

## ABSTRACT

In this study, the ion-exchange constant,  $K_X^{\text{Br}}$  for the ion-exchange process  $X^-/\text{Br}^-$  involving different halo-substituted organic salts, MX and CTABr micelle in aqueous system were determined by a semiempirical kinetic approach with the interest of investigating the relationship of the ion-exchange constant to the micellar aggregation behavior. The first chapter contains the reviews of literature studies on this area. Chapter 2 listed all the materials used as well as the experimental details for the study. It consists of 2 parts: (a) kinetic measurements which show the effect of [MX] on the rate of piperidinolysis of phenyl salicylate in the absence and presence of CTABr; and (b) the rheological investigation. In chapter 3, the results of the kinetic measurements and rheological behavior of the reaction mixtures are presented. The mean values of  $K_X^{\text{Br}}$  are  $12.8 \pm 0.9$ ,  $13.4 \pm 0.6$ ,  $4.67 \pm 0.7$ ,  $50.3 \pm 2.0$ ,  $47.9 \pm 2.5$ ,  $8.82 \pm 0.3$ ,  $71.2 \pm 5.6$ ,  $62.1 \pm 5.2$ ,  $11.2 \pm 0.9$  and  $144 \pm 12$  for MX = 3- and 4- $\text{FC}_6\text{H}_4\text{CO}_2\text{Na}$ ; 2-, 3- and 4- $\text{ClC}_6\text{H}_4\text{CO}_2\text{Na}$ ; 2-, 3- and 4- $\text{BrC}_6\text{H}_4\text{CO}_2\text{Na}$ ; and 2- and 4- $\text{IC}_6\text{H}_4\text{CO}_2\text{Na}$ , respectively. Shear thinning behavior of the plots of shear viscosity versus shear rate at constant [MX] and  $[\text{CTABr}]_{\text{T}}$  are observed in all systems except when MX = 2- $\text{ClC}_6\text{H}_4\text{CO}_2\text{Na}$  for which the value of  $K_X^{\text{Br}}$  is the lowest. In Chapter 4, detailed discussions of the results are given. The values of  $K_X^{\text{Br}}$  offer quantitative evidence of the perception that the strong micellar binding of certain counterions is the cause of the micellar structural transition from spherical to cylindrical to wormlike entangled micelles. Viscosity maxima of the plots of shear viscosity as a function of [MX] are known as the characteristic features of the wormlike micellar solution. Thus, it may be concluded that the magnitudes of the thermodynamic ion-exchange constant,  $K_X^{\text{Y}}$  for ion-exchange process  $X^-/\text{Y}^-$  on the cationic micellar surface in aqueous solution could affect the physical properties such as the structure of micelles of ionic surfactant solutions.

## ABSTRAK

Dalam kajian ini, pemalar penukaran ion,  $K_X^{Br}$  untuk proses penukaran ion  $X^-/Br^-$  melibatkan pelbagai garam organik dengan kumpulan penukarganti halogen, MX dan misel CTABr di dalam system akues telah ditentukan dengan menggunakan satu pendekatan semiempirikal kinetic dengan minat untuk mengkaji perhubungan pemalar penukaran ion kepada sifat aggregasi misel. Bab pertama mengandungi rumusan kajian terdahulu mengenai bidang ini. Bab 2 menyenaraikan semua bahan yang digunakan dan juga kaedah eksperimen untuk kajian ini. Ia mengandungi 2 bahagian: (a) pengukuran kinetik yang menunjukkan kesan [MX] terhadap kadar piperidinolisis fenil salisilat tanpa kehadiran dan kehadiran CTABr; dan (b) kajian rheologi. Di dalam Bab 3, keputusan dari kajian kinetik dan rheologi terhadap campuran tindak balas turut disenaraikan. Purata nilai  $K_X^{Br}$  adalah  $12.8 \pm 0.9$ ,  $13.4 \pm 0.6$ ,  $4.67 \pm 0.7$ ,  $50.3 \pm 2.0$ ,  $47.9 \pm 2.5$ ,  $8.82 \pm 0.3$ ,  $71.2 \pm 5.6$ ,  $62.1 \pm 5.2$ ,  $11.2 \pm 0.9$  dan  $144 \pm 12$  yang masing-masing merujuk kepada MX = 3- dan 4-FC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Na; 2-, 3- dan 4-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Na; 2-, 3- dan 4-BrC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Na; dan 2- dan 4-IC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Na. Sifat peluncuran menipis pada plot kelikatan melawan kadar putaran pada keadaan [MX] dan [CTABr]<sub>T</sub> malar telah dilihat dalam semua system kecuali apabila MX = 2-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Na di mana nilai  $K_X^{Br}$  adalah terendah. Di dalam Bab 4, perbincangan terperinci tentang keputusan turut disertakan. Nilai  $K_X^{Br}$  menawarkan bukti kuantitatif terhadap persepsi bahawa pengikatan yang kuat terhadap misel oleh sesetengah ion berlawanan cas adalah penyebab perubahan struktur misel daripada berbentuk sfera kepada silinder dan kepada misel cecacing yang berselirat. Kelikatan maksima pada plot kelikatan sebagai fungsi [MX] adalah diketahui sebagai ciri misel cecacing. Maka, boleh dirumuskan bahawa magnitud pemalar termodinamik penukaran ion,  $K_X^Y$  untuk proses penukaran ion

