Study of Cationic and Nonionic Mixed Micelles with NaBr and 3,5-Cl₂C₆H₃CO₂Na by Use of Probe Nucleophilic Reaction of Piperidine with Ionized Phenyl Salicylate

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Abstract: Behaviors of cationic and nonionic mixed micelles in the form of hexadecyltrimethylammonium bromide (HDABr) and hexadecyltrimethylammonium bromide-Polyethylene glycol hexadecyl ether (C₁₆E₂₀), in the presence of inert salts (NaBr and 3,5-dichlorosodium benzoate), by the use of reaction probe between Pp and ionized PhSH (Pp = piperidine and PhSH = phenyl salicylate), has been reported in this work. The values of R_X^{Br} (R_X^{Br} denotes ion exchange constants obtained in the presence of micelles of different structural features) or K_X^{Br} (K_X^{Br} denotes ion exchange constants obtained in the presence of micelles of the same structural features) for 3,5-Cl₂C₆H₃CO₂⁻ were almost the same at three different [HDABr]_T (0.006, 0.010 and 0.015 M). The average value of R_X^{Br} or K_X^{Br} determined, in the presence of pure HDABr micelles, using semi empirical kinetic (SEK) method appeared to be almost 2½-fold larger (R_X^{Br} or K_X^{Br} = 198) than that in the presence of mixed HDABr-C₁₆E₂₀ micelles (R_X^{Br} or K_X^{Br} = 78). Rheological measurements indicated the existence of wormlike/twisted micelles and vesicle at 0.015 M pure HDABr, various [3,5-Cl₂C₆H₃CO₂Na], and 25 and 35°C whereas there were evidence of only spherical micelles in the presence of mixed HDABr-C₁₆E₂₀ ([HDABr]_T = 0.015 M and [C₁₆E₂₀]_T = 0.006 M) at both temperatures.

Key words: piperidine, phenyl salicylate, hexadecyltrimethylammonium bromide, polyethylene glycol hexadecyl ether, wormlike micelles, vesicle

1 Introduction

There is no dispute on the recent rises and needs for new and consistent scientific information in the field of research on micelles¹. Surface active substances (SAS), popularly called surfactants, form micelles of different characteristics and they have been discovered for the past 10 decades². It has also been unanimously believed that changes in micelles behaviors, from one structural feature to another, are related to the counterion (X) affinity to their surfaces³⁻⁸ and different studies on qualitative NMR studies on the affinity of X ions^{4, 6, 8}. Some di-substituted benzoate salts were studied based on NMR and the counterions X (including 3,5-Cl₂C₆H₃CO₂⁻) were reported to be inserted into the micellar hydrophobic core/hydrophilic

head interface⁹. Rheological studies, small angle neutron scattering (SANS), and cryo-TEM images have also revealed the micellar growth and its formation for the X ions¹⁰.

There have been quite a number of studies that provided various kinetic models which were used to correlate quantitatively the observed data for the rate of micellar catalyzed reactions¹¹. However, most of the studies were focused on pure micellar system¹² and very few were reported based on mixed micellar system¹³. Furthermore, theoretical studies on the structure of mixed micelles began a few decades ago¹⁴ and the detail explanations on their characteristic features are not yet well cleared relative to those of pure micellar systems. There was an

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attempt, in 1998¹⁵⁾, to explain observations based upon the effects of mixed micelles on the kinetic reaction rate using Multiple Micellar Pseudo Phase (MMPP) models. But that was carried out to study the mixed anionic-nonionic micellar combination. Another study¹⁶⁾, however, presented the use of Pseudo Phase Micellar (PPM) model to explain the rate of reactions affected by the mixed cationic-nonionic micellar system. The PPM model merged with an empirical equation (equation (1))¹⁷⁾ was used to treat the results obtained in this study.

$$K_S = K_S^0 / (1 + K_{XS}[MX]) \quad (1)$$

where K_S is the HDABr micellar binding constant of the anionic reactant, S^- , (and equals to K_S^0 in the absence of X^-), K_{XS} denotes empirical constant and its value indicates the ability of X^- to transfer anionic reactant, S^- , from pure HDABr micelles to bulk aqueous phase¹⁸⁾.

The behavior of pure cationic micelles (HDABr), for the reaction of piperidine with ionized phenyl salicylate, in the presence of MX, 3,5-dichlorosodium benzoate ($3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$), was recently studied¹⁹⁾. However, the article has not reported such behavior in the presence of mixed micelles. It has been known for nearly three decades that the counterionic salts affect the physicochemical properties of mixed aqueous ionic-nonionic surfactants^{20–22)}. Effects of the concentrations of moderately hydrophobic counterions on the structural features of mixed aqueous ionic-nonionic surfactants have been reported rarely, although such systems are very important industrially as well as technologically²⁰⁾. The effects of sodium benzoate (NaBz), sodium hexanoate (NaHx) and NaCl on the associated physicochemical properties of polymer-cationic surfactant mixed system have been studied and the qualitative interpretation of the findings is given in detail^{20, 23–25)}. A quantitative interpretation of the results of these^{20–25)} and related studies^{26–29)} is difficult because of the unavailability of the values of the counterion binding constants with the ionic surfactants in the absence and presence of nonionic surfactant or polymer. In the continuation of our study on the determination of the hydrophilic and moderately hydrophobic counterions binding constants with HDABr in the absence and presence of $\text{C}_{16}\text{E}_{20}$ ³⁰⁾, we wish to report the following new findings on: (i) the effects of $[\text{C}_{16}\text{E}_{20}]$ on the binding affinity of X^- with HDABr, (ii) the rheological study of mixed aqueous HDABr/MX/ $\text{C}_{16}\text{E}_{20}$ / H_2O (MX = $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$) solution and (iii) the possible quantitative relationship between the values of ion exchange constants (R_X^{Br} or K_X^{Br}) and the structural features of HDABr/MX/ $\text{C}_{16}\text{E}_{20}$ / H_2O (MX = $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$). The choice of MX as $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$ was motivated by nearly 4-fold larger mean value of R_X^{Br} or K_X^{Br} for $X = 3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2^-$ than that for $X = \text{salicylate ion}$ ³⁰⁾. The results and their plausible explanations are described in this manuscript. It is perhaps noteworthy that the present manuscript constitutes the second report

where the effect of mixed micelles, HDABr- $\text{C}_{16}\text{E}_{20}$ / H_2O , on the counterion binding constant have been studied quantitatively.

