A Comparative Analysis of Pseudophase Ion-Exchange (PIE) Model and Berezin Pseudophase (BPP) Model: Analysis of Kinetic Data for Ionic Micellar-mediated Semi-ionic Bimolecular Reaction

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Pseudo-first-order rate constants (k_{obs}) for the reaction of *N*-benzylphthalimide (NBPT) with HO^- have been determined at 2.0×10^{-4} M NBPT, 1.0×10^{-3} and 2.0×10^{-3} M NaOH as well as varying concentrations of cetyltrimethylammonium bromide ($[CTABr]_T$ = 0.0-1.7×10^{-1} M). The effects of $[CTABr]_T$ – CMC (with CMC representing the critical micelle concentration of CTABr) on k_{obs} have been analyzed in terms of Berezin's pseudophase (BPP) model and pseudophase ion-exchange (PIE) model. Although both models give the best observed data fit with least-squares values not significantly different from each other, the calculated values of K_S from BPP model appear to be more reliable compared to those from PIE model because the values of K_S from BPP model are similar to the corresponding K_S values determined spectrophotometrically.

Key Words : *N*-Benzylphthalimide, Rate constant, Binding constant, Pseudophase ion-exchange (PIE) model, Berezin pseudophase (BPP) model

Introduction

The occurrence of ion-exchange between counterions and ionic reactants of charge similar to the charge of counterions of micellar-mediated ionic reactions or semi-ionic reactions has been detected kinetically in the late 1960 s.[1] The quantitative analysis of the kinetic data on such reactions involves largely the following two alternative theoretical approaches for the distribution of counterion-like reactants between micellar and aqueous pseudophase. (i) The most commonly used approach is the pseudophase ion-exchange (PIE) model[2] and (ii) a less commonly used approach is to write micellar counterion binding in terms of ionic micellar surface electrical potential.[3] Both approaches are semi-empirical and have limitations.[3] The frequent use of PIE model may be attributed, at least partly, to its practical and theoretical simplicity. Both approaches might result in kinetic parameters of varying degree of reliability. The parameters, such as micellar binding constants (K_S) of reactants and ion-exchange constant (K_X^Y), seem to be the only kinetic parameters which could be compared with those obtained independently by using different experimental techniques. The reports on a comparison of this sort are rare especially under strictly kinetic conditions. An attempt is made in the present study to compare K_S values obtained by the use of kinetic models (PIE model and Berezin's pseudophase model) and UV-visible spectrophotometric technique. The results and probable explanations are described in this manuscript.

Experimental Section

Materials. Reagent-grade chemicals such as cetyltrimethylammonium bromide (CTABr) and sodium hydroxide (NaOH) were of the highest commercially available purity. All other chemicals used were also of reagent grade. *N*-benzylphthalimide (NBPT) was synthesized as described elsewhere.[4] Stock solutions of NBPT (0.01 M) were prepared in CH_3CN and stored at low temperature whenever they were not in use.

Kinetic Measurements. *(a) Alkaline Hydrolysis of N-Benzylphthalimide (NBPT) in the Presence of Different Total Concentration of CTABr ($[CTABr]_T$) at 35 ºC:* The rate of alkaline hydrolysis of NBPT was studied by monitoring the disappearance of reactant (NBPT) spectrophotometrically at 300 nm using Shimadzu UV-Visible Spectrophotometer with the help of UV-1601 PC software. Details of the kinetic procedure have been described elsewhere.[5] The observed data followed eqn. (1)

$$A_{obs} = \delta_{app}[X_0]\exp(-k_{obs}t) + A_\infty \quad (1)$$

where A_{obs} is the absorbance at any reaction time t, δ_{app} is the apparent molar extinction coefficient of reaction mixtures, $[X_0]$ is the initial concentration of the reactant, $A_\infty = A_{obs}$ at $t = \infty$ and k_{obs} represents pseudo first-order rate constant for alkaline hydrolysis of NBPT. The rates of reactions were generally monitored for the reaction period of more than 7-9 halflives.

(b) Spectrophotometric Determination of Cationic Micellar Binding Constant of NBPT: Since the rate of cationic micellar-mediated hydrolysis of NBPT is highly sensitive to $[HO^-]$ at $\geq 1.0 \times 10^{-3}$ M NaOH, the CTABr micellar binding constant of NBPT was determined spectrophotometrically at [NaOH] = 0. The maximum initial absorbance, A_{obs}^0, (*i.e.* observed absorbance at reaction time $t = 0$) change within $[CTABr]_T$ (total concentration of CTABr) range 0.0-1.7×10^{-1} M was observed at 314 nm and 35 °C. The values of A_{obs}^0 were determined at 2.0×10^{-4} M NBPT and within $[CTABr]_T$ range $6.0 \times 10^{-4} - 1.7 \times 10^{-1}$ M. These values of

