa

Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

Received 15 August 2001; accepted 8 October 2001

## Abstract

Pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for alkaline hydrolysis of 4-nitrophthalimide decrease with the increase in  $[\text{CTABr}]_{\text{T}}$  (total concentration of cetyltrimethylammonium bromide) at constant  $[\text{CH}_3\text{CN}]$  and  $[\text{NaOH}]$ . This micellar effect is explained in terms of pseudophase model of micelle. The increase in the content of  $\text{CH}_3\text{CN}$  from 5 to 15% v/v decreases CTABr micellar binding constant ( $K_{\text{S}}$ ) of ionized 4-nitrophthalimide ( $\text{NPT}^-$ ) from 3650 to 370  $\text{M}^{-1}$ , increases the critical micelle concentration (cmc) from  $2.8 \times 10^{-4}$  to  $7.0 \times 10^{-4}$  M and decreases the pseudo-first-order rate constants ( $k_{\text{M}}^{\text{h}}$ ) for hydrolysis of  $\text{NPT}^-$  in the micellar pseudophase from  $3.57 \times 10^{-4}$  to  $2.24 \times 10^{-4}$   $\text{s}^{-1}$ . The rate constants  $k_{\text{obs}}$ , obtained at constant  $[\text{NaOH}]$ ,  $[\text{CH}_3\text{CN}]$ ,  $[\text{CTABr}]_{\text{T}}$  and varying concentrations of NaX ( $\text{X}^- = \text{Br}^-$  and  $\text{Cl}^-$ ), follow the relationship:  $k_{\text{obs}} = (k'_0 + \theta K[\text{NaX}]) / (1 + K[\text{NaX}])$ , where  $\theta$  and  $K$  are empirical parameters. The values of  $\theta$  and  $K$  are explained in terms of pseudophase model of micelle coupled with an empirical relationship:  $K_{\text{S}} = K_{\text{S}}^0 / (1 + K_{\text{X/S}}[\text{NaX}])$ , where  $K_{\text{S}}$  is the CTABr micellar binding constant of  $\text{NPT}^-$  in the presence of NaX. The value of  $K_{\text{Br/S}}/K_{\text{Cl/S}} (= K_{\text{Br}}^{\text{Cl}})$  is 3.5. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** 4-Nitrophthalimide; Base; Hydrolysis; Kinetics; Salts; Mixed solvents; Micelles; Cationic surfactants

## 1. Introduction

The occurrence of ion-exchange in ionic micellar-mediated semi-ionic reactions was realized nearly three decades before by the studies on the effects of micelles on the reaction rates [1]. Romsted [2] proposed pseudophase ion-exchange (PIE) model to explain such kinetic observations quantitatively. Some of the weaknesses of PIE model were detected soon after its development and consequently a few additional kinetic models [3] have been proposed to explain the kinetic data which could not be explained in terms of PIE model. Some more general weaknesses of PIE

model which could be due to over-parameterization in its treatment have been realized recently [4,5].

Pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for methanolysis [6], *n*-butylaminolysis and piperidinolysis [7] of ionized phenyl salicylate ( $\text{PS}^-$ ) in the presence of cetyltrimethylammonium bromide (CTABr) resulted in CTABr micellar binding constants ( $K_{\text{S}}$ ) of  $\text{PS}^-$  which showed the variation with inert salt concentration ( $[\text{MX}]$ ) according to the following empirical equation:

$$K_{\text{S}} = \frac{K_{\text{S}}^0}{1 + K_{\text{X/S}}[\text{MX}]} \quad (1)$$

where  $K_{\text{S}}^0 = K_{\text{S}}$  at  $[\text{MX}] = 0$  and  $K_{\text{X/S}}$  is an empirical parameter whose magnitude is the measure of the

\* Corresponding author.

E-mail address: niyaz@kimia.um.edu.my (M. Niyaz Khan).

ability of  $X^-$  to expel  $S^-$  from cationic micellar pseudophase to the aqueous pseudophase. The validity of Eq. (1) has been verified by a few other related studies involving  $X^-/PS^-$  [8–10] and  $X^-/PT^-$  [11,12] ion-exchange processes ( $PT^-$  represents anionic phthalimide).

The effects of mixed aqueous-organic solvents on rate of methanolysis [13], ethanediolysis [14] of  $PS^-$  and alkaline hydrolysis of phenyl benzoate [15] have been reported. The increase in critical micelle concentration (cmc) and decrease in  $K_S$  with the increase in the contents of organic co-solvents have been shown to follow empirical linear equations.

Eq. (1) is an empirical equation and hence its generality must be tested under variety of experimental conditions, especially the one which involves exchanging ions of considerably different hydrophobicity and structural features. Anionic 4-nitrophthalimide ( $NPT^-$ ) is expected to be more hydrophobic than  $PT^-$  and it is different from  $PS^-$  in terms of structural aspects. We, therefore, decided to test the validity of Eq. (1) by using ion-exchange  $X^-/NPT^-$  and the validity of empirical equations exhibiting the effects of mixed  $H_2O-CH_3CN$  solvents on cmc and  $K_S$  in the presence of CTABr micelles. Thus, the effects of [NaCl], [NaBr] and mixed  $H_2O-CH_3CN$  solvents on the rate of alkaline hydrolysis of anionic 4-nitrophthalimide in the presence of CTABr micelles have been studied and the observed results and their probable explanation(s) are described in this paper.

## 2. Experimental section

### 2.1. Materials

Reagent grade chemicals such as 4-nitrophthalimide, CTABr, and inorganic salts were supplied by Fluka, BDH or Aldrich and were of the highest commercially available purity. All other chemicals used were also of reagent grade. The stock solutions (0.01 M) of 4-nitrophthalimide were prepared in acetonitrile.

### 2.2. Kinetic measurements

The rate of alkaline hydrolysis of 4-nitrophthalimide was studied by monitoring the disappearance of reactant, 4-nitrophthalimide, spectrophotometrically at 260 nm as a function of reaction time in the presence

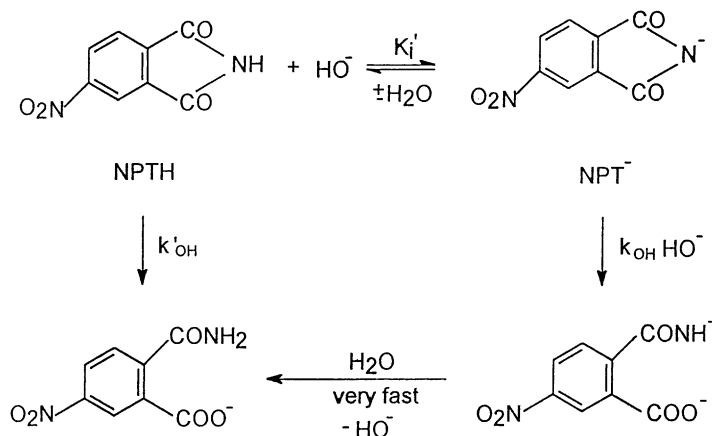
of CTABr micelles. The details of the kinetic procedure, and data analysis were same as described elsewhere [16].