2 Experimental

Commercially and commonly found reagent-grade chemicals such as piperidine (Pp), phenyl salicylate (PhSH), hexadecyltrimethylammonium bromide (HDABr), polyethylene glycol hexadecyl ether ($\text{C}_{16}\text{E}_{20}$), and sodium bromide (NaBr) were used as received. 3,5-Dichlorobenzoic acid ($3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$) was obtained from Aldrich with 97% purity but it was recrystallized before use. The standard solutions of 0.2 M MX ($3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$) were prepared by adding 0.25 M NaOH to 0.2 M solution of $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$. The 0.01 M stock solution of PhSH was prepared in acetonitrile while that of 1.0 M Pp was prepared using distilled deionized water.

2.1 Kinetic Method

Pseudo first order rate law kinetics has been used to monitor the rate of nucleophilic reaction of Pp with ionized PhSH (PhS^-) in this study. A large number of experiments involving mixture of substances – 0.10 M Pp, 0.2 mM PhSH, 0.03 M NaOH and various concentrations of MX (= $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$) were subjected to spectrophotometric studies to monitor the disappearance of PhS^- at 370 nm and 35°C (in the presence of pure HDABr and mixed HDABr- $\text{C}_{16}\text{E}_{20}$). The details and the outcome of the investigation were described elsewhere¹⁷⁾. The rate law was taken care of by maintaining the ratio of $[\text{PhS}^-]_T : [\text{Pp}]_T$ as 1 : 500 with $[\]_T$ signifying the total concentration. The time taken for the reaction and the UV light absorbed by the mixture is related to equation (2).

$$A_{\text{obs}} = [\text{PhS}^-]_0 \delta_{\text{app}} \exp(-k_{\text{obs}} t) + A_{\infty} \quad (2)$$

where A_{obs} = absorbance at time, t , $[\text{PhS}^-]_0$ = initial concentration of PhS^- , δ_{app} = apparent molar extinction coefficient/molar extinction coefficient times the optical path length, k_{obs} = observed pseudo first order rate constant, and $A_{\infty} = A_{\text{obs}}$ at $t = \infty$. Equation (2) was used to find the values of δ_{app} using the nonlinear least-squares method and the results were analyzed as described elsewhere¹⁷⁾. The values of k_{obs} were obtained in the presence of pure $[\text{HDABr}]_T$ and mixed $[\text{HDABr}]_T$ - $[\text{C}_{16}\text{E}_{20}]_T$ micelles at different $[\text{MX}]$. Different values of k_{obs} , in the absence of HDABr, were also determined and are required in the use of the SEK method and the brief reaction pathway for the piperidinolysis of PhS^- is demonstrated in **Scheme 1**. Details of this technique and explanations of the reaction mechanisms are according to what was described in the earlier report¹⁷⁾.

Scheme 1 Brief reaction mechanism of the aqueous piperidinolysis of PhS^- .

2.2 Use of semi empirical kinetic, SEK, method to find the values of K_X^{Br} or R_X^{Br} for $X=3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2^-$

The determination of K_X^{Br} or R_X^{Br} for the counterion was done by the use of SEK method and specific kinetic probe. This SEK method is the only way to estimate the ion exchange constant of dichlorobenzoate ion on cationic micelles. The pseudo first order rate constants for the reaction of Pp and PhS^- , in the presence of pure HDABr micelles, at various $[\text{MX}]$ ($\text{MX} = 3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$) and 35°C have been used as an evidence to use the method. Further explanations are presented in the past^{17–19}. The SEK method was used to calculate the values of ion exchange constants (K_X^{Br} or R_X^{Br}) and the theoretical value of K_S^0 (7000 M^{-1}) was used to obtain the values of kinetic parameters, K_{XS}^{n} , in presence of pure HDABr micelles. These values are required to use the SEK method³¹ and this has been explained elsewhere³¹.

2.3 Rheological study

This study was conducted with the total volume of the sample of 10 mL at (i) constant concentration of Pp, PhSH, NaOH, and MX in the presence of pure HDABr and (ii) constant concentration of Pp, PhSH, NaOH, and MX in the presence of mixed HDABr- $\text{C}_{16}\text{E}_{20}$. Both were achieved at various $[\text{MX}]$ range (0.004 to 0.070 M) using Anton Paar MCR301 rheometer at two different temperatures (25 and 35°C). The double gap cylinder (DG26.7/T200/SS having 26.661 mm external diameter and 24.656 mm internal diameter) was used as a sample container. During the flow curve measurement, the values of steady-shear viscosity (η) were determined and the shear rate was at the range of $0.010\text{--}1000 \text{ s}^{-1}$. The details of the rheometric measurements are according to what were described in the past³².

3 Results

3.1 Effect of $[\text{NaBr}]$ on k_{obs} for the piperidinolysis of PhS^- at lower concentrations of pure HDABr and mixed HDABr- $\text{C}_{16}\text{E}_{20}$ and 35°C

The kinetic experiments on the effects of $[\text{NaBr}]$ for the

Fig. 1 Sketches showing the relationship between $^m k_{\text{obs}}$ and $[\text{NaBr}]$ for the reaction of Pp and PhS^- at three different constant $[\text{HDABr}]_T + [\text{C}_{16}\text{E}_{20}]_T = 0.006 \text{ M} + 0.00 \text{ M}$ (●), $0.006 \text{ M} + 0.6 \mu\text{M}$ (◆) and $0.006 \text{ M} + 0.060 \text{ mM}$ (■), and 35°C . The solid lines are drawn via the calculated values of the rate constant (k_{calcd}). Insert: The plots for magnified scale for the data points at lower values of $[\text{MX}]$.

reaction of 0.10 M Pp, 0.20 mM PhSH and 0.030 M NaOH in the presence of pure HDABr and mixed HDABr- $\text{C}_{16}\text{E}_{20}$ on k_{obs} (with the NaBr concentration range from 0.00–0.700 M) were conducted at 35°C and 370 nm. The value of $[\text{HDABr}]_T$ is 0.006 with 0.00 M $\text{C}_{16}\text{E}_{20}$. Similar observations were obtained by increasing $[\text{C}_{16}\text{E}_{20}]$ to 0.6 μM and 0.06 mM. The results are presented graphically in Fig. 1.

3.2 Effect of $[\text{NaBr}]$ on k_{obs} for the piperidinolysis of PhS^- at higher concentrations of mixed HDABr- $\text{C}_{16}\text{E}_{20}$ and 35°C

Other kinetic experiments (similar to the one in section 3.1) at comparatively higher $[\text{C}_{16}\text{E}_{20}]_T$ were conducted at 35°C and 370 nm³⁰. The values of $[\text{HDABr}]_T$ are 0.006, 0.010 and 0.015 M with 0.006 M $\text{C}_{16}\text{E}_{20}$. Similar observations were obtained by increasing $[\text{C}_{16}\text{E}_{20}]_T$ to 0.010 and 0.015 M³².