Table 1. Values of parameters, δ_W, δ_M and K_S, calculated from eqn. (2)[a]

10^4 [X_0] M	10^4 CMC M	K_S M^{-1}	δ_W $M^{-1}cm^{-1}$	δ_M $M^{-1}cm^{-1}$	$10^4 \Sigma d_i^2$
2.0[b]	3.01	1105 ± 251[c]	1520 ± 68[c]	721 ± 335[c]	3.800
	3.66	1031 ± 219	1466 ± 54	721 ± 313	3.800
	3.84	1012 ± 210	1453 ± 50	721 ± 307	3.800
	4.99	907 ± 169	1376 ± 33	721 ± 276	3.800
3.0[d]	3.01	1019 ± 188	1410 ± 52	697 ± 267	3.541
	3.66	955 ± 165	1366 ± 43	697 ± 251	3.541
	3.84	939 ± 160	1355 ± 40	697 ± 247	3.541
	4.99	848 ± 130	1290 ± 29	697 ± 224	3.541
5.0[e]	3.01	975 ± 91	1503 ± 29	670 ± 130	5.514
	3.66	917 ± 81	1454 ± 24	670 ± 123	5.514
	3.84	902 ± 78	1441 ± 22	670 ± 121	5.514
	4.99	818 ± 64	1368 ± 16	670 ± 110	5.514
3.0[f]	5.00	1580 ± 410	1470 ± 50	810 ± 430	22.47
	6.00	1370 ± 305	1380 ± 32	810 ± 380	22.47

[a][NaOH] = 0, T = 35 ºC, λ = 314 nm. [b]2% v/v CH_3CN in the aqueous reaction mixture. [c]Error limits are standard deviations. [d]2% v/v CH_3CN in the aqueous reaction mixture. [e]5% v/v CH_3CN in the aqueous reaction mixture. [f][NaOH] = 1.2×10^{-3} M.

A^0_{obs} were used to calculate K_S, δ_W, and δ_M from eqn. (2)

$$A^0_{obs} = \frac{(\delta_W + \delta_M K_S[D_n])[X_0]}{1 + K_S[D_n]} \quad (2)$$

where K_S is CTABr micellar binding constant of NBPT, $[D_n]$ = $[CTABr]_T$ – CMC with CMC representing critical micelle concentration of CTABr surfactant, δ_W and δ_M represent molar extinction coefficients of NBPT at 314 nm in aqueous pseudophase and micellar pseudophase, respectively, and $[X_0]$ is the initial concentration of NBPT. In the absence of experimentally known value of CMC, the values of δ_W, δ_M and K_S were calculated from eqn. (2) at different presumed values of CMC ranging from $3.01 \times 10^{-4} - 4.99 \times 10^{-4}$ M. These results, as summarized in Table 1, show the values of least-squares, Σd_i^2 (where $d_i = A^0_{obs\,i} - A^0_{calcd\,i}$ with $A^0_{obs\,i}$ and $A^0_{calcd\,i}$ representing observed and calculated initial absorbance at *i*th total concentration of CTABr), remain almost unchanged with change in CMC from $3.01 \times 10^{-4} - 4.99 \times 10^{-4}$ M. The quality of the fitting of observed data to eqn. 2 is evident from the standard deviations associated with the calculated parameters, δ_W, δ_M and K_S, and from the plot of Figure 1 where solid line is drawn through the calculated values of absorbance using eqn. (2) with parameters listed in Table 1.

The initial absorbance change ΔA^0_{obs} {= $(\delta_W$-$\delta_M)$ $[X_0]$} is rather low (≈ 0.14) at $[X_0] = 2.0 \times 10^{-4}$ M and consequently the calculated values of δ_W, δ_M and K_S under such conditions are rather less reliable. In order to increase the value of ΔA^0_{obs}, the value of A^0_{obs} at different $[CTABr]_T$ were also determined at $[X_0] = 5.0 \times 10^{-4}$ M. These observed data were used to calculate δ_W, δ_M, K_S and Σd_i^2 from eqn. (2) and these results are summarized in Table 1. Although the values of δ_W, δ_M and K_S are not appreciably different from the corresponding values obtained at $[X_0] = 2.0 \times 10^{-4}$ M (Table 1), the standard deviations associated with these parameters are significantly lower at $[X_0] = 5.0 \times 10^{-4}$ M than those at $[X_0] = 2.0 \times 10^{-4}$ M. The satisfactory fit of observed data, obtained at $[X_0] = 5.0 \times 10^{-4}$ M, to eqn. (2) is evident from the plot of Figure 1 where solid line is drawn through the calculated data points.