## 3. Results and discussion

All the kinetic runs were carried out at 0.01 M NaOH and within the  $[CTABr]_T$  (total concentration of cetyltrimethylammonium bromide) range of 0.0 to  $\leq 0.10$  M. 4-Nitrophthalimide molecules are expected to remain in fully ionized form ( $NPT^-$ ) because under similar conditions, phenyl salicylate (PSH) molecules exist in fully ionized form and  $pK_a$  of phenyl salicylate and 4-nitrophthalimide are 9.09 and 8.51, respectively, in the absence of CTABr micelles at 35 °C. The rate of hydrolysis of 4-nitrophthalimide at 0.01 M NaOH and  $[CTABr]_T = 0$  follows kinetic equation:  $k_{obs} = k_0 + k_{OH}[HO^-]$ , where  $k_{obs}$  is pseudo-first-order rate constant for alkaline hydrolysis of 4-nitrophthalimide,  $k_0 (= 2 \times 10^{-3} s^{-1})$  represents rate constant for pH-independent hydrolysis of 4-nitrophthalimide, and  $k_{OH} (= 46.3 \times 10^{-3} M^{-1} s^{-1})$  is the rate constant for the reaction between  $HO^-$  and  $NPT^-$  [17]. A brief reaction scheme for alkaline hydrolysis of 4-nitrophthalimide under the present reaction conditions may be shown in Scheme 1. A huge amount of kinetic data on micellar-mediated organic reactions reveals that the reaction mechanism of a particular reaction is generally same in both aqueous and micellar pseudophase. Thus, we presume the occurrence of the same reaction mechanism in both aqueous and micellar pseudophases for alkaline hydrolysis of 4-nitrophthalimide under the present reaction conditions. It should be noted that pH-independent rate of hydrolysis of 4-nitrophthalimide is governed by the rate law:  $rate = k'_{OH}[HO^-][NPTH]$ , where NPTH represents nonionized 4-nitrophthalimide. Thus,  $k_0 = k'_{OH}K_W/K_a$ , where  $K_W = [HO^-][H^+]$  and  $K_a = [NPT^-][H^+]/[NPTH]$ . The values of  $k_0$  and  $k_{OH}$  show that the contribution of  $k_0$  and  $k_{OH}$  towards  $k_{obs}$  at 0.01 M NaOH are 80 and 20%, respectively.

### 3.1. Effect of mixed $H_2O-CH_3CN$ solvent on the rate of alkaline hydrolysis of $NPT^-$ in the presence of CTABr micelles

Several kinetic runs were carried out within the  $[CTABr]_T$  range  $6 \times 10^{-5}$  to 0.03 M at 0.01 M NaOH,



Scheme 1.

5% v/v CH<sub>3</sub>CN,  $1 \times 10^{-4}$  M NPT<sup>-</sup> and 35 °C. Similar observations were obtained at 8, 10 and 15% v/v CH<sub>3</sub>CN. These observations show an approximate monotonic decrease in  $k_{obs}$  with the increase in [CTABr]<sub>T</sub> at its value >cmc under a constant [NaOH], [NPT<sup>-</sup>], % v/v content of CH<sub>3</sub>CN and temperature. Such an effect of [CTABr]<sub>T</sub> on  $k_{obs}$  is generally explained in terms of pseudophase model (PM) of micelle [18]. The general reaction scheme in view of PM model of micelle and observed rate law (rate =  $k_{obs}[NPT^-]_T$ , where  $[NPT^-]_T = [NPT^-]_W + [NPT^-]_M$  with subscripts W and M representing aqueous pseudophase and micellar pseudophase, respectively, and  $[NPTH] \approx 0$ ) can lead to the following equation

$$k_{obs} = \frac{k_W^h + k_M^h K_S [D_n]}{1 + K_S [D_n]} \quad (2)$$

where  $k_W^h$  and  $k_M^h$  are pseudo-first-order rate constants for hydrolysis of 4-nitrophthalimide in aqueous pseudophase and micellar pseudophase, respectively,  $K_S$  represents CTABr micellar binding constant of NPT<sup>-</sup> and  $[D_n] = [CTABr]_T - \text{cmc}$  (cmc represents critical micelle concentration).

The value of cmc was determined by using both iterative [19] and graphical [20] techniques and these values at different contents of CH<sub>3</sub>CN are summarized in Table 1. The value of  $k_W^h$  was taken as the average value of  $k_{obs}$  obtained at  $[CTABr]_T < \text{cmc}$ . The unknown parameters,  $k_M^h$  and  $K_S$ , were calculated from Eq. (2) using the nonlinear least-squares tech-

nique and these results are summarized in Table 1. The fitting of the observed data to Eq. (2) seems to be satisfactory within the domain of the residual errors ( $d_i = k_{obs i} - k_{calc i}$ ) and standard deviations associated with the calculated values of  $k_M^h$  and  $K_S$  (Table 1).

The increase in the content of CH<sub>3</sub>CN from 5 to 15% v/v decreased  $k_W^h$  and  $k_M^h$  by nearly 50 and 40%, respectively. But the values of pseudo-first-order rate constants for methanolysis of PS<sup>-</sup> in aqueous pseudophase and micellar pseudophase decreased and increased by nearly 6 and 35%, respectively, under similar conditions [21]. This difference of effects of the content of CH<sub>3</sub>CN on the rates of hydrolysis of NPT<sup>-</sup> and methanolysis of PS<sup>-</sup> in the presence of CTABr micelles is possibly due to the following reason. The respective pH-independent rates of hydrolysis of NPT<sup>-</sup> and methanolysis of PS<sup>-</sup> involve NPTH and HO<sup>-</sup> as well as PS<sup>-</sup> and CH<sub>3</sub>OH as the reactants. Nearly 5- to 6-fold lower rate of hydrolysis of NPT<sup>-</sup> in micellar pseudophase than that in the aqueous pseudophase under the presence of 5–15% v/v CH<sub>3</sub>CN may be attributed to certain factors as described elsewhere [22].