Table 1 Pseudo-first-order rate constants (k_{obs}) for the reaction of Pp with PhS^- at 0.006, 0.010 and 0.015 M HDABr at different $[\text{3,5-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]^a$.

$[\text{MX}]^b$ (M)	$[\text{HDABr}]_T^c = 0.006 \text{ M}$		0.010 M		0.015 M	
	$10^4 k_{\text{obs}} (\text{s}^{-1})$	$10^4 k_{\text{calcd}} (\text{s}^{-1})$	$10^4 k_{\text{obs}} (\text{s}^{-1})$	$10^4 k_{\text{calcd}} (\text{s}^{-1})$	$10^4 k_{\text{obs}} (\text{s}^{-1})$	$10^4 k_{\text{calcd}} (\text{s}^{-1})$
0.00	$28.7^d \pm 0.2$		26.6 ± 0.3^f		25.4 ± 0.2	
0.001	28.3 ± 0.4		26.8 ± 0.3		25.1 ± 0.3	
0.002	28.8 ± 0.2		27.3 ± 0.2		26.8 ± 0.2	
0.004	31.8 ± 0.3		29.2 ± 0.3		27.7 ± 0.2	
0.006	51.3 ± 0.6		42.4 ± 0.2	42.5	33.0 ± 0.3	31.5
0.008	94.4 ± 0.6	93.2 ^e	75.0 ± 0.6	73.0	54.5 ± 0.3	53.8
0.010	123.0 ± 1.3	123.2	98.3 ± 0.9	96.3	70.6 ± 0.6	72.2
0.012	143.9 ± 1.3	144.9	114.5 ± 1.5	114.7	86.3 ± 0.4	87.4
0.014	163.4 ± 1.4	161.3	127.8 ± 1.7	129.6	99.2 ± 0.7	100.3
0.016	176.7 ± 1.6	174.2	138.1 ± 1.7	142.0	110.4 ± 1.2	111.4
0.018	182.8 ± 1.9	184.6	149.3 ± 1.9	152.3	118.9 ± 1.1	121.1
0.020	192.3 ± 2.2	193.1	157.5 ± 2.1	161.1	127.5 ± 1.2	129.5
0.022	198.5 ± 2.2	200.3	166.7 ± 1.8	168.8	137.0 ± 1.2	136.9
0.026	212.0 ± 1.9	211.5	183.2 ± 2.0	181.3	149.6 ± 1.2	149.4
0.030	222.4 ± 1.4	220.0	196.2 ± 2.0	191.1	162.5 ± 1.4	159.6
0.034	229.8 ± 2.0	226.7	206.0 ± 2.1	199.0	172.1 ± 1.8	168.0
0.040	237.5 ± 1.8	234.3	211.7 ± 1.8	208.3	180.7 ± 1.5	178.1
0.060	247.3 ± 2.0	249.1	224.6 ± 2.7	227.3	198.0 ± 1.4	199.8
0.080	254.0 ± 1.7	256.7	233.1 ± 1.9	237.6	209.1 ± 1.6	212.1

^a $[\text{PhSH}]_0 = 0.2 \text{ mM}$, $[\text{Pp}] = 0.1 \text{ M}$, $[\text{NaOH}] = 0.03 \text{ M}$, $\lambda = 370 \text{ nm}$ and aqueous reaction mixture for each kinetic run contains 2% v/v acetonitrile

^b Total concentration of $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$

^c Total concentration of HDABr

^d Observed pseudo first order rate constant

^e Calculated pseudo first order rate constant

^f Error limits are standard deviations

3.3 Effect of $[\text{3,5-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ on k_{obs} for the piperidinolysis of PhS^- at a constant concentration of HDABr and 35°C

A number of kinetic experiments were also conducted at constant 0.1 M Pp, 0.2 mM PhSH and 0.03 M NaOH in the presence of 0.006 M HDABr and various values $[\text{3,5-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ (0.00–0.08 M). Similar outcomes were obtained by further increasing the concentration of HDABr to 0.010 and 0.015 M. The values of k_{obs} obtained are shown in Table 1.

3.4 Effect of $[\text{3,5-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ on k_{obs} for the piperidinolysis of PhS^- at lower concentrations of mixed HDABr- $\text{C}_{16}\text{E}_{20}$ and 35°C

Other sets of kinetic experiments were also conducted at constant 0.1 M Pp, 0.2 mM PhS^- and 0.03 M NaOH at lower concentrations of mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micelles ($[\text{HDABr}]_T = 0.006 \text{ M}$ with $[\text{C}_{16}\text{E}_{20}]_T = 6.0 \mu\text{M}$) and different

$[\text{3,5-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ (0.00–0.04 M), to investigate whether the small amount of the nonionic micelles can bring about changes to the values of rate constants as well as the empirical constants. Complementary outcomes were obtained upon increasing $[\text{C}_{16}\text{E}_{20}]_T$ to 0.06 mM. The obtained results are presented in Table 2.

3.5 Effect of higher concentration of mixed HDABr- $\text{C}_{16}\text{E}_{20}$ on k_{obs} for the reaction of Pp with PhS^- at various $[\text{3,5-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ and 35°C

Other sets of kinetic experiments were also conducted at constant 0.1 M Pp, 0.2 mM PhS^- and 0.03 M NaOH in the presence of mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micelles ($[\text{C}_{16}\text{E}_{20}]_T = 0.006, 0.010$ and 0.015 M with 0.006 M HDABr) and different $[\text{3,5-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ (0.00–0.08 M), with the purpose to investigate the influence of introducing the nonionic micelles to the reaction mixture. Complementary outcomes were obtained upon increasing $[\text{C}_{16}\text{E}_{20}]_T$ to 0.010 and 0.015

Table 2 Pseudo-first-order rate constants ($^m k_{\text{obs}}$) for the reaction of Pp with PhS^- at 0.006 M HDABr in the presence of 0.600 μM , and 0.060 mM $\text{C}_{16}\text{E}_{20}$ and different $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]^a$.