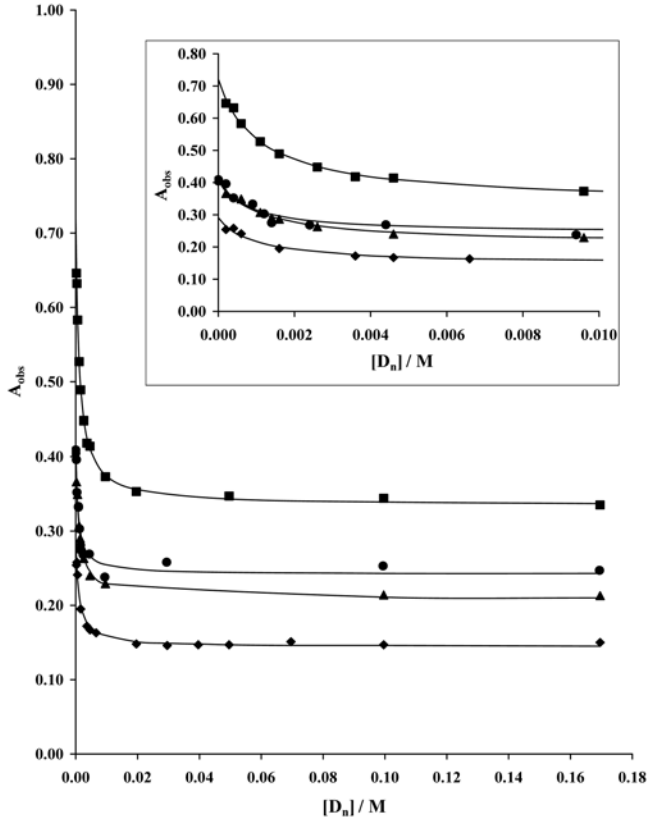


Figure 1. Plots of A_{obs} versus $[D_n]$ for (◆), $[X_0] = 2.0 \times 10^{-4}$ M, [NaOH] = 0; (▲), $[X_0] = 3.0 \times 10^{-4}$ M, [NaOH] = 0; (●), $[X_0] = 3.0 \times 10^{-4}$ M, [NaOH] = 1.2×10^{-3} M; and (■), $[X_0] = 5.0 \times 10^{-4}$ M, [NaOH] = 0. The solid lines are drawn through the calculated values of absorbance using eqn. (2) for (◆), 10^4 CMC = 3.84 M, K_S = 1012 M^{-1}, δ_W = 1453 $M^{-1}cm^{-1}$, δ_M = 721 $M^{-1}cm^{-1}$; (▲), 10^4 CMC = 3.84 M, K_S = 939 M^{-1}, δ_W = 1355 $M^{-1}cm^{-1}$, δ_M = 697 $M^{-1}cm^{-1}$; (●), 10^4 CMC = 6.00 M, K_S = 1370 M^{-1}, δ_W = 1380 $M^{-1}cm^{-1}$, δ_M = 810 $M^{-1}cm^{-1}$; and (■), 10^4 CMC = 3.84 M, K_S = 902 M^{-1}, δ_W = 1441 $M^{-1}cm^{-1}$, δ_M = 670 $M^{-1}cm^{-1}$.

Although the rate of alkaline hydrolysis of NBPT is very sensitive to $[HO^-]$ both in the presence and absence of CTABr micelles, an attempt has been made to determine K_S at 1.2×10^{-3} M NaOH. The values of were obtained at 314 nm and different values of $[CTABr]_T$ in the presence of 1.2×10^{-3} M NaOH and 3.0×10^{-4} M NBPT. The least squares calculated values of δ_W, δ_M, K_S and Σd_i^2 from eqn. (2) using these values are shown in Table 1. The calculated parameters, K_S and δ_M, are associated with unusually large standard deviations which could be attributed to rather low value of ΔA^0_{obs} (≈ 0.15) and large uncertainty in the determination of A^0_{obs} values due to high rate of hydrolysis of NBPT under such conditions.

(c) Product Characterization: The alkaline hydrolysis product of NBPT is affirmed as *N*-benzylphthalamate ion ($NBPA^-$) by comparing the final UV absorption spectra of hydrolytic products with the authentic sample of *N*-benzyl-

Table 2. Alkaline hydrolysis (1.0×10^{-3} M NaOH) of NBPT at different $[CTABr]_T$, calculated from eqn. (3)[a]