The increase in the content of acetonitrile from 5 to 15% v/v increased the cmc of CTABr from  $2.8 \times 10^{-4}$  to  $7.0 \times 10^{-4}$  M in mixed aqueous solvents containing 0.01 M NaOH and  $1 \times 10^{-4}$  M NPT<sup>-</sup> at 35 °C. Similar observations were obtained in methanolysis [13], ethanediolysis [14] of PS<sup>-</sup> and alkaline hydrolysis of phenyl benzoate [15]. The values of cmc at different contents of CH<sub>3</sub>CN were found to follow

Table 1

Pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for alkaline hydrolysis of  $\text{NPT}^-$  at different  $[\text{CTABr}]_{\text{T}}^{\text{a}}$ 

[C] <sup>b</sup> ( $\times 10^4$ M)	CH <sub>3</sub> CN content							
	5% v/v		8% v/v		10% v/v		15% v/v	
	$k_{\text{obs}}$ ( $\times 10^4$ s <sup>-1</sup> )	$k_{\text{cald}}^{\text{c}}$ ( $\times 10^4$ s <sup>-1</sup> )	$k_{\text{obs}}$ ( $\times 10^4$ s <sup>-1</sup> )	$k_{\text{cald}}^{\text{c}}$ ( $\times 10^4$ s <sup>-1</sup> )	$k_{\text{obs}}$ ( $\times 10^4$ s <sup>-1</sup> )	$k_{\text{cald}}^{\text{c}}$ ( $\times 10^4$ s <sup>-1</sup> )	$k_{\text{obs}}$ ( $\times 10^4$ s <sup>-1</sup> )	$k_{\text{cald}}^{\text{c}}$ ( $\times 10^4$ s <sup>-1</sup> )
0.6	20.8 ± 0.4 <sup>d</sup>		16.9 ± 0.2 <sup>d</sup>		15.3 ± 0.3 <sup>d</sup>		11.1 ± 0.1 <sup>d</sup>	
0.6			17.3 ± 0.2					
1.0	21.1 ± 0.2		16.3 ± 0.3		14.8 ± 0.5			
1.0			16.2 ± 0.2					
2.0	19.9 ± 0.1						10.7 ± 0.2	
3.0	19.1 ± 0.3	19.4	16.4 ± 0.3		15.7 ± 0.3			
3.5	17.4 ± 0.5	17.1						
4.0	16.7 ± 0.6	15.4	15.5 ± 0.2				11.0 ± 0.2	
4.5	13.4 ± 0.4	14.1						
5.0	12.2 ± 0.3	13.0	14.5 ± 0.5		15.8 ± 0.2		10.8 ± 0.1	
5.0			14.4 ± 0.2					
6.0			13.4 ± 0.3	12.6	14.3 ± 0.3	14.1		
6.0			12.4 ± 0.4	12.6				
7.0	10.7 ± 0.2	10.3	11.2 ± 0.3	11.4	13.3 ± 0.7	12.8	11.1 ± 0.2	
7.0			11.0 ± 0.7	11.4				
8.0	9.74 ± 0.12	9.45	10.7 ± 0.3	10.5	11.0 ± 0.2	11.8		
8.0			10.5 ± 0.3	10.5				
10.0	7.34 ± 0.25	8.26	8.83 ± 0.24	9.13	9.91 ± 0.18	10.3	10.9 ± 0.2	
10.0			8.50 ± 0.26	9.13				
14.0			7.47 ± 0.25	7.51	8.47 ± 0.08	8.43		
14.0			7.53 ± 0.14	7.51				
15.0							9.13 ± 0.17	8.93
20.0	6.21 ± 0.13	5.91	5.93 ± 0.10	6.21	7.17 ± 0.15	6.94	7.85 ± 0.12	8.10
20.0			6.42 ± 0.11	6.21				
40.0	5.55 ± 0.04	4.74	4.91 ± 0.10	4.61	5.70 ± 0.11	5.07	6.12 ± 0.03	6.15
40.0			5.70 ± 0.04	4.61				
100.0	4.38 ± 0.05	4.04	4.18 ± 0.04	3.61	4.35 ± 0.04	3.88	4.24 ± 0.08	4.19
100.0			4.21 ± 0.02	3.61				
200.0	3.66 ± 0.03	3.80	3.24 ± 0.03	3.26	3.52 ± 0.02	3.47	3.51 ± 0.03	3.30
200.0			2.91 ± 0.05	3.26				
300.0	2.94 ± 0.02	3.73	2.84 ± 0.03	3.14	2.98 ± 0.04	3.34	3.08 ± 0.06	2.97
300.0			2.79 ± 0.04	3.14				
400.0			2.64 ± 0.03	3.09	2.63 ± 0.02	3.27	2.79 ± 0.06	2.80
400.0			2.68 ± 0.03	3.09				
500.0			2.41 ± 0.02				2.56 ± 0.05	2.69
500.0			2.41 ± 0.04					
600.0			2.17 ± 0.03				2.47 ± 0.03	2.61
600.0			2.29 ± 0.02					
800.0			1.93 ± 0.03					
800.0			2.16 ± 0.11					
1000.0			1.70 ± 0.04					
$k_{\text{M}}^{\text{h}}$ ( $\times 10^4$ s <sup>-1</sup> ) <sup>d</sup>	3.57 ± 0.37		2.92 ± 0.17 <sup>d</sup>		3.06 ± 0.27 <sup>d</sup>		2.24 ± 0.10 <sup>d</sup>	
$K_{\text{S}}$ (M <sup>-1</sup> )	3651 ± 328		1893 ± 105		1472 ± 144		368 ± 22	
cmc ( $\times 10^4$ M) <sup>e</sup>	2.8 (2.5) <sup>e</sup>		4.0 (3.6) <sup>e</sup>		5.2 (5.3) <sup>e</sup>		7.0 (9.0) <sup>e</sup>	
$k_{\text{W}}^{\text{h}}$ ( $\times 10^4$ s <sup>-1</sup> )	20.6		16.2		15.4		10.9	

<sup>a</sup> Conditions: [4-nitrothalimide]<sub>0</sub> =  $1 \times 10^{-4}$  M; [NaOH] = 0.01 M; 35 °C;  $\lambda$  = 260 nm.<sup>b</sup> [C] = [CTABr]<sub>T</sub>.<sup>c</sup> Calculated from Eq. (2) as described in the text.<sup>d</sup> Error limits are standard deviations.<sup>e</sup> Values in parenthesis were obtained from Broxton's graphical technique.

Table 2  
Values of  $\ln(\text{cmc})_0$ ,  $\chi$  and  $\ln K_S^0$ ,  $\Gamma$  calculated from respective Eqs. (3) and (4)

OS <sup>a</sup>	Micelle	COC <sup>b</sup>	VOC <sup>c</sup>	$-\ln(\text{cmc})_0$	$\chi (\times 10^2)$ (% v/v) <sup>-1</sup>	$\ln K_S^0$	$\Gamma (\times 10^2)$ (% v/v) <sup>-1</sup>
NPT <sup>-</sup>	CTABr	None	CH <sub>3</sub> CN	8.58 ± 0.10 <sup>d</sup>	9.05 ± 1.0 <sup>d</sup>	9.40 ± 0.19 <sup>d</sup>	22.0 ± 2.0 <sup>d</sup>
PS <sup>-</sup>	CTABr	2% v/v CH <sub>3</sub> CN	CH <sub>3</sub> OH <sup>e</sup>	9.67	11.9	9.53	7.59
PS <sup>-</sup>	CTABr	2% v/v CH <sub>3</sub> N	HOCH <sub>2</sub> CH <sub>2</sub> OH <sup>f</sup>	10.22	9.70	9.38	5.40
PS <sup>-</sup>	CTABr	10% v/v CH <sub>3</sub> OH	CH <sub>3</sub> CN <sup>g</sup>	9.00	17.7	9.72	22.0
PB <sup>h</sup>	SDS	None	CH <sub>3</sub> CN <sup>i</sup>	5.72	2.65	6.69	10.8

<sup>a</sup> Organic substrate.