$[\text{MX}]^b$ (M)	$[\text{HDABr}]_T^c = 0.006 \text{ M}$		0.006 M	
	$[\text{C}_{16}\text{E}_{20}]_T^d = 0.600 \mu\text{M}$		0.060 mM	
	$10^4 m k_{\text{obs}} (\text{s}^{-1})$	$10^4 m k_{\text{calcd}} (\text{s}^{-1})$	$10^4 m k_{\text{obs}} (\text{s}^{-1})$	$10^4 m k_{\text{calcd}} (\text{s}^{-1})$
0.00	20.3 ± 0.30^e		21.1 ± 0.40^g	
0.001	21.1 ± 0.29		21.3 ± 0.30	32.5
0.002	22.7 ± 0.32		21.5 ± 0.35	37.0
0.004	33.3 ± 0.38	32.7^f	29.4 ± 0.67	29.7
0.006	75.7 ± 0.47	78.3	73.5 ± 0.89	73.4
0.008	106.0 ± 0.55	106.5	101.1 ± 1.31	99.7
0.010	125.3 ± 0.63	125.7	118.3 ± 1.48	117.2
0.012	139.8 ± 0.72	139.6	129.8 ± 1.69	129.8
0.014	150.4 ± 0.43	150.2	137.6 ± 2.91	139.2
0.016	159.2 ± 0.53	158.4	146.0 ± 2.04	146.5
0.018	165.1 ± 0.75	165.1	151.0 ± 1.98	152.3
0.020	170.8 ± 1.10	170.5	156.2 ± 2.04	157.1
0.022	176.4 ± 0.92	175.1	161.4 ± 2.15	161.1
0.026	182.7 ± 1.20	182.3	165.5 ± 1.68	167.4
0.030	188.3 ± 1.14	187.7	170.5 ± 1.49	174.1
0.034	192.2 ± 1.31	192.0	176.8 ± 1.39	175.7
0.040	194.5 ± 1.64	196.9	180.6 ± 1.52	179.9

Footnote a, b, and c are the same as in Table 1

^d Total concentration of $\text{C}_{16}\text{E}_{20}$

^e Observed pseudo first order rate constant

^f Calculated pseudo first order rate constant

^g Error limits are standard deviations

Fig. 2 Sketches showing the relationship between $^m k_{\text{obs}}$ and $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ for the reaction of Pp and PhS^- at three different constant $[\text{HDABr}]_T + [\text{C}_{16}\text{E}_{20}]_T/M = 0.006 + 0.006$ (●), $0.006 + 0.010$ (■) and $0.006 + 0.015$ (◆), and 35°C . The dotted lines are drawn via the calculated values of the rate constant (k_{calcd}). Insert: The plots for magnified scale for the data points at lower values of $[\text{MX}]$.

Fig. 3 Sketches showing the relationship between $^m k_{\text{obs}}$ and $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ for the reaction of Pp and PhS^- at three different constant $[\text{HDABr}]_T + [\text{C}_{16}\text{E}_{20}]_T/M = 0.010 + 0.006$ (●), $0.010 + 0.010$ (■) and $0.010 + 0.015$ (◆), and 35°C . The dotted lines are drawn via the calculated values of the rate constant (k_{calcd}). Insert: The plots for magnified scale for the data points at lower values of $[\text{MX}]$.

Fig. 4 Sketches showing the relationship between $m k_{\text{obs}}$ and $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ for the reaction of Pp and PhS^- at three different constant $[\text{HDABr}]_{\text{T}} + [\text{C}_{16}\text{E}_{20}]_{\text{T}}/M = 0.015 + 0.006$ (●), $0.015 + 0.010$ (■) and $0.015 + 0.015$ (◆), and 35°C . The dotted lines are drawn via the calculated values of the rate constant (k_{calcd}). Insert: The plots for magnified scale for the data points at lower values of $[\text{MX}]$.

M and the sketches of k_{obs} against $[\text{MX}]$ are presented in Figs. 2, 3 and 4, respectively.

3.6 Rheological characteristics of aqueous pure HDABr micellar solutions at various $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, 25 and 35°C

Aqueous form of solution mixtures of constant $[\text{Pp}]$, $[\text{PhS}^-]$, and $[\text{NaOH}]$ in the presence of 0.015 M HDABr and different $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ were rheologically measured. The experiments were conducted at the steady-shear response and two distinct temperatures (25 and 35°C). Different values of shear viscosity (η) at various shear rates ($\dot{\gamma}$) were determined. The results are presented, using log-log sketches of η vs $\dot{\gamma}$, in Figs. 5a and 5b at, respectively, 25 and 35°C .

3.7 Rheological characteristics of aqueous mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micellar solutions at various $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, 25 and 35°C

To study the effects of mixed micelles, another aqueous solution mixtures of constant $[\text{Pp}]$, $[\text{PhS}^-]$, $[\text{NaOH}]$, and mixed 0.015 M HDABr and 0.006 M $\text{C}_{16}\text{E}_{20}$ at different $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, were subjected to rheometric measurements. The experimental conditions were similar as that in 3.6 above and different values of η at different $\dot{\gamma}$ were also determined. Different observations were obtained in the presence of 0.006 M $\text{C}_{16}\text{E}_{20}$ and the results are presented, using log-log sketches of η vs $\dot{\gamma}$, in Figs. 6a and 6b at, respectively, 25 and 35°C .

Fig. 5 Sketches representing zero shear viscosity (η) against shear rate ($\dot{\gamma}$) for the piperidinolysis of PhS^- containing 0.015 M HDABr and $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]/M =$ (a) 0.004 (●) 0.007 (□) 0.015 (▲) 0.025 (◆) 0.040 (○) and 0.070 (◇) at 25°C and (b) 0.004 (●) 0.007 (□) 0.015 (▲) 0.025 (◆) 0.040 (○) and 0.070 (◇) at 35°C .

4 Discussion

4.1 Explanation of kinetic results at constant concentration of HDABr micelles and various values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ and 35°C

The values of k_{obs} for the reaction of 0.1 M Pp and 0.2 mM PhSH in basic medium with $[\text{HDABr}]_{\text{T}} = 0.006$, 0.010 or 0.015 M, $[\text{C}_{16}\text{E}_{20}]_{\text{T}} = 0$, and different concentration of $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$ obey semi empirical equation (3)

$$k_{\text{obs}} = \frac{k_0 + \theta K^{X/S} ([\text{MX}] - [\text{MX}]_0^{\text{op}})}{1 + K^{X/S} ([\text{MX}] - [\text{MX}]_0^{\text{op}})} \quad (3)$$

or

$$k_{\text{obs}} = \frac{k_0 + {}^X k_{\text{cat}} ([\text{MX}] - [\text{MX}]_0^{\text{op}})}{1 + K^{X/S} ([\text{MX}] - [\text{MX}]_0^{\text{op}})} \quad (4)$$

where $k_0 = k_{\text{obs}}$ at $[\text{MX}] = [\text{MX}]_0^{\text{op}}$ ($[\text{MX}]_0^{\text{op}}$ optimum values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$) were obtained by the use of iterative method explained in detail in the literature^{17, 33}). Symbols $K^{X/S}$ and θ are empirical constants and their values were determined by the use of nonlinear least squares method. The values of k_0 were found experimentally by carrying out kinetic runs at constant $[\text{HDABr}]_{\text{T}}$ and $[\text{MX}] = [\text{MX}]_0^{\text{op}}$ (Table 3). The optimum values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ ($[\text{MX}]_0^{\text{op}}$) at various $[\text{HDABr}]_{\text{T}}$ were determined as described in the past¹⁷) and are presented in Table 3.