[CTABr] M	$10^3 k_{obs}$[b] s^{-1}	δ_{app}[b] $M^{-1}cm^{-1}$	10^3 A_∞[b]	$10^3 k_{calcd}$[c] s^{-1}
5.0×10^{-4}	24.2 ± 0.2[d]	2343 ± 11[d]	8 ± 1[d]	31.4
6.0×10^{-4}	30.9 ± 0.5	2452 ± 26	11 ± 1	37.3
7.0×10^{-4}	36.0 ± 0.5	2228 ± 19	12 ± 1	42.4
8.0×10^{-4}	40.9 ± 0.9	2116 ± 34	13 ± 1	46.9
1.0×10^{-3}	48.2 ± 1.2	2269 ± 51	15 ± 1	54.0
1.5×10^{-3}	62.7 ± 1.4	2006 ± 48	19 ± 1	65.6
2.0×10^{-3}	81.9 ± 2.1	2315 ± 75	11 ± 1	72.1
3.0×10^{-3}	92.4 ± 1.3	2049 ± 37	8 ± 1	77.9
5.0×10^{-3}	88.2 ± 1.6	2025 ± 45	10 ± 1	78.9
7.0×10^{-3}	77.5 ± 1.5	2254 ± 47	10 ± 1	75.9
1.0×10^{-2}	67.8 ± 0.9	2119 ± 23	10 ± 1	70.0
2.0×10^{-2}	43.0 ± 0.8	2113 ± 25	11 ± 1	53.1
3.0×10^{-2}	34.2 ± 0.7	2251 ± 21	14 ± 2	42.3
5.0×10^{-2}	22.7 ± 0.5	2151 ± 23	17 ± 2	29.9
7.0×10^{-2}	16.4 ± 0.4	2052 ± 20	20 ± 2	23.1
1.0×10^{-1}	11.6 ± 0.3	2016 ± 18	19 ± 2	17.2
1.7×10^{-1}	7.40 ± 0.23	2105 ± 24	30 ± 3	10.8

[a]$[NBPT]_0 = 2.0 \times 10^{-4}$ M, [NaOH] = 1.0×10^{-3} M, T = 35 °C, λ = 300 nm, 2% v/v CH_3CN in the aqueous reaction mixture. [b]Calculated from eqn. (1). [c]Calculated from eqn. (3) with 10^4 CMC = 3.66 M, k_W^2 = 21.6 $M^{-1}s^{-1}$, $10^3 k_M$ = 2.03 ± 0.13 M s^{-1}, K_{OH} = 60 M^{-1} and K_S = 831 ± 195 M^{-1} where $10^4 \Sigma d_i^2$ = 9.229. [d]Error limits are standard deviations.

Table 3. Alkaline hydrolysis (2.0×10^{-3} M NaOH) of NBPT at different $[CTABr]_T$, calculated from eqn. (3)[a]

[CTABr] M	$10^3 k_{obs}$[b] s^{-1}	δ_{app}[b] $M^{-1}cm^{-1}$	10^3 A_∞[b]	$10^3 k_{calcd}$[c] s^{-1}
6.0×10^{-4}	65.5 ± 0.8[d]	2197 ± 24[d]	7 ± 1[d]	71.9
8.0×10^{-4}	75.9 ± 1.6	2136 ± 40	11 ± 1	85.5
1.0×10^{-3}	105 ± 2	1905 ± 56	9 ± 1	95.4
2.0×10^{-3}	125 ± 3	1946 ± 67	11 ± 1	119.2
4.0×10^{-3}	130 ± 3	1964 ± 76	12 ± 1	128.1
5.0×10^{-3}	124 ± 3	1960 ± 65	12 ± 1	127.4
7.0×10^{-3}	117 ± 3	1999 ± 53	12 ± 1	123.2
2.0×10^{-2}	97.2 ± 1.5	2128 ± 34	11 ± 1	90.8
3.0×10^{-2}	77.6 ± 1.0	2292 ± 26	11 ± 1	74.3
4.0×10^{-2}	57.1 ± 0.7	2168 ± 18	13 ± 1	62.7
5.0×10^{-2}	56.4 ± 0.5	2229 ± 16	12 ± 1	54.2
7.0×10^{-2}	41.7 ± 0.5	2336 ± 16	14 ± 1	42.6
1.0×10^{-1}	29.8 ± 0.4	2286 ± 14	17 ± 1	32.2
1.7×10^{-1}	20.4 ± 0.5	2342 ± 19	27 ± 3	20.5

[a]$[NBPT]_0 = 2.0 \times 10^{-4}$ M, [NaOH] = 2.0×10^{-3} M, T = 35 °C, λ = 300 nm, 2% v/v CH_3CN in the aqueous reaction mixture. [b]Calculated from eqn. (1). [c]Calculated from eqn. (3) with 10^4 CMC = 3.84 M, k_W^2 = 25.25 $M^{-1}s^{-1}$, $10^3 k_M$ = 39.6 ± 3.0 M s^{-1}, K_{OH} = 44 ± 7 M^{-1} and K_S = 986 ± 240 M^{-1} where $10^4 \Sigma d_i^2$ = 4.090. [d]Error limits are standard deviations.

phthalamic acid under the same condition.[4] Molar absorptivities of $NBPA^-$ ion and phthalic acid at 300 nm are nearly zero. Therefore, the apparent molar absorptivity of the reaction mixture, $\delta_{app} \approx \delta_{NBPT}$ at 300 nm because $\delta_{app} = \delta_{NBPT} - \delta_P$ where δ_{NBPT} and δ_P represent the molar absorptivity of NBPT and products, respectively. The calculated values of δ_{app} turned out to be almost independent of the total concentration of CTABr and NaOH (Tables 2 and 3). The values of A_∞ (Tables 2 and 3) show that the products of the reaction do not absorb to a detectable level at 300 nm.