$X/Y^-$  pada permukaan misel kationik di dalam keadaan akues boleh mempengaruhi sifat fizikalnya seperti struktur misel pada larutan surfaktan ionik.

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## LIST OF SYMBOLS AND ABBREVIATIONS

$[ ]_T$	total concentration
$\alpha$	degree of counterion dissociation
$\delta_{app}$	apparent molar absorptivity
$\theta$	empirical parameter in Eq. 4.5
$\eta_\gamma$	shear viscosity value at fixed shear rate
$A_0$	observed absorbance at $t = 0$
$A_{calc}$	calculated absorbance
$A_{obs}$	observed absorbance
$A_\infty$	observed absorbance at $t = \infty$
$Bz^-$	$C_6H_4CO_2^-$
$BzNa$	$C_6H_4CO_2Na$
CTABr	cetyltrimethylammonium bromide
$D_n$	detergent / micelle
Eq.	equation
$F_{X/S}$	empirical constant whose magnitude should be $> 0$ and $\leq 1$
$k_{calc}$	calculated rate constant
$k_{calc\ i}$	rate constants determined by calculation at the $i$ -th value of $[MX]$
$k_d^M$	rate constants for micelle disintegration
$k_f^M$	rate constants for micelle formation
$k_M$	rate constant for the reaction in micellar phase
$K_M$	equilibrium constant for micelle formation
$k_W^{n, MX}$	nucleophilic second-order rate constant for the reaction of Piperidine with $PS^-$ in aqueous phase and $[MX] \neq 0$

$K_N$	micellar binding constant of piperidine
$k_{\text{obs}}$	observed pseudo-first-order rate constant
$k_{\text{obs } i}$	rate constants determined by experiment at the i-th value of [MX]
$k_{\text{obs}}^{\text{MX}}$	$k_{\text{obs}}$ at a typical value of [MX] and $[\text{CTABr}]_{\text{T}} = 0$
$K_S$	micellar binding constants of $\text{PS}^-$
$K_S^0$	$K_S$ at $[\text{MX}] = 0$
$K^{\text{X/S}}$	empirical constant in Eq. 4.5
$K_{\text{X/S}}$	empirical constant which the magnitude represents the ability of counterion $\text{X}^-$ to expel $\text{S}^-$ from cationic micellar pseudophase
$k_{\text{M}}^{\text{n}}$	nucleophilic second order rate constant for reaction of piperidine with $\text{PS}^-$ in micellar pseudophase
$k_{\text{W}}^{\text{n}}$	nucleophilic second order rate constant for reaction of piperidine with $\text{PS}^-$ in aqueous phase
$k_{\text{W}}$	rate constant for the reaction in aqueous phase
$K_{\text{X}}^{\text{Y}}$	ion-exchange constant for ion-exchange process $\text{X}^-/\text{Y}^-$
$M$	Molarity
$\text{MX}$	inert organic salt
$[\text{MX}]_0^{\text{op}}$	optimum concentration of MX needed to expel both $\text{HO}^-$ and $\text{Br}^-$ ions from micellar pseudophase to aqueous phase
$[\text{MX}]_{\text{OH}}^{\text{op}}$	optimum concentration of MX to expel $\text{HO}^-$ ion
$[\text{MX}]_{\text{Br}}^{\text{op}}$	optimum concentration of MX to expel $\text{Br}^-$ ion
$[\text{MX}]_{\text{S}}^{\text{ef}}$	effective concentration of MX to expel $\text{PS}^-$ from micellar pseudophase to aqueous phase
$N_{\text{a}}$	Avogadro's number

NMR	nuclear magnetic resonance
PIE	Pseudophase Ion Exchange
Pip	piperidine
pK <sub>a</sub>	acid dissociation constant at logarithmic scale
PM	Pseudophase Micellar
PS <sup>-</sup>	ionized phenyl salicylate
PSH	phenyl salicylate
RE	residual error
s	second
S	substrate / solubilizate
TEM	transmission electron microscopy
TTABr	tetradecyltrimethylammonium bromide
V <sub>M</sub>	micellar volume

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### Appendix A

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