The values of $K^{X/S}$ and θ , obtained at different $[\text{HDABr}]_{\text{T}}$, were calculated using equation (3) and are presented in

Table 3 Values of empirical constants, θ , and $K^{X/S}$ obtained using equations 3 with the $[MX]_0^{op}$ values for $MX = 3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$ at different $[\text{HDABr}]_T$ ^a.

$[\text{HDABr}]_T$ (M)	$10^4 k_0^c$ (s ⁻¹)	$[\text{MX}]_0^{op}$ (M)	$10^3 \theta^d$ (s ⁻¹)	$K^{X/Sde}$ (M ⁻¹)	$10^4 {}^X k_{cat}^e$ (M ⁻¹ s ⁻¹)	$F_{X/S}$	$K^{X/S}$ (M ⁻¹)	$K_{X/S}^n$ (M ⁻¹)	K_X^{Br} or R_X^{Br}
0.006 ^b	28.7 ± 0.2	0.00531	28.1 ± 0.2	128.0 ± 3.1	32.6 ± 0.7 ^f	0.90 ^g	5504 ^h	4954.0 ⁱ	198 ^j
0.010	26.6 ± 0.3	0.00515	27.2 ± 0.4	81.7 ± 3.5	22.2 ± 0.7	0.87	5727	4982.7	199
0.015	25.4 ± 0.2	0.00552	25.6 ± 0.3	56.7 ± 1.8	14.5 ± 0.3	0.82	6010	4928.2	197

Footnote a is the same as in Table 1.

^b Total concentration of HDABr^c $k_0 = k_{obs}$ at $[\text{MX}] = [\text{MX}]_0^{op}$ ^d The values of θ and $K^{X/S}$ were calculated from equation (3)^e The values of ${}^X k_{cat}$ and $K^{X/S}$ were calculated from equation (4) with the replacement of $\theta K^{X/S}$ in equation (3) by ${}^X k_{cat}$ ^f Limits of error signifies standard deviations^g $F_{X/S} = \theta / (k_w^2 [\text{Pp}]_T)$, where $k_w^2 = k_{obs}^2$ at $[\text{HDABr}]_T = [\text{C}_{16}\text{E}_{20}]_T = 0$ and $[\text{Pp}]_T = 0.1$ M and the value of k_w^n , under such conditions is $0.322 \text{ M}^{-1} \text{ s}^{-1}$ ^h $K_{X/S} = K_{X/S} (1 + K_S^0 [\text{HDABr}]_T)$, where $K_S^0 = 7 \times 10^3 \text{ M}^{-1}$ ⁱ $K_{X/S}^n = F_{X/S} K_{X/S}$ ^j K_X^{Br} or $R_X^{Br} = K_{X/S}^n / K_{Br/S}^n$, where $K_{Br/S}^n = 25 \text{ M}^{-1} \text{ }^{36)}$

Table 3. It has been described in detail elsewhere³⁴⁾ that a plausible reaction mechanism in terms of pseudophase micellar model and empirical equation (equation (1)) can lead to equation (3) with $K^{X/S}$ and θ represented by equations (5) and (6), respectively. It has been noticed from equation (5) that increase in $[\text{HDABr}]_T$ results in the corresponding decrease in the values of $K^{X/S}$ (so long as $K_{X/S}$ does not depend on $[\text{HDABr}]_T$). This observation agrees with the results in **Table 3** where $K^{X/S} = 128, 82$ and 57 M^{-1} at respectively $[\text{HDABr}]_T = 0.006, 0.010$ and 0.015 M. But the values of $K_{X/S}$ (**Table 3**) were determined using equation (5) with 7000 M^{-1} as the literature value of $K_S^{0(11)}$.

$$K^{X/S} = K_{X/S} / (1 + K_S^0 [\text{HDABr}]_T) \quad (5)$$

$$\theta = F_{X/S} (k_w^2 [\text{Pp}]_T) \quad (6)$$

or

$${}^X k_{cat} = F_{X/S} (k_w^2 [\text{Pp}]_T) K^{X/S} \quad (7)$$

where $F_{X/S}$ is an empirical constant and its appearance in equation (6) is described in detail elsewhere³⁴⁾, k_w^2 represents second-order rate constant for the nucleophilic reaction of Pp with ionized PhSH (PhS⁻).

4.2 Ion exchange catalysis

Perhaps it is noteworthy that the observed data described in **Tables 1** and **2**, and the plots of **Figs. 1-4** where the increase in k_{obs} with increasing $[\text{MX}]$ represents catalytic effects of MX. The study carried out to discover the effects of MX (= sodium 4-chlorobenzoate) on k_{obs} for piperidinolysis of PhS⁻ revealed the decrease of nearly 10% with the increase in $[\text{MX}]$ from 0.0 to ≤ 0.2 M at constant $[\text{C}_{16}\text{E}_{20}]$ within its range $5\text{--}15$ mM and $[\text{HDABr}]_T = 0$ ³⁵⁾. Thus, the observed results exhibited by **Tables 1, 2** and

Figs. 1-4 cannot be attributed to ionic strength/salt effect. Similar observations have been presented in several reports on related studies where the nonlinear increase of k_{obs} with an increase of $[\text{MX}]$ at a constant [cationic micelles] is ascribed to the occurrence of ion exchange process X^-/PhS^- at the cationic micellar surface^{11, 18, 34)}. This characteristic behavior of HDABr/MX/H₂O/C₁₆E₂₀ catalysis is referred to ion exchange catalysis, where the origin of catalysis of MX is the ion exchange X^-/PhS^- .

It is evident from equation (4) that the apparent catalytic constant, ${}^X k_{cat}$, which measures the ability of MX to catalyze the semi ionic reactions at constant $[\text{HDABr}]_T$ is expressed as ${}^X k_{cat} = \theta K^{X/S}$. Thus, the values of ${}^X k_{cat}$ can be calculated from equation (4) with the replacement of $\theta K^{X/S}$ in equation (3) by ${}^X k_{cat}$. The values of unknown parameters $K^{X/S}$ and ${}^X k_{cat}$ were also calculated from modified equation (3) (i.e. equation (4)) where $\theta K^{X/S}$ is changed to ${}^X k_{cat}$. These calculated data are also summarized in **Tables 3** and **4**. Perhaps, it is noteworthy that the calculated values of $K^{X/S}$ and k_{calc} were turned out to be exactly the same at a particular value of $[\text{HDABr}]_T$ which is evident from **Tables 1, 2** and the plots of **Figs. 1-4** where the solid lines are drawn through the calculated values of the rate constant, k_{calc} .