Results and Discussion

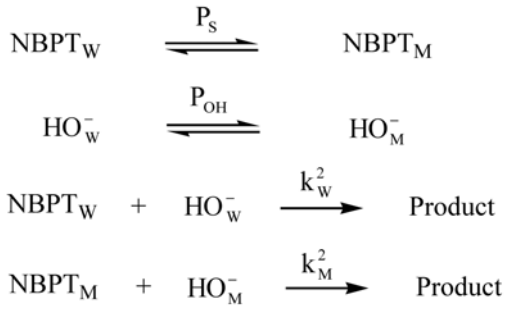
The cleavage of *N*-benzylphthalimide (NBPT) was studied within $[CTABr]_T$ range 0.0-1.7×10^{-1} M at 1.0×10^{-3} M NaOH. Pseudo-first-order rate constants, k_{obs}, are shown in Table 2. Similar observations were obtained at 2.0×10^{-3} M NaOH and the observed data are summarized in Table 3. The study[4] on alkaline hydrolysis of NBPT reveals that the reactants for the reaction under present experimental conditions are HO^- and NBPT. The variation of k_{obs} with $[CTABr]_T$ at the constant [NaOH] clearly reveals the well defined maxima at both 1.0×10^{-3} and 2.0×10^{-3} M NaOH. Such observations on related reaction systems have been explained in terms of either less commonly used Berezin's pseudophase (BPP) model[6] or more widely used pseudophase ion-exchange (PIE) model.[2,7,8]

Berezin's Pseudophase (BPP) Model. The reaction scheme for the alkaline hydrolysis of NBPT, in the presence of CTABr micelles, D_n, is shown in Scheme 1, where subscripts *W* and *M* represent aqueous pseudophase and micellar pseudophase, respectively, P_S and P_{OH} are the partition coefficients for the distribution of respective NBPT and HO^- between aqueous and micellar pseudophases. Observed rate law (rate = k_{obs} $[NBPT]_T$ with $[NBPT]_T$ = $[NBPT_W]$ + $[NBPT_M]$) and Scheme 1 can lead to eqn. (3) provided $P_S >> 1$, $P_{OH} >> 1$ and $[D_n]V_M << 1$ where $[D_n]$ and V_M represent molar concentration of micelles and molar volume of the micellar reaction region, respectively.[9]

$$k_{obs} = \frac{k_W + k_M K_S K_{OH}[D_n]}{(1 + K_S[D_n])(1 + K_{OH}[D_n])} \quad (3)$$

In eqn. (3), $k_W = k_W^2 [HO^-]_T$, $k_M = k_M^{mr} [HO^-]_T$ and $k_M^{mr} = k_M^2 / V_M$.

An attempt to fit the observed data (k_{obs} versus $[D_n]$) to eqn. 3 requires knowledge of CMC values under the present experimental conditions. The values of CMC were determined by graphical technique[10] as 3.66×10^{-4} and 3.84×10^{-4} M at 1.0×10^{-3} and 2.0×10^{-3} M NaOH, respectively. The values of k_M^{mr}, K_S and K_{OH} were calculated from eqn. (3) considering k_W^2 as known parameter. The values of k_W^2