<sup>b</sup> Constant organic co-solvent.

<sup>c</sup> Variable organic co-solvent.

<sup>d</sup> Error limits are standard deviations.

<sup>e</sup> Ref. [13].

<sup>f</sup> Ref. [14].

<sup>g</sup> Ref. [21].

<sup>h</sup> Phenyl benzoate.

<sup>i</sup> Ref. [15].

the following empirical equation:

$$\ln(\text{cmc}) = \ln(\text{cmc})_0 + \chi X \quad (3)$$

where  $\chi$  is an empirical parameter and  $X$  represents the % v/v content of organic co-solvent in the mixed aqueous solvent. Apparently, the magnitude of  $\chi$  is the measure of the ability of organic co-solvent to inhibit micelle formation.

The values of  $\ln(\text{cmc})_0$  and  $\chi$  were calculated from Eq. (3) using the linear least-squares technique and these results are summarized in Table 2. The fitting of the observed data to Eq. (3) is evident from the plots of Fig. 1, where solid line is drawn from the calculated data points. The value of  $\chi \{=9.05(\% \text{ v/v})^{-1}\}$  is lower than  $\chi \{=11.9(\% \text{ v/v})^{-1}\}$  [13] for methanol and  $\chi \{=17.7(\% \text{ v/v})^{-1}\}$  [15] for mixed methanol–acetonitrile. Complete absence of CTABr micelles has been reported in mixed aqueous solvents containing 10–15% v/v methanol or 15–20% v/v acetonitrile [23]. Thus, the existence of CTABr micelles in mixed aqueous solvent containing 15% v/v acetonitrile, 0.01 M NaOH and  $1 \times 10^{-4}$  M NPT<sup>-</sup> indicates that NPT<sup>-</sup> ions promote micelle formation.

The values of  $K_S$  decreased from 3650 to 370 M<sup>-1</sup> with the increase in acetonitrile content from 5 to 15% v/v at 35 °C. These values of  $K_S$  were found to follow the following empirical equation:

$$\ln K_S = \ln K_S^0 - \Gamma X \quad (4)$$

where  $\Gamma$  is an empirical parameter whose magnitude is the measure of the ability of organic co-solvent to

decrease the CTABr micellar affinity of anionic solute. The fitting of the observed data to Eq. (4) is evident from the plot of Fig. 1 where solid line is drawn through the calculated data points. The linear least-squares calculated values of  $\ln K_S^0$  and  $\Gamma$  are summarized in Table 2

It is interesting to note that the value of  $\chi$  is smaller while the value of  $\Gamma$  is larger (by nearly 3-fold) for acetonitrile than for methanol (Table 2). Mixed H<sub>2</sub>O–CH<sub>3</sub>OH and H<sub>2</sub>O–CH<sub>3</sub>CN solvents are known as typically aqueous (TA) and typically nonaqueous (TNA) solvent, respectively. These TA and TNA solvents display characteristically different solution properties. At low content of organic co-solvent, acetonitrile molecules disrupt whereas methanol molecules promote the water-structure [24]. Thus, the water-structure breaking ability of acetonitrile molecules causes larger solubilizing capacity of H<sub>2</sub>O–CH<sub>3</sub>CN compared to that of H<sub>2</sub>O–CH<sub>3</sub>OH where methanol molecules strengthen the water-structure. This could be one of the various possible reasons for larger value of  $\Gamma$  for acetonitrile than for methanol (Table 2). It should be noted that CTABr monomers are expected to increase water-structure [25].

The stability of an ionic micelle is expected to be governed by, at least, three basic factors: (i) effect of the medium of nonmicellar pseudophase on stability of monomers which are in equilibrium with micelle, (ii) electrostatic repulsion between the adjacent ionic headgroups, and (iii) hydrophobic interaction between the hydrophobic segments of micelle-forming

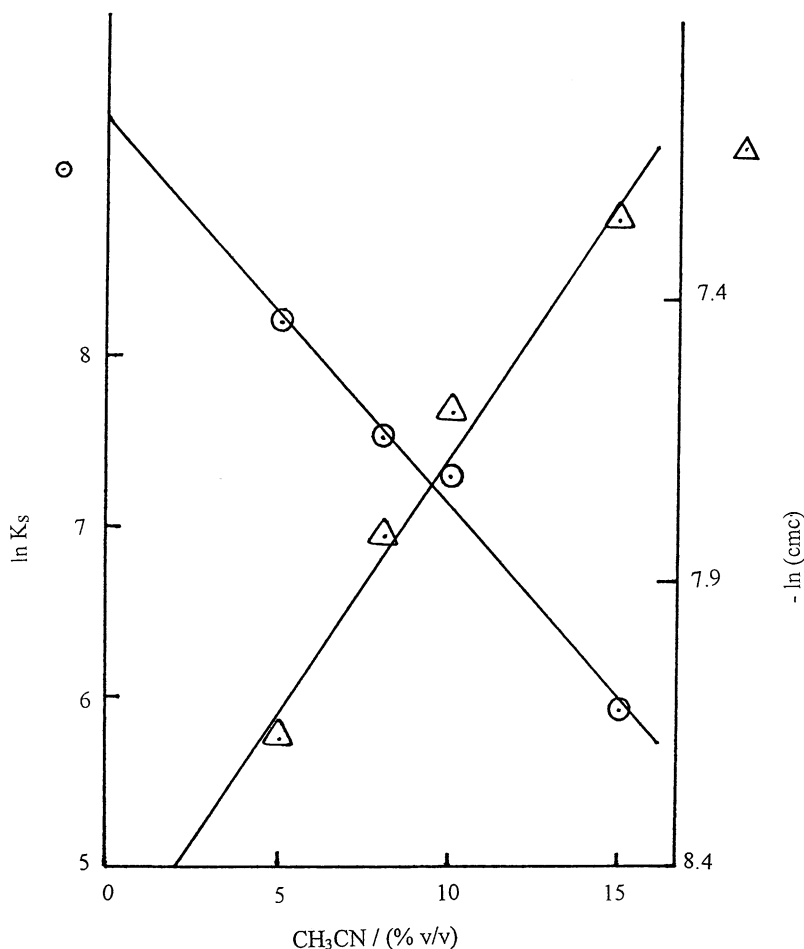


Fig. 1. Plots showing the dependence of  $\ln K_S$  (⊙) and  $\ln(\text{cmc})$  (Δ) vs. % v/v content of  $\text{CH}_3\text{CN}$ . The solid lines are drawn through the least-squares calculated points.

surfactant molecules. Although the dielectric constant of methanol is almost similar to that of acetonitrile, methanol, being protic solvent, can solvate both ionic headgroups and their counterions while acetonitrile, being aprotic solvent, can solvate only cationic charge. Thus, at constant composition ( $X$ ) of mixed  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  solvents, the Stern layer, i.e. the CTABr micellar region of bound counterions ( $\text{Br}^-$ ) should contain larger number of water molecules in mixed  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  than in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  solvent. This effect would cause slight larger local effective dielectric constant of Stern layer in mixed  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  solvent than in  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  solvent at a constant  $X$ . This shows that the destabilization

of micelle formation due to electrostatic repulsion between adjacent headgroups would be slightly larger in mixed  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  solvent than in  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  solvent at a constant  $X$ . This effect may be partially or fully responsible for slightly larger value of  $\chi$  for  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  than for  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  solvent.