To determine the values of ion exchange constant (R_X^{Br} or K_X^{Br}), the normalized values of both $K_{X/S}^n (F_{X/S} K_{X/S}^n)$ and $K_{Br/S}^n (F_{Br/S} K_{Br/S}^n)$ are required. The values of $K_{X/S}^n$ are presented in **Table 3**. The HDABr micellar binding constant for X and S (K_X and K_S), where $S = \text{PhS}^-$, has the relationship with $K_{X/S}^n$ as; $K_{X/S}^n = K_X / K_S$ ³²⁾. Similarly, the reference counterion, Br (from NaBr), has the HDABr micellar binding constant as; $K_{Br/S}^n = K_{Br} / K_S$. For the two different counterions with identical micelles structural behavior, the following equation (equation (8)) can be used to calculate the values of ion exchange constants³⁴⁾.

Table 4 Values of empirical constants, ${}^m\theta$ and ${}^mK^{X/S}$ obtained using equation 3 with the $[MX]_0^{op}$ values for $MX = 3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$ at different concentrations of mixed HDABr- $\text{C}_{16}\text{E}_{20}$ ^a.

[HDABr] _T ^b (M)	[C ₁₆ E ₂₀] _T ^c (M)	$10^4 k_0$ ^d (s ⁻¹)	${}^m[\text{MX}]_0^{op}$ (M)	$10^3 {}^m\theta$ ^e (s ⁻¹)	${}^mK^{X/Sef}$ (M ⁻¹)	$10 {}^mK_{cat}^f$ (M ⁻¹ s ⁻¹)	${}^mF_{X/S}$	${}^nK^{X/S}$ (M ⁻¹)	${}^nK^{Br/Sj}$ (M ⁻¹)	${}^mR_X^{Br}$ or ${}^mK_X^{Br}$
0.006	0.0000006	20.3 ± 0.3	0.00311	22.7 ± 0.1	178.2 ± 2.0	40.4 ± 0.3 ^g	0.8 ^h	142.6 ⁱ	1.4	102 ^k
0.006	0.00006	21.1 ± 0.4	0.00318	20.5 ± 0.1	192.6 ± 2.5	39.5 ± 0.4	0.8	154.1	1.8	85.1
0.006	0.006	33.4 ± 0.4	0.00352	27.2 ± 0.3	120.8 ± 4.2	32.9 ± 0.9	1.1	132.9	1.4 ⁱ	81.5
0.006	0.010	34.5 ± 0.4	0.00317	25.4 ± 0.2	117.6 ± 3.5	29.8 ± 0.7	1.3	152.9	2.2 ⁱ	60.0
0.006	0.015	35.7 ± 0.4	0.00318	23.3 ± 0.2	122.2 ± 3.3	28.5 ± 0.6	1.3	158.9	1.8 ⁱ	73.9
0.010	0.006	30.9 ± 0.3	0.00534	26.2 ± 0.2	67.2 ± 1.7	17.6 ± 0.3	1.1	73.9	1.0 ⁱ	85.9
0.010	0.010	43.4 ± 0.4	0.00989	21.2 ± 0.2	54.3 ± 1.9	11.5 ± 0.3	1.1	59.7	1.1 ⁱ	61.1
0.010	0.015	33.8 ± 0.2	0.00547	22.5 ± 0.3	75.4 ± 3.0	17.0 ± 0.5	1.2	89.5	0.9 ⁱ	105.3
0.015	0.006	28.3 ± 0.2	0.00866	25.7 ± 0.2	32.2 ± 0.5	8.3 ± 0.1	1.1	35.4	0.8 ⁱ	46.6
0.015	0.010	39.8 ± 0.5	0.01185	17.2 ± 0.1	59.4 ± 1.4	10.2 ± 0.2	0.9	52.9	0.6 ⁱ	85.3
0.015	0.015	28.5 ± 0.3	0.00964	22.3 ± 0.2	48.4 ± 1.3	10.7 ± 0.2	1.2	58.1	0.8 ⁱ	73.5

Footnote *a* is the same as in Table 1^b Total concentration of HDABr^c Total concentration of C₁₆E₂₀^d $k_0 = k_{obs}$ at $[MX] = [MX]_0^{op}$ ^e The values of ${}^m\theta$ and ${}^mK^{X/S}$ were calculated from equation (3)^f The values of ${}^mK_{cat}$ and ${}^mK^{X/S}$ were calculated from equation (4) with the replacement of ${}^m\theta$ in equation (3) by ${}^mK_{cat}$ ^g Limits of error signifies standard deviations^h ${}^mF_{X/S} = {}^m\theta/{}^mK_{obs}^W$ with ${}^mK_{obs}^W = {}^mK_{obs} (= {}^mK_W^2 [Pp]_T) = 303.5 \times 10^{-4}$, 273.0×10^{-4} , 240×10^{-4} , 193.2×10^{-4} and $184.2 \times 10^{-4} \text{ s}^{-1}$ at constant $[C_{16}E_{20}]_T$ (6×10^{-7} , 6×10^{-5} , 0.006, 0.010 and 0.015 M $[C_{16}E_{20}]$ respectively) and $[MX] = [\text{HDABr}] = 0$ ⁱ ${}^nK^{X/S} = {}^mF_{X/S} {}^mK_{X/S}$ ^j ${}^nK^{Br/S} = {}^mF_{Br/S} {}^mK^{Br/S}$ for $MX = \text{NaBr}$ and ⁱData are obtained from reference³⁰⁾^k ${}^mR_X^{Br}$ or ${}^mK_X^{Br} = {}^nK^{X/S}/{}^nK^{Br/S}$

$$K_X^{Br} = K_X/K_{Br} = K_{X/S}^n/K_{Br/S}^n \quad (8)$$

On the other hand, if the two systems have different micellar structural behaviors, equation (8) can no longer give conventional ion exchange constant (K_X^{Br}) and under such condition, K_X/K_{Br} is referred to as R_X^{Br} ³⁴⁾. The calculated values of K_X^{Br} (Table 3) and the literature value of $K_{Br/S}^n$ were used to calculate the values of K_X^{Br} using equation (8)³⁶⁾ and are presented in Table 3.