Scheme 1

$[HO^-]_T$ at 1.0×10^{-3} and 2.0×10^{-3} M NaOH were obtained from k_{obs} values determined experimentally at $[CTABr]_T <$ CMC including at $[CTABr]_T = 0$ and thus the values of $k_W^2[HO^-]_T$ at 1.0×10^{-3} and 2.0×10^{-3} M NaOH are $(21.6 \pm 0.3) \times 10^{-3}$ and $(50.5 \pm 1.7) \times 10^{-3}$ s^{-1}, respectively. The observed data at 2.0×10^{-3} M NaOH (Table 3) fit to eqn. 3 and nonlinear least-squares calculated values of k_M, K_S, K_{OH} and least-squares (Σd_i^2) are $(39.6 \pm 3.0) \times 10^{-4}$ M s^{-1}, 986 ± 240 M^{-1}, 44 ± 7 M^{-1}, and 4.09×10^{-4}, respectively. The extent of reliable fit of observed data to eqn. (3) is evident from the calculated values of rate constants (k_{calcd}) as shown in Table 3. The values of k_M, K_S and K_{OH} were also calculated at different presumed values of CMC (ranging from 3.84×10^{-4} M to 5.26×10^{-4} M) at which the percent residual errors {RE = $100 \times (k_{obs\,i} - k_{calcd\,i})/k_{obs\,i}$ where $k_{obs\,i}$ and $k_{calcd\,i}$ represent respective experimentally determined and calculated values of rate constant at the *i*th value of $[CTABr]_T$} were only slightly changed. But the respective values of k_M, K_S and K_{OH} changed from 39.6×10^{-4} M s^{-1} to 41.3×10^{-4} M s^{-1}, 986 M^{-1} to 1710 M^{-1}, and 44 M^{-1} to 39 M^{-1}, with change in CMC from 3.84×10^{-4} M to 5.26×10^{-4} M.

The observed data at 1.0×10^{-3} M NaOH (Table 2) did not fit to eqn. (3) in the sense that the nonlinear least-squares regression analysis could not converge such a data fit to a minimum least-squares value when k_M, K_S and K_{OH} were considered as unknown parameters. However, the same observed data fit to eqn. (3) when only k_M, and K_S were considered as unknown parameters. The nonlinear least-squares treatment of observed data to eqn. (3) gave $10^3 k_M = 2.03 \pm 0.13$ M s^{-1}, $K_S = 831 \pm 195$ M^{-1}, and $10^4 \Sigma d_i^2 = 9.229$ with 10^4 CMC = 3.66 M, $10^3 k_W = 21.6$ s^{-1} and $K_{OH} = 60$ M^{-1}. The value of K_{OH} (69 M^{-1} at 25 °C) was determined experimentally as described elsewhere.[3] The increase in CMC from 3.66×10^{-4} M to 4.99×10^{-4} M resulted in the change in k_M from 2.03×10^{-3} M s^{-1} to 1.95×10^{-3} M s^{-1} and in K_S from 831 M^{-1} to 1141 M^{-1} while the RE values were slightly (≤ 5%) changed within $[CTABr]_T$ range $5.0 \times 10^{-4} - 1.7 \times 10^{-1}$ M.

Although the fitting of observed data to eqn. (3) is better at 2.0×10^{-3} M NaOH than at 1.0×10^{-3} M NaOH in terms of RE values, the values of k_M^{mr} (= $k_M/[HO^-]_T$) and K_S are almost independent of [NaOH] within the domain of experimental uncertainties. In view of the basic assumptions of BPP and pseudophase (PP) micellar models, k_M^{mr} and K_S should be independent of [NaOH]. The values k_M^2 (= $k_M^{mr} V_M$ with $V_M = 0.3$ M^{-1})[3] are 0.61 and 0.59 $M^{-1}s^{-1}$ at 1.0×10^{-3} and 2.0×10^{-3} M NaOH, respectively. These k_M^2 values are ~35- to 40-fold smaller than k_W^2 (= 22 to 25 $M^{-1}s^{-1}$) which cannot be attributed to only lower polarity of the reaction medium for micellar-mediated reaction because the increase in the content of acetonitrile from 2 – 70% v/v in mixed aqueous solvent decreases k_{obs} for alkaline hydrolysis of NBPT at 2.0×10^{-3} M NaOH by only ~7.5-fold.[4] Experimental observations indirectly show that the polarity and concentration of water decrease continuously as the distance increases from Stern region to the micellar centre *i.e.* core and consequently the micellar pseudophase is non-homogeneous in terms of the distribution of micellized molecules of different hydrophilicity. Hydroxide ion is certainly highly hydrophilic while NBPT is highly hydrophobic. Hence it is plausible to propose that either different average locations of HO^- ions and NBPT molecules in the micellar pseudophase or considerably low value of HO_M^- in the vicinity of $NBPT_M$ molecules due to continuous decrease in $[H_2O]$ with increase in distance from exterior to core of micelle are partly responsible for considerably lower value of k_M^2 compared with k_W^2.