### 3.2. Effects of $[\text{NaBr}]$ and $[\text{NaCl}]$ on $k_{\text{obs}}$ at a constant $[\text{CTABr}]_T$

A series of kinetic runs was carried out at  $1 \times 10^{-4}$  M 4-nitrophenalimide, 0.01 M NaOH, 0.006 M CTABr,  $35^\circ\text{C}$  and different  $[\text{NaBr}]$  ranging from 0.0 to 1.0 M. Similar results were obtained at 0.01, 0.015

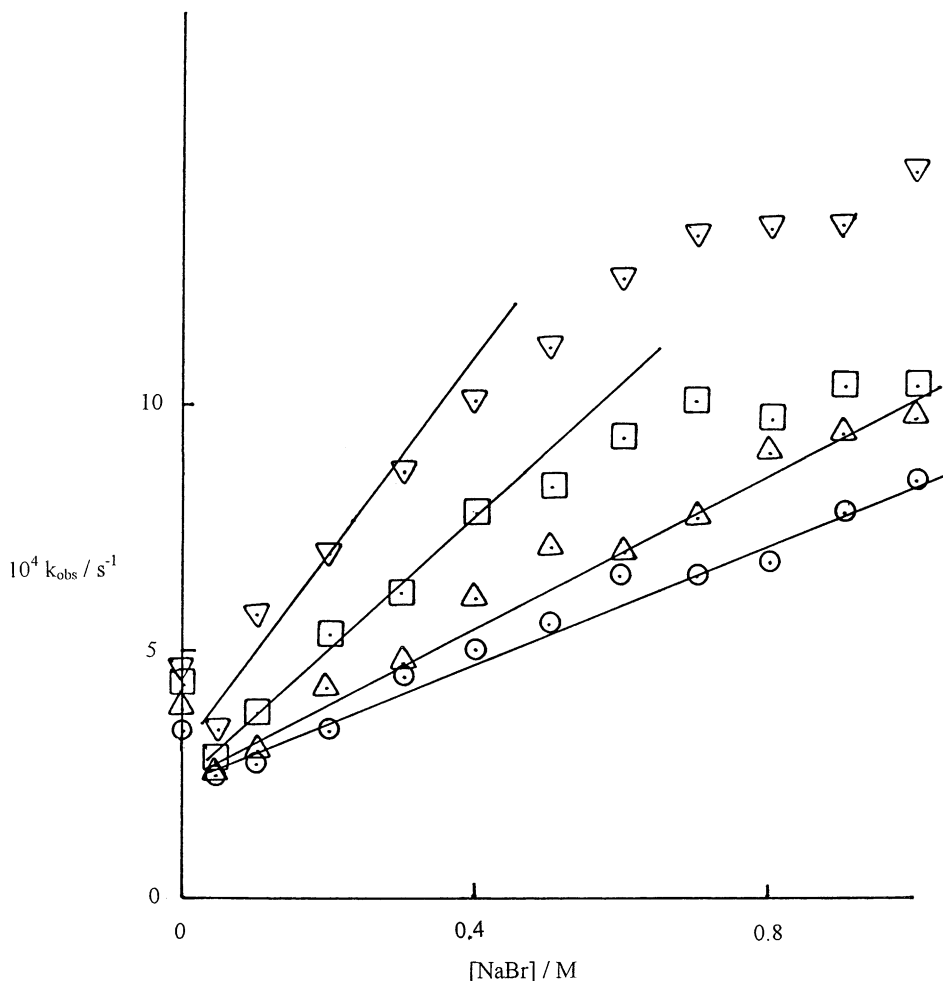


Fig. 2. Plots showing the dependence of  $k_{\text{obs}}$  upon  $[\text{NaBr}]$  at 0.020 (○), 0.015 (△), 0.010 (□) and 0.006 M CTABr (▽) in mixed aqueous solvent containing 1% v/v  $\text{CH}_3\text{CN}$ . The solid lines are drawn through the least-squares calculated points.

and 0.02 M CTABr. These results are shown graphically as the plots of  $k_{\text{obs}}$  versus  $[\text{NaBr}]$  in Fig. 2. Similar observations as shown graphically in Fig. 3 were obtained in the presence of NaCl. It may be noted that the reaction mixture at 1.0 M NaBr and 0.02 M CTABr became visibly highly viscous but the solution was still apparently clear solution. The reaction mixtures at 0.02 M CTABr and  $\geq 0.5$  M NaBr became cloudy after nearly 24 h at room temperature. But this cloudiness disappeared when the reaction mixtures were heated to 35 °C. Such observations were not noticed at  $[\text{CTABr}]_{\text{T}} \leq 0.015$  M. These observations and other related studies [26–28] show that the addition of  $\text{Br}^-$

to CTABr micellar solution changes the structure of micelle. Such micellar structural changes are relatively less sensitive to  $[\text{Cl}^-]$ . However, micellar structural changes appeared to be kinetically insensitive [1].

The plots of Figs. 2 and 3 demonstrate a modest but definite decrease ( $\sim 20$ – $30\%$ ) in  $k_{\text{obs}}$  with the increase in  $[\text{NaX}]$  (where  $\text{X} = \text{Br}$  and  $\text{Cl}$ ) from 0.0 to 0.05 M. The increase in  $[\text{NaX}]$  beyond 0.05 M caused an increase in  $k_{\text{obs}}$ . A qualitative explanation of these observations may be found in terms of the occurrence of ion-exchange processes such as  $\text{X}^-/\text{HO}^-$  and  $\text{X}^-/\text{NPT}^-$ . The occurrence of ion-exchange in ionic micellar-mediated ionic or semi-ionic reactions has