Apparent experimental proof reported that there exists a consistently respective increase and a decrease in hydrophobicity and hydrophilicity of micellar region when the separation between the interior and exterior surfaces of the micelles is increased³⁷⁾. The counterion X ($3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2^-$) has chloro substituents (Cl) and a carboxylate ion (COO^-) which are, respectively, hydrophobic and hydrophilic in nature. The two chloro substituents, at position 3 and 5 of X, are assumed to be in a micellar region of almost similar hydrophilic and hydrophobic character. Thus, considering the reported value of K_X^{Br} ($= 50$) for $3\text{-ClC}_6\text{H}_4\text{CO}_2^-$ ¹⁹⁾, the value of K_X^{Br} for $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2^-$ supposed to have been around 100 if, and only if, the free energy factor (at the expense of groups located at the aromatic segment) would be significant. However, the mean value of K_X^{Br} , (Table 3)

for $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2^-$ is 198. This prediction of K_X^{Br} value, based upon the number of substituents and their locations in an aromatic region, has a probably failed assumption which depends only on structural behaviors of HDABr/MX. It has not taken into account the changes in shapes and sizes of HDABr/MX with the decrease or increase in values of K_X^{Br} ¹⁹⁾. The published results show the existence of mixed vesicle-wormlike micelles at 0.006–0.015 M range of HDABr and various values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ ³⁸⁾.

4.3 Explanation of kinetic results at constant mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micelles, various $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ and 35°C

The mixed cationic-nonionic (HDABr- $\text{C}_{16}\text{E}_{20}$) micellar system is different from the pure micellar system. To differentiate between the parameters obtained in the mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micellar systems and those in the pure ones, a letter “m” is used as a superscript to the former throughout the text. Hence, the parameters k_{obs} , k_0 , $[MX]_0^{op}$, k_W^2 , θ , ${}^mK_{cat}$, $K_{X/S}^{X/S}$, K_S^0 , $F_{X/S}$ and R_X^{Br} or K_X^{Br} are regarded as ${}^m k_{obs}$, ${}^m k_0$, ${}^m [MX]_0^{op}$, ${}^m k_W^2$, ${}^m \theta$, ${}^m K_{cat}$, ${}^m K_{X/S}$, ${}^m K_S^{X/S}$, ${}^m K_S^0$, ${}^m F_{X/S}$ and ${}^m R_X^{Br}$ or ${}^m K_X^{Br}$, respectively. It has been explained in section 4.1 (the case of pure HDABr micelles) that the values of k_0 were determined at constant $[\text{HDABr}]_T$ and

$[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}] = 0$. However, in the case of mixed HDABr- $\text{C}_{16}\text{E}_{20}$, the condition has been changed by adding constant concentrations of $\text{C}_{16}\text{E}_{20}$ (6.0×10^{-7} , 6.0×10^{-5} , 6.0×10^{-3} , 1.0×10^{-2} and 1.5×10^{-2} M) and the corresponding values of ${}^m k_0$ are presented in Table 4. The values of ${}^m k_{\text{obs}}$ were also found to fit equation (3). The values of ${}^m [\text{MX}]_0^{\text{op}}$ (Table 4) were found to increase with the increase in $[\text{HDABr}]_T$ and almost independent of $[\text{C}_{16}\text{E}_{20}]_T$. However, these values are comparatively higher than those obtained in the presence of pure HDABr (Table 3). The relationship between ${}^m \theta$ and ${}^m F_{X/S}$ has now become; ${}^m F_{X/S} = {}^m \theta / {}^m k_{\text{obs}}^w$, (${}^m k_{\text{obs}}^w = {}^m k_{\text{obs}}$ at various $[\text{C}_{16}\text{E}_{20}]_T$ and $[\text{HDABr}]_T = [\text{MX}] = 0$) with ${}^m k_{\text{obs}}^w = {}^m k_W^2 [\text{Pp}]_T = 303.5 \times 10^{-4}$, 273.0×10^{-4} , 240.0×10^{-4} , 193.2×10^{-4} and $184.2 \times 10^{-4} \text{ s}^{-1}$ at constant $[\text{C}_{16}\text{E}_{20}]_T$ (6.0×10^{-7} , 6.0×10^{-5} , 6.0×10^{-3} , 1.0×10^{-2} and 1.5×10^{-2} M $\text{C}_{16}\text{E}_{20}$, respectively) and $[\text{MX}] = [\text{HDABr}]_T = 0$. The values of ${}^m F_{X/S}$ (Table 4) are independent of both $[\text{HDABr}]_T$ and $[\text{C}_{16}\text{E}_{20}]_T$ and increased (compared to those in Table 3). These seem different from the previously reported study³⁹⁾ and the reason, however, could be because of the 3.3 to 8.3×10^4 -fold larger (0.05 M) concentration of $\text{C}_{16}\text{E}_{20}$ than those reported in this manuscript (6.0×10^{-7} , 6.0×10^{-5} , 6.0×10^{-3} , 1.0×10^{-2} and $1.5 \times 10^{-2} \text{ M}$).

The values of ${}^m K^{X/S}$ and ${}^m \theta$ were found to be independent of both $[\text{HDABr}]_T$ and $[\text{C}_{16}\text{E}_{20}]_T$ and were calculated using equation (3). The values of ${}^m K_{X/S}$ could not be calculated due to the fact that the values of K_s^0 for mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micelles are not available for the present study. It has been described, in section 4.1, how to derive equations (5), (6) and (7). Similarly, it can be easily shown in view of (respectively) equations (5), (6) and (7) that

$${}^m K^{X/S} = {}^m K_{X/S} / (1 + {}^m K_s^0 [\text{HDABr}]_T) \quad (9)$$

and

$${}^m \theta = {}^m F_{X/S} ({}^m k_W^2 {}^m [\text{Pp}]_T) \quad (10)$$

or

$${}^m K_{\text{cat}} = {}^m F_{X/S} ({}^m k_W^2 {}^m [\text{Pp}]_T) K^{X/S} \quad (11)$$

In view of equation (9) and (10), it is evident that

${}^m K_{X/S}^n = {}^m K^{X/S} (1 + {}^m K_s^0 [\text{HDABr}]_T)$ and $K_{Br/S}^n = {}^m K^{Br/S} (1 + {}^m K_s^0 [\text{HDABr}]_T)$. These relationships can lead to equation (12) where ${}^n m K^{X/S} = F_{X/S} {}^m K^{X/S}$ and ${}^n m K^{Br/S} = F_{Br/S} {}^m K^{Br/S}$.

$${}^m P_X^{Br} = {}^n m K^{X/S} / {}^n m K^{Br/S} \quad (12)$$

It is evident that in aqueous solution containing mixed cationic-nonionic surfactants (e.g. HDABr- $\text{C}_{16}\text{E}_{20}$), the relatively large hydrophilic headgroup of $\text{C}_{16}\text{E}_{20}$ shields the small sized hydrophobic micellar parts of HDABr⁴⁰⁾.