Pseudophase Ion Exchange (PIE) Model. This model uses pseudophase micellar model coupled with an ion-exchange formalism at ionic micellar surface as shown by eqn. (4)[2,7-10]

$$HO_M^- + Br_W^- \underset{}{\overset{K_{OH}^{Br}}{\rightleftharpoons}} HO_W^- + Br_M^- \qquad (4)$$

where Br^- is inert counterion of CTABr surfactant, $K_{OH}^{Br} = K_{Br}/K_{OH}$ with $K_{Br} = [Br_M^-]/[Br_W^-][D_n]$ and $K_{OH} = [HO_M^-]/[HO_W^-][D_n]$. The observed rate law (rate = $k_{obs}[NBPT]_T$) and pseudophase micellar model coupled with eqn. (4) can lead to eqn. (5)[2,7-9]

$$k_{obs} = \frac{k_W^2[HO^-]_T + (k_M^{mr}K_S - k_W^2)m_{OH}[D_n]}{1 + K_S[D_n]} \qquad (5)$$

where $[HO^-]_T = [HO_W^-] + [HO_M^-]$, $m_{OH} = [HO_M^-]/[D_n]$, k_W^2 is second-order rate constant for the reaction of HO_W^- with $NBPT_W$ and $k_M^{mr} = k_M^2/V_M$. The values of m_{OH} at different $[D_n]$ and at a constant $[HO^-]_T$ were calculated from eqn. (6) at a given value of K_{OH}^{Br} with known values of $[HO^-]_T$, $[Br^-]_T$, and β (= 0.8)[2c] where $[Br^-]_T = [Br_W^-] + [Br_M^-]$ (= $[D_n]$ + CMC), $\beta = m_{OH} + m_{Br}$ and $m_{Br} = [Br_M^-]/[D_n]$. These calculated values of m_{OH}

$$m_{OH}^2 + m_{OH}\left\{\frac{[HO^-]_T + [Br^-]_T K_{OH}^{Br}}{(K_{OH}^{Br}-1)[D_n]} - \beta\right\} - \frac{\beta[HO^-]_T}{(K_{OH}^{Br}-1)[D_n]} = 0 \qquad (6)$$

were subsequently used in eqn. (5) to calculate k_M^{mr}, K_S and least-squares, Σd_i^2, values using the nonlinear least-squares technique. Such calculations were carried out at different arbitrarily assigned values of K_{OH}^{Br} and the calculated values of k_M^{mr}, K_S and Σd_i^2 are shown in Tables 4 and 5 at a 1.0×10^{-3} and 2.0×10^{-3} M NaOH, respectively.

It is evident from Tables 4 and 5 that the values of Σd_i^2 and K_S are almost invariant while the value of k_M^{mr} increases by ~10-fold with increase in K_{OH}^{Br} from 5 to 100. Thus, it is almost impossible to decide the correct value of K_{OH}^{Br}. This seems to be a general problem with PIE model.[11] However, the reported values of K_{OH}^{Br}, and β determined experimentally under conditions not strictly similar to those of reaction kinetics, are 7-31[2a] and 0.8[2c], respectively. But, the kinetic data are generally fitted with values of K_{OH}^{Br} in the range 12-20[2c]. The values of k_M^{mr} are almost independent of [NaOH] while the values of K_S decrease by ~40% with increase in [NaOH] from 1.0×10^{-3} M to 2.0×10^{-3} M at a constant value of K_{OH}^{Br} and β. Nearly 40% decrease in K_S with increase in [NaOH] from 1.0×10^{-3} M to 2.0×10^{-3} M is apparently

Table 4. Alkaline hydrolysis (1.0×10^{-3} M NaOH) of NBPT at different $[CTABr]_T$, calculated from eqn. 5[a]

$[CTABr]_T$ M	K_{OH}^{Br} =	5	10	20	100
	$10^3 k_{obs}$[b] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}
5.0×10^{-4}	24.2 ± 0.2[d]	32.4	32.1	31.8	31.3
6.0×10^{-4}	30.9 ± 0.5	38.8	38.5	38.1	37.4
7.0×10^{-4}	36.0 ± 0.5	44.2	43.9	43.4	42.8
8.0×10^{-4}	40.9 ± 0.9	48.8	48.5	48.1	47.5
1.0×10^{-3}	48.2 ± 1.2	56.2	56.0	55.7	55.3
1.5×10^{-3}	62.7 ± 1.4	68.3	68.3	68.3	68.5
2.0×10^{-3}	81.9 ± 2.1	75.0	75.2	75.5	75.9
3.0×10^{-3}	92.4 ± 1.3	80.9	81.2	81.6	82.4
5.0×10^{-3}	88.2 ± 1.6	80.8	81.2	81.6	82.2
7.0×10^{-3}	77.5 ± 1.5	76.3	76.5	76.8	77.1
1.0×10^{-2}	67.8 ± 0.9	68.4	68.5	68.5	68.5
2.0×10^{-2}	43.0 ± 0.8	48.5	48.4	48.2	47.9
3.0×10^{-2}	34.2 ± 0.7	37.1	36.9	36.7	36.3
5.0×10^{-2}	22.7 ± 0.5	25.1	24.9	24.7	24.4
7.0×10^{-2}	16.4 ± 0.4	18.9	18.8	18.6	18.3
1.0×10^{-1}	11.6 ± 0.3	13.8	13.7	13.6	13.4
1.7×10^{-1}	7.40 ± 0.23	8.49	8.41	8.31	8.17
$10^4 \Sigma d_i^2$ =		6.480	6.069	5.555	4.761
k_M^{mr} /s^{-1} =		3.21 ± 0.34[d]	4.85 ± 0.48[d]	8.07 ± 0.76[d]	33.6 ± 2.9[d]
K_S/M^{-1} =		112 ± 18[d]	115 ± 18[d]	116 ± 17[d]	115 ± 16[d]