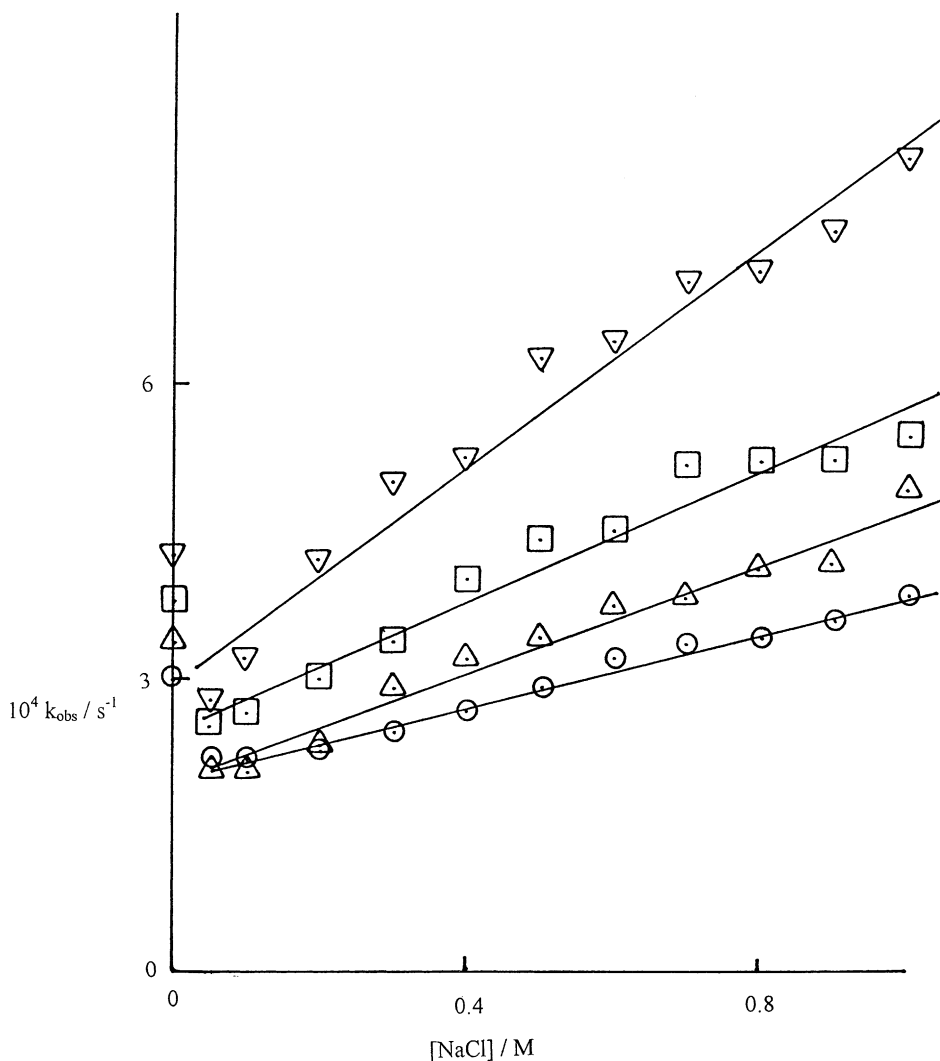


Fig. 3. Plots showing the dependence of  $k_{\text{obs}}$  upon  $[\text{NaCl}]$  at 0.020 ( $\odot$ ), 0.015 ( $\triangle$ ), 0.010 ( $\square$ ) and 0.006 M CTABr ( $\nabla$ ) in mixed aqueous solvent containing 1% v/v  $\text{CH}_3\text{CN}$ . The solid lines are drawn through the least-squares calculated points.

been unequivocally established [29–31]. The possible ion-exchange processes, in the present reacting system, are  $\text{X}^-/\text{HO}^-$ ,  $\text{X}^-/\text{NPT}^-$  and  $\text{HO}^-/\text{NPT}^-$ . The effectiveness of an ion-exchange is expected to depend upon, at least, two factors: (i) the difference in the hydrophilicity, and (ii) the relative concentrations of two exchanging ions. Thus, the ion-exchange  $\text{HO}^-/\text{NPT}^-$  is considered to be least effective among three possible ion-exchange processes for the fact that the difference in hydrophilicity of  $\text{HO}^-$  and  $\text{NPT}^-$  is largest

one and the concentrations of both  $\text{HO}^-$  and  $\text{NPT}^-$  have been kept constant at relatively low values compared with that of  $\text{X}^-$ . The ion-exchange  $\text{X}^-/\text{NPT}^-$  may be ignored compared with  $\text{X}^-/\text{HO}^-$  at relatively low value of  $[\text{NaX}]$  because of the large difference in hydrophilicity of  $\text{NPT}^-$  and  $\text{X}^-$  compared to that of  $\text{X}^-$  and  $\text{HO}^-$ . Although the contribution of  $k_{\text{OH}}$  [ $\text{HO}^-$ ] towards  $k_{\text{obs}}$  is only  $\sim 20\%$  at 0.01 M NaOH, the increase in  $[\text{NaX}]$  from 0.0 to 0.05 M decreased  $k_{\text{obs}}$  by  $\sim 20\text{--}30\%$  due to most effective transfer of



one,  $\text{HO}^-$ , of the two reactants from micellar pseudophase to the aqueous pseudophase by added  $\text{X}^-$ .

It should be noted that the transfer of both  $\text{HO}^-$  and  $\text{NPT}^-$  and exclusive transfer of  $\text{HO}^-$  from micellar pseudophase to the aqueous pseudophase by added  $\text{X}^-$  would cause an increase and decrease in  $k_{\text{obs}}$ , respectively, because the value of  $k_{\text{obs}}$  decreased from  $23.0 \times 10^{-4}$  to  $2.8 \times 10^{-4} \text{ s}^{-1}$  with the increase in  $[\text{CTABr}]_{\text{T}}$  from 0.0 to 0.02 M at 0.01 M NaOH. But the decrease in  $k_{\text{obs}}$  due to increase in  $[\text{X}^-]$  from 0.0 to 0.05 M does not necessarily mean that the  $\text{X}^-$  ions are singularly ineffective in expelling  $\text{NPT}^-$  ions from micellar pseudophase to the aqueous pseudophase at  $[\text{NaX}] \leq 0.05 \text{ M}$ . It merely shows that the rate-increasing effect of the expulsion of both  $\text{HO}^-$  and  $\text{NPT}^-$  is dominated by the rate-decreasing effect of the exclusive expulsion of  $\text{HO}^-$  from micellar pseudophase to the aqueous pseudophase by added  $\text{X}^-$  at  $[\text{NaX}] \leq 0.05 \text{ M}$ .