4.4 Explanation of rheometric data in the presence of pure HDABr and mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micelles at various $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$

Rheological data reveal that different flow curves show

Fig. 6 Sketches representing zero shear viscosity (η) against shear rate ($\dot{\gamma}$) for the piperidinolysis of PhS^- containing 0.015 M HDABr, 0.006 M $\text{C}_{16}\text{E}_{20}$ and $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]/M =$ (a) 0.004 (●) 0.007 (□) 0.015 (▲) 0.025 (◆) 0.040 (○) and 0.070 (◇) at 25°C and (b) 0.004 (●) 0.007 (□) 0.015 (▲) 0.025 (◆) 0.040 (○) and 0.070 (◇) at 35°C .

various micellar structural behaviors. For pure HDABr (0.015 M), at ≥ 0.004 to $\leq 0.007 \text{ M}$ $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, there exist flow curves with mild shear thickening behavior at a reasonably high shear rate and at both 25 and 35°C (Figs. 5a and 5b) which show unique characteristics of spherical micelles. Some flow curves, at ≥ 0.015 to $\leq 0.025 \text{ M}$ $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, experience shear thinning which indicates a non-Newtonian fluid system. This characteristic shows the existence of wormlike micelles⁴¹⁾ in the solution. However, at ≥ 0.040 to $\leq 0.070 \text{ M}$ $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, the system turned back to the shear thickening behavior with relatively higher viscosity values (Figs. 5a and 5b)⁴²⁾. The presence of 0.006 M $\text{C}_{16}\text{E}_{20}$ in the mixed HDABr- $\text{C}_{16}\text{E}_{20}$ micelles gives different results at the same $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$. All the 12 flow curves in Figs. 6a and 6b give mild shear thickening behavior at a reasonably high shear rate under the entire experimental conditions. It has been concluded that very dilute solution with a very low shear viscosity at a very high shear rate exhibits what is called “Taylor effect” and these could be caused by the presence of $\text{C}_{16}\text{E}_{20}$ as a nonionic surfactant. These observations revealed the presence of only spherical micelles under such experimental conditions.

The plot in Fig. 7 (representing η_0 against $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$) reveals the existence of two well-defined maxima

Fig. 7 Graphs representing shear viscosity (η_0) at constant shear rate ($\dot{\gamma}$) against $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$ with 0.015 M HDABr in the absence of $\text{C}_{16}\text{E}_{20}$ at 25°C ($\square$) and 35°C ($\diamond$), and the presence of 0.006 M $\text{C}_{16}\text{E}_{20}$ at 25°C ($\circ$) and 35°C ($\triangle$).

in the absence of $\text{C}_{16}\text{E}_{20}$ at constant shear rate, 0.015 M HDABr and both 25°C ($\square$) and 35°C ($\diamond$). These maxima appeared at specific values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]$, ($[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]_{\text{sp}}$); (i) 0.015 M ($\eta_0 = 31.2$ mPa.s) and 0.040 M ($\eta_0 = 9.3$ mPa.s) at 25°C and (ii) 0.015 M ($\eta_0 = 13.5$ mPa.s) and 0.040 M ($\eta_0 = 4.8$ mPa.s) at 35°C. It is clearly evident, therefore, that at both temperatures, the two maxima occurred at the same values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]_{\text{sp}}$. But the increase in the temperature (from 25 to 35°C) decreased the values of η_0 from 31.2 to 13.9 mPa.s and 9.3 to 4.8 mPa.s, at respectively, 0.015 and 0.040 M values of $[3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}]_{\text{sp}}$. Despite the fact that reports on the occurrence of maxima in the graph of shear viscosity against $[\text{MX}]$ (for a solution of cationic surfactants) are almost common^{43–45}, the detailed explanation of the reaction for the source of those maxima has not yet been apprehended at the molecular level^{43, 46}. Nonetheless, it has been accepted from previous reports^{43, 47} that the appearance of these maxima (under such experimental conditions) is a sign of the presence of wormlike/twisted wormlike micelles in a solution. Contrarily, there was no existence of maxima (Fig. 7) in the presence of mixed HDABr- $\text{C}_{16}\text{E}_{20}$ ($[\text{HDABr}]_{\text{T}} = 0.015$ M and $[\text{C}_{16}\text{E}_{20}]_{\text{T}} = 0.006$ M) at constant shear rate and both 25°C ($\circ$) and 35°C ($\triangle$). But the values of η_0 , not different from that of water, have also decreased due to the temperature variation from 25 to 35°C.

Although specific ion effects on structural features of aqueous ionic surfactant aggregates have been known for the last nearly more than ten decades and thousands of papers have published, the basic forces responsible for such specific effect remain unclear both theoretically and experimentally⁴⁸. It is considered to be useful to develop reversible micelle-vesicle conversions by changing a physi-

cal parameter such as pH, temperature or pressure of the medium. Such approach might provide an understanding of fundamental principles of aqueous surfactants structural transitions from micelles to vesicles⁴⁹. The study described in the present manuscript reveals that the presence of 6 mM $\text{C}_{16}\text{E}_{20}$ has caused almost complete transformation of mixed vesicles and wormlike micelles to mere spherical micelles. Similarly, the presence of 6 mM $\text{C}_{16}\text{E}_{20}$ reduced the values of R_{X}^{Br} or K_{X}^{Br} from 198 to 81. This is considered to be a quantitative correlation between the values of R_{X}^{Br} or K_{X}^{Br} and X-induced HDABr micellar growth. It is interesting to note that the similar effect of $\text{C}_{16}\text{E}_{20}$ could be observed at its concentration of 0.06 mM (Table 3).

5 Conclusions

Perhaps the most notable finding of present study is the reduction of the value of R_{X}^{Br} or K_{X}^{Br} from 198 to 78 due to presence of 0.06 M $\text{C}_{16}\text{E}_{20}$ in the mixed aqueous solution containing 15 mM HDABr and different values of $[\text{NaX}]$ with $\text{X} = 3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{CO}_2^-$. The values of R_{X}^{Br} remain independent of $[\text{C}_{16}\text{E}_{20}]$ within the range of 0.06–15 mM. Varying the concentration of $\text{C}_{16}\text{E}_{20}$ could be a method to achieving changes in the structural as well as the viscoelastic behavior of aqueous HDABr/ $\text{C}_{16}\text{E}_{20}$ /MX (MX = inert organic salt). It can be concluded that the nearly 2½-fold lower values of R_{X}^{Br} or K_{X}^{Br} for the aqueous mixed HDABr/ $\text{C}_{16}\text{E}_{20}$ /3,5- $\text{Cl}_2\text{C}_6\text{H}_3\text{CO}_2\text{Na}$ micellar solution is related to the addition of a nonionic surfactant, $\text{C}_{16}\text{E}_{20}$. This quantitative correlation allows the prediction of structural behaviors of aqueous solutions of both pure HDABr and mixed HDABr- $\text{C}_{16}\text{E}_{20}$ surfactant at different $[\text{MX}]$ on the basis of experimentally determined R_{X}^{Br} or K_{X}^{Br} values.

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