[a]$[NBPT]_0 = 2.0 \times 10^{-4}$ M, [NaOH] = 1.0×10^{-3} M, T = 35 ºC, λ = 300 nm, 2% v/v CH_3CN in the aqueous reaction mixture. [b]Calculated from eqn. (1). [c]Calculated from eqns. (5) and (6) with β = 0.8, 10^4 CMC = 3.66 M, and k_W^2 = 21.6 $M^{-1}s^{-1}$. [d]Error limits are standard deviations.

Table 5. Alkaline hydrolysis (2.0×10^{-3} M NaOH) of NBPT at different $[CTABr]_T$, calculated from eqn. (5)[a]

$[CTABr]_T$ M	K_{OH}^{Br} =	5	10	20	100
	$10^3 k_{obs}$[b] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}	$10^3 k_{calcd}$[c] s^{-1}
6.0×10^{-4}	65.5 ± 0.8	68.0	68.2	67.9	67.0
8.0×10^{-4}	75.9 ± 1.6	79.9	80.1	79.8	78.9
1.0×10^{-3}	105 ± 2	89.1	89.3	89.1	88.3
2.0×10^{-3}	125 ± 3	115	115	115	116
4.0×10^{-3}	130 ± 3	130	130	130	131
5.0×10^{-3}	124 ± 3	131	131	131	131
7.0×10^{-3}	117 ± 3	128	128	128	128
2.0×10^{-2}	97.2 ± 1.5	92.3	92.3	92.2	92.0
3.0×10^{-2}	77.6 ± 1.0	73.5	73.5	73.6	73.5
4.0×10^{-2}	57.1 ± 0.7	60.8	60.9	60.9	61.0
5.0×10^{-2}	56.4 ± 0.5	51.8	51.9	51.9	52.0
7.0×10^{-2}	41.7 ± 0.5	39.8	39.9	40.0	40.2
1.0×10^{-1}	29.8 ± 0.4	29.6	29.7	29.7	29.9
1.7×10^{-1}	20.4 ± 0.5	18.5	18.5	18.6	18.7
$10^4 \Sigma d_i^2$ =		6.408	6.278	6.313	6.483
k_M^{mr} /s^{-1} =		3.46 ± 0.25[d]	5.21 ± 0.36[d]	8.64 ± 0.61[d]	35.8 ± 2.6[d]
K_S/M^{-1} =		79 ± 9[d]	77 ± 9[d]	73 ± 9[d]	65 ± 8[d]

[a]$[NBPT]_0 = 2.0 \times 10^{-4}$ M, [NaOH] = 2.0×10^{-3} M, T = 35 ºC, λ = 300 nm, 2% v/v CH_3CN in the aqueous reaction mixture. [b]Calculated from eqn. (1). [c]Calculated from eqns. (5) and (6) with β = 0.8, 10^4 cmc = 3.84 M, and k_W^2 = 25.25 $M^{-1}s^{-1}$. [d]Error limits are standard deviations.

inconceivable in terms of PIE model[2] and reported data.[12]

A Comparative Look at the Kinetic Parameters, k_M^{mr} and K_S, Derived Using BPP Model (Eqn. 3) and PIE Model (Eqn. 5):

i. The values of k_M^{mr}, obtained from BPP model, are ~2-fold smaller than those obtained from PIE model.

ii. The values of K_S, obtained from BPP model, are ~8- to 9-fold larger than those obtained from PIE model.

iii. The values of K_S, obtained by spectrophotometric technique at 2.0×10^{-4} and 5.0×10^{-4} M NBPT and [NaOH] = 0, are almost similar to K_S values obtained from BPP model at 2.0×10^{-4} M NBPT as well as 1.0×10^{-3} and 2.0×10^{-3} M NaOH.

Conclusion

Although the values of least-squares, Σd_i^2, do not differ significantly in the observed data fit to equations derived based upon BPP and PIE models, the calculated kinetic parameters, especially K_S from BPP model appear to be more reliable compared to those obtained from PIE model because the values of K_S from BPP model are, within the limits of experimental uncertainties, similar to the corresponding K_S values determined spectrophotometrically. However, both BPP and PIE models have their own known intrinsic limitations and therefore present conclusion based upon just present single study cannot be considered as a general one.

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