The rate constants,  $k_{\text{obs}}$ , increased with the increase in  $[\text{NaX}]$  at  $>0.05 \text{ M}$  (Figs. 2 and 3). These results cannot be attributed to the salt effect for the reason that the rate constants,  $k_{\text{obs}}$ , for alkaline hydrolysis of  $\text{NPT}^-$  remained almost unchanged with the change in  $[\text{NaCl}]$  from 0.0 to 2.5 M at 0.03 M NaOH [17]. A quantitative or semi quantitative explanation for these results may be given in terms of PM of micelle [32] coupled with ion-exchange  $\text{X}^-/\text{NPT}^-$ . It should be noted that since  $\text{HO}^-$  is more hydrophilic than  $\text{X}^-$  ( $\text{X}^- = \text{Br}^-$  and  $\text{Cl}^-$ ), the effect of ion-exchange  $\text{X}^-/\text{HO}^-$  on  $k_{\text{obs}}$  should be nearly leveled off at  $[\text{NaX}] > 0.05 \text{ M}$ . Thus, the increase in  $k_{\text{obs}}$  due to increase in  $[\text{NaX}]$  at  $>0.05 \text{ M}$  is basically due to ion-exchange  $\text{X}^-/\text{NPT}^-$ . The effect of the increase in  $[\text{NaX}]$  on the distribution of counterion  $\text{NPT}^-$  between micellar- and aqueous-pseudophases may be represented by the empirical Eq. (1), where  $\text{MX} = \text{NaX}$  and  $\text{S}^- = \text{NPT}^-$ . Eqs. (1) and (2) can lead to the following equation

$$k_{\text{obs}} = \frac{k'_0 + \theta K [\text{NaX}]}{1 + K [\text{NaX}]} \quad (5)$$

where

$$k'_0 = \frac{k_{\text{W}}^{\text{h}} + k_{\text{M}}^{\text{h}} K_{\text{S}}^0 [\text{D}_n]}{1 + K_{\text{S}}^0 [\text{D}_n]} \quad (6)$$

$$K = \frac{K_{\text{X/S}}}{1 + K_{\text{S}}^0 [\text{D}_n]} \quad (7)$$

$$\theta = k_{\text{W}}^{\text{h}} \quad (8)$$

Eq. (5) predicts that the plot of  $k_{\text{obs}}$  versus  $[\text{NaX}]$  should be nonlinear with high gradient at low  $[\text{NaX}]$  and low gradient at high  $[\text{NaX}]$  at a constant  $[\text{CTABr}]_{\text{T}}$ . But the observed plots, shown in Figs. 2 and 3 seem to be linear at  $[\text{CTABr}]_{\text{T}} \geq 0.015 \text{ M}$  for NaBr and at  $[\text{CTABr}]_{\text{T}} \geq 0.006 \text{ M}$  for NaCl. It is evident from Eq. (7) that the value of  $K$  depends upon the values of  $K_{\text{X/S}}$  and  $K_{\text{S}}^0$ . The kinetically determined value of  $K_{\text{S}}^0$  in aqueous solvent containing 1% v/v  $\text{CH}_3\text{CN}$  is  $6600 \text{ M}^{-1}$  [17] and hence  $1 + K_{\text{S}}^0 [\text{D}_n] \approx K_{\text{S}}^0 [\text{CTABr}]_{\text{T}}$  at  $[\text{CTABr}]_{\text{T}} \geq 0.006 \text{ M}$  because  $\text{cmc} < 2 \times 10^{-4} \text{ M}$  under such conditions. Thus,  $K \approx K_{\text{X/S}} / (K_{\text{S}}^0 [\text{CTABr}]_{\text{T}})$  and it shows that  $K$  should decrease with the increase in  $[\text{CTABr}]_{\text{T}}$ .

The value of  $K_{\text{Br/PS}}$  (where  $\text{PS}^-$  represents ionized phenyl salicylate), obtained from kinetic data on piperidinolysis of  $\text{PS}^-$ , is  $25 \text{ M}^{-1}$  [6] and CTABr micellar binding constant of  $\text{PS}^-$  is  $6700 \text{ M}^{-1}$  [33]. The similarity in the CTABr micellar binding constants of  $\text{PS}^-$  and  $\text{NPT}^-$  indicates that  $K_{\text{Br/NPT}}$  may not be significantly different from  $25 \text{ M}^{-1}$ . Thus, the expected value of  $K_{\text{Br/NPT}}$  and  $K_{\text{S}}^0$  value of  $6600 \text{ M}^{-1}$  reveal that  $K$  should be  $< 1$  at  $[\text{CTABr}]_{\text{T}} \geq 0.006 \text{ M}$ . The value of  $K_{\text{Cl/NPT}}$  may be 2- to 5-fold smaller than that of  $K_{\text{Br/NPT}}$  because the value of ion-exchange constant  $K_{\text{Br}}^{\text{Cl}} (= [\text{Br}_M^-][\text{Cl}_W^-] / [\text{Br}_W^-][\text{Cl}_M^-])$ , obtained directly through spectrophotometric [34] and trapping of free counterions [35] measurements, is 3–5. Thus, the linear plots of  $k_{\text{obs}}$  versus  $[\text{NaX}]$  in Figs. 2 and 3 are due to inequality  $1 \gg K [\text{NaX}]$  within the  $[\text{NaX}]$  range where linearity of the plot exists.

Eq. (5) reduced to Eq. (9) under the conditions where  $1 \gg K [\text{NaX}]$ . The values of  $k'_0$  and  $\theta K$

$$k_{\text{obs}} = k'_0 + \theta K [\text{NaX}] \quad (9)$$

were calculated from Eq. (9) for the linear plots of Figs. 2 and 3. These results for NaBr and NaCl are summarized in Table 3. The values of  $\theta K$  show a decrease with the increase in  $[\text{CTABr}]_{\text{T}}$  for both NaBr and NaCl (Table 3) which is expected in view of Eqs. (7) and (8). The value of  $K$  was obtained from the calculated values of  $\theta K$  with  $\theta = k_{\text{W}}^{\text{h}} = 23 \times 10^{-4} \text{ s}^{-1}$  and subsequently the value of  $K_{\text{X/NPT}}$  was calculated from Eq. (7) with  $[\text{D}_n] \approx [\text{CTABr}]_{\text{T}}$ ,  $K_{\text{S}}^0 = 6600 \text{ M}^{-1}$  and  $K_{\text{X/S}}$  replaced by  $K_{\text{X/NPT}}$ . These calculated values of  $K$  and  $K_{\text{X/NPT}}$  are summarized in Table 3 for  $\text{X}^- = \text{Br}^-$  and  $\text{Cl}^-$ .

Table 3

Values of  $k'_0$  and  $\theta K$  calculated from Eq. (9) for NaX<sup>a</sup>

NaX	[CTABr] <sub>T</sub> (M)	$k'_0$ ( $\times 10^4$ s <sup>-1</sup> )	$\theta K$ ( $\times 10^4$ M <sup>-1</sup> s <sup>-1</sup> )	[NaX] range <sup>b</sup> (M)	$K^c$ (M <sup>-1</sup> )	$K_{X/NPT}^d$ (M <sup>-1</sup> )
NaBr	0.006	3.01 ± 0.69 <sup>e</sup>	19.4 ± 3.7 <sup>e</sup>	0.05–0.30	0.84	34
	0.010	2.22 ± 0.21	13.9 ± 0.8	0.05–0.40	0.60	40
	0.015	2.84 ± 0.38	7.41 ± 0.63	0.05–1.0	0.32	32
	0.020	2.35 ± 0.21	6.09 ± 0.33	0.05–1.0	0.26	35
NaCl	0.006	2.97 ± 0.19	5.48 ± 0.33	0.05–1.0	0.24	9.7
	0.010	2.51 ± 0.17	3.24 ± 0.27	0.10–1.0	0.14	9.4
	0.015	1.96 ± 0.13	2.74 ± 0.21	0.20–1.0	0.12	12.0
	0.020	1.97 ± 0.06	1.86 ± 0.09	0.10–1.0	0.08	10.4

<sup>a</sup> Conditions: [4-nitrothalamide]<sub>0</sub> =  $1 \times 10^{-4}$  M, [NaOH] = 0.01 M, 35 °C,  $\lambda$  = 260 nm, aqueous reaction mixture for each kinetic run contained 1% v/v CH<sub>3</sub>CN.

