ABSTRACT

In this study, the ion-exchange constant, K_X^{Br} for the ion-exchange process X^-/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^{Br} are 12.8 ± 0.9, 13.4 ± 0.6, 4.67 ± 0.7, 50.3 ± 2.0, 47.9 ± 2.5, 8.82 ± 0.3, 71.2 ± 5.6, 62.1 ± 5.2, 11.2 ± 0.9 and 144 ± 12 for MX = 3- and 4-$FC_6H_4CO_2Na$; 2-, 3- and 4-$ClC_6H_4CO_2Na$; 2-, 3- and 4-$BrC_6H_4CO_2Na$; and 2- and 4-$IC_6H_4CO_2Na$, respectively. Shear thinning behavior of the plots of shear viscosity versus shear rate at constant [MX] and $[CTABr]_T$ are observed in all systems except when MX = 2-$ClC_6H_4CO_2Na$ for which the value of K_X^{Br} is the lowest. In Chapter 4, detailed discussions of the results are given. The values of K_X^{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^Y for ion-exchange process X^-/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 ± 0.9, 13.4 ± 0.6, 4.67 ± 0.7, 50.3 ± 2.0, 47.9 ± 2.5, 8.82 ± 0.3, 71.2 ± 5.6, 62.1 ± 5.2, 11.2 ± 0.9 dan 144 ± 12 yang masing-masing merujuk kepada MX = 3- dan 4-$FC_6H_4CO_2Na$; 2-, 3- dan 4-$ClC_6H_4CO_2Na$; 2-, 3- dan 4-$BrC_6H_4CO_2Na$; dan 2- dan 4-$IC_6H_4CO_2Na$. Sifat peluncuran menipis pada plot kelikatan melawan kadar putaran pada keadaan [MX] dan $[CTABr]_T$ malar telah dilihat dalam semua system kecuali apabila MX = 2-$ClC_6H_4CO_2Na$ 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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$[\ ]_T$	total concentration
α	degree of counterion dissociation
δ_{app}	apparent molar absorptivity
θ	empirical parameter in Eq. 4.5
η_γ	shear viscosity value at fixed shear rate
A_0	observed absorbance at t = 0
A_{calc}	calculated absorbance
A_{obs}	observed absorbance
A_∞	observed absorbance at t = ∞
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
$k^n{}_W^{MX}$	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_{obs}	observed pseudo-first-order rate constant
$k_{obs\ i}$	rate constants determined by experiment at the i-th value of [MX]
k_{obs}^{MX}	k_{obs} at a typical value of [MX] and $[CTABr]_T = 0$
K_S	micellar binding constants of PS^-
K_S^0	K_S at [MX] = 0
$K^{X/S}$	empirical constant in Eq. 4.5
$K_{X/S}$	empirical constant which the magnitude represents the ability of counterion X^- to expel S^- from cationic micellar pseudophase
k^n_M	nucleophilic second order rate constant for reaction of piperidine with PS^- in micellar pseudophase
k^n_W	nucleophilic second order rate constant for reaction of piperidine with PS^- in aqueous phase
k_W	rate constant for the reaction in aqueous phase
K_X^Y	ion-exchange constant for ion-exchange process X^-/Y^-
M	Molarity
MX	inert organic salt
$[MX]_0^{op}$	optimum concentration of MX needed to expel both HO^- and Br^- ions from micellar pseudophase to aqueous phase
$[MX]_{OH}^{op}$	optimum concentration of MX to expel HO^- ion
$[MX]_{Br}^{op}$	optimum concentration of MX to expel Br^- ion
$[MX]_S^{ef}$	effective concentration of MX to expel PS^- from micellar pseudophase to aqueous phase
N_a	Avogadro's number

NMR	nuclear magnetic resonance
PIE	Pseudophase Ion Exchange
Pip	piperidine
pK_a	acid dissociation constant at logarithmic scale
PM	Pseudophase Micellar
PS^-	ionized phenyl salicylate
PSH	phenyl salicylate
RE	residual error
s	second
S	substrate / solubilizate
TEM	transmission electron microscopy
TTABr	tetradecyltrimethylammonium bromide
V_M	micellar volume

LIST OF APPENDICES

Appendix A