<sup>b</sup> The linearity of  $k_{\text{obs}}$  vs. [NaX] was considered within this [NaX] range.

<sup>c</sup>  $K = \theta K/k_{\text{W}}^{\text{h}}$  with  $10^4 k_{\text{W}}^{\text{h}} = 23$  s<sup>-1</sup>.

<sup>d</sup>  $K_{X/NPT} = K(1 + K_{\text{S}}^0[\text{CTABr}]_{\text{T}})$  with  $K_{\text{S}}^0 = 6600$  M<sup>-1</sup>.

<sup>e</sup> Error limits are standard deviations.

The empirical definition of  $K_{X/S}$  shows that  $K_{X/S}/K_{Y/S}$  should be equal to usual ion-exchange constant  $K_{\text{X}}^{\text{Y}} (= [X_{\text{M}}^-][Y_{\text{W}}^-]/[X_{\text{W}}^-][Y_{\text{M}}^-])$  [12]. The average calculated values of  $K_{\text{Br}/\text{NPT}} (= 35 \pm 3 \text{ M}^{-1})$  and  $K_{\text{Cl}/\text{NPT}} (= 10 \pm 1 \text{ M}^{-1})$  give  $K_{\text{Br}}^{\text{Cl}} = K_{\text{Br}/\text{NPT}}/K_{\text{Cl}/\text{NPT}} = 3.5$  which is well within the limits of the reported values of  $K_{\text{Br}}^{\text{Cl}} (= 2.7$  and  $5.0$ , obtained by trapping of free counterions [35] and spectrophotometric [34] measurements, respectively).

## Acknowledgements

The authors thank the National Scientific Research Development Council of Malaysia under IRPA program for financial support (Grant No. 09-02-03-0785).

## References

- [1] C.A. Bunton, G. Savelli, Adv. Phys. Org. Chem. 22 (1986) 213 and references cited therein.
- [2] L.S. Romsted, in: K.L. Mittal, B. Lindman (Eds.), Surfactants in Solution, Vol. 2, Plenum Press, New York, 1984, p. 1015.
- [3] C.A. Bunton, in: K.L. Mittal, D.O. Shah (Eds.), Surfactants in Solution, Vol. 11, Plenum Press, New York, 1991, p. 17.
- [4] R.R. Germani, G. Savelli, T. Romeo, N. Spreti, G. Cerichelli, C.A. Bunton, Langmuir 9 (1993) 55.
- [5] N.H. Lajis, M.N. Khan, J. Phys. Org. Chem. 11 (1998) 209.
- [6] M.N. Khan, J. Org. Chem. 62 (1997) 3190.
- [7] M.N. Khan, Z. Arifin, E. Ismail, S.F.M. Ali, J. Org. Chem. 65 (2000) 1331.
- [8] M.N. Khan, Z. Arifin, E. Ismail, S.F.M. Ali, Colloids Surf. A 161 (2000) 381.
- [9] M.N. Khan, M.R. Yusoff, J. Phys. Org. Chem. 14 (2001) 74.
- [10] M.N. Khan, M.R. Yusoff, J. Chem. Res. S (2001) 143.
- [11] M.N. Khan, Z. Arifin, J. Chem. Soc., Perkin Trans. 2 (2000) 2503.
- [12] M.N. Khan, S.Y. Kun, J. Chem. Soc., Perkin Trans. 2 (2001) 1325.
- [13] M.N. Khan, Z. Arifin, Langmuir 12 (1996) 261.
- [14] M.N. Khan, Z. Arifin, Langmuir 13 (1997) 6626.
- [15] M.N. Khan, Colloids Surf. A 139 (1998) 63.
- [16] M.N. Khan, J. Chem. Soc., Perkin Trans. 2 (1990) 435.
- [17] M.N. Khan, Z. Abdullah, Int. J. Chem. Kinet. 33 (2001) 407.
- [18] C.A. Bunton, Catal. Rev. Sci. Eng. 20 (1979) 1.
- [19] M.N. Khan, Z. Arifin, J. Colloid Interf. Sci. 180 (1996) 9.
- [20] T.J. Broxton, J.R. Christie, A.J. Dole, J. Phys. Org. Chem. 7 (1994) 437 and reference cited therein.
- [21] M.N. Khan, Z. Arifin, Colloids Surf. A 125 (1997) 149.
- [22] M.N. Khan, Z. Arifin, Malaysian J. Sci. B 15 (1994) 41.
- [23] L.G. Ionescu, L.S. Romanesco, F. Nome, Sarmisegetuza research group, in: K.L. Mittal, B. Lindman (Eds.), Surfactants in Solution, Vol. 2, Plenum Press, New York, 1984, p. 789.
- [24] J.B.F.N. Engberts, in: F. Franks (Ed.), Water: A Comprehensive Treatise, Vol. 6, Plenum Press, New York, 1979 (Chapter 4).
- [25] W.P. Jencks, Catalysis in Chemistry and Enzymology, McGraw-Hill, New York, 1969.
- [26] A. Heindl, J. Strand, H.-H. Kohler, J. Phys. Chem. 97 (1993) 742.
- [27] P. Mukerjee, in: K.L. Mittal (Ed.), Solution Chemistry of Surfactants, Vol. 1, Plenum Press, New York, 1979, p. 153.
- [28] B.K. Mishra, S.D. Samant, P. Pradhan, S.B. Mishra, C. Manohar, Langmuir 9 (1993) 894.

- [29] S.J. Bachofer, U. Simonis, *Langmuir* 12 (1996) 1744.
- [30] A.L. Underwood, E.W. Anacker, *J. Phys. Chem.* 88 (1984) 2390.
- [31] L.J. Magid, Z. Han, G.G. Warr, M.A. Cassidy, P.D. Butler, W.A. Hamilton, *J. Phys. Chem. B* 101 (1997) 7919.
- [32] F.M. Menger, C.E. Portnoy, *J. Am. Chem. Soc.* 89 (1967) 4698.
- [33] M.N. Khan, Z. Arifin, I.A. Wahab, S.F.M. Ali, E. Ismail, *Colloids Surf. A* 163 (2000) 271.
- [34] D. Bartet, C. Gamboa, L. Sepulveda, *J. Phys. Chem.* 84 (1980) 272.
- [35] I.M. Cuccovia, I.N. da Silva, H. Chaimovich, L.S. Romsted, *Langmuir* 13 (1997) 647.