Kinetics of the Reaction of Methyl 4-Nitrobenzenesulfonate + Br⁻ in Ethanol Amine Based Surfactants

MICHAEL M. MOHAREB, KALLOL K. GHOSH, RAMA M. PALEPU

Department of Chemistry, St. Francis Xavier University, Antigonish, NS B2G 2V8, Canada

ABSTRACT: The kinetics of the reaction of methyl 4-nitrobenzenesulfonate + Br⁻ ions has been studied in ethanol amine based (alkyldimethylethanolammonium bromide and alkyldiethylethanolammonium bromide) surfactant solutions. The observed first-order rate constants increase monotonically with surfactant concentration, with hydrophobic chain length and with head group bulk in a manner similar to other quaternary ammonium surfactants. The results were analyzed using the pseudophase model of micellar rate effects in conjunction with a Langmuir form to describe micellar binding of bromide ion. An attempt to estimate activation parameters of the reaction from temperature variance of micellar pseudophase rate constants has also been made. © 2006 Wiley Periodicals, Inc. Int J Chem Kinet 38: 303–308, 2006

INTRODUCTION

Self-organizing assemblies like micelles, microemulsions, and vesicles have emerged as novel reaction media for investigating the reactivity and selectivity of a large number of S_N1 and S_N2 reactions. In such media, organic reactants are partitioned into the surfactant aggregates by electrostatic and hydrophobic interactions, and the observed rate accelerations are largely due to the increased localization of the reactants [1] and also the typical physicochemical properties of the micellar environment [1a].

The S_N2 reaction (Scheme 1) of Br⁻ with methyl 4-nitrobenzenesulfonate (MNBS) in the presence of cationic surfactants has been studied extensively [2–7], and the mechanism of this process is well known. Most previous authors have used alkyltrimethylammonium bromides or chlorides. Recently, we have investigated the preparation and micellar properties of ethanol amine based surfactants [8].

In the present investigation, we have used quaternary ammonium bromides (Scheme 2) having ethanol groups that would affect the binding of bromide and possibly of the substrate. From the viewpoint of usability, self-organization of a surfactant at a lower concentration is preferable. It is quite relevant to study how these novel ethanol amine based surfactants affect the reaction. Moreover, the applicability of the pseudophase kinetic model and the effects of surfactant head and tail groups have been explored.

Scheme 1

R = C$_{12}$, C$_{14}$, and C$_{16}$
R' = CH$_3$ and CH$_2$CH$_3$
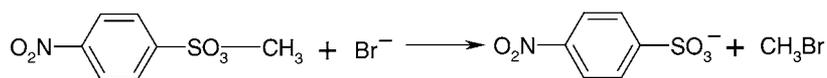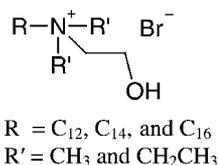
Scheme 2

EXPERIMENTAL

Materials

Alkyl dimethylethanol, diethylethanol amines (C$_{12}$–C$_{16}$), n-alkyl bromides (C$_{12}$–C$_{16}$), methyl 4-nitro-bezenesulfonate (MNBS), and sodium bromide were obtained from Sigma-Aldrich and were used as received. The quaternary alkyldimethylethanolam-monium bromides (C$_{12}$–, C$_{14}$–, and C$_{16}$ DMEA) and alkyldiethylethanolammonium bromides (C$_{12}$–, C$_{14}$–, and C$_{16}$DEEA) were synthesized as described previously [8]. All of the ionic bromide surfactants proved to be >99.2% pure. All surfactant solutions were prepared freshly in triply deionized water before use.

Kinetic Measurements

The reaction rates were followed spectrophotometri-cally at 280 nm using a Hewlett Packard 8452A diode array single beam spectrophotometer. The substrate was added as 25 μL of stock solution in acetonitrile to the reaction cell so that reaction solutions never contained more than 1% by volume acetonitrile, and the final substrate concentration was 1.0×10^{-4} M. The solution under investigation without the substrate was used as the reference solution. The temperature for the kinetic runs was maintained using a thermostated Haake DC-3 water bath and water-jacketed cell compartment. Figure 1 shows sample overlaid spectra for the reaction in 12.5 mM C$_{14}$DEEA solution.

Observed pseudo-first-order rate constants (k_{obs}) were obtained from the slopes of $\ln((A_\infty - A_0)/(A_\infty - A_t))$ against time plots, where A_∞, A_t, and A_0 are absorbences at the end of the reaction, at time t, and at time zero, respectively. Under the working conditions, the pseudo-first-order kinetic plots were linear for at least five half-lives. Experiments were repeated at least twice to show that rate constants were reproducible within a precision of 5% or better.
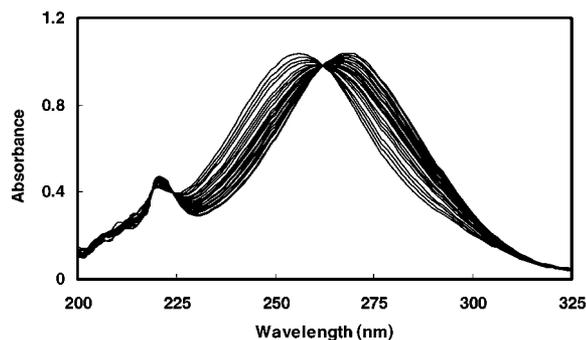
Figure 1   Sample overlaid spectra of MNBS + Br$^-$ reaction in 12.5 mM C$_{14}$DEEA solution at 298 K.

RESULTS AND DISCUSSION

The rates of the reaction of MNBS and Br$^-$ in the presence of micelles of C$_{12}$–, C$_{14}$–, and C$_{16}$DMEA and C$_{12}$–, C$_{14}$–, and C$_{16}$DEEA have been determined at 298.2 K for a range of surfactant concentrations under pseudo-first-order conditions. The kinetics of the reaction was obtained by monitoring the appearance of 4-nitrobenzenesulfonate ion spectrophotometrically at 280 nm. In all cases, an isosbestic point was observed at 262 nm that indicates the reaction does not proceed through any relatively long-lived intermediates, and its kinetics therefore can be approximated to describe the rate-limiting elementary step of the process. The observed pseudo-first-order rate constants (k_{obs}) were determined in each of the surfactants.

Variation of k_{obs} as a function of the concentration of the surfactants is shown in Figs. 2 and 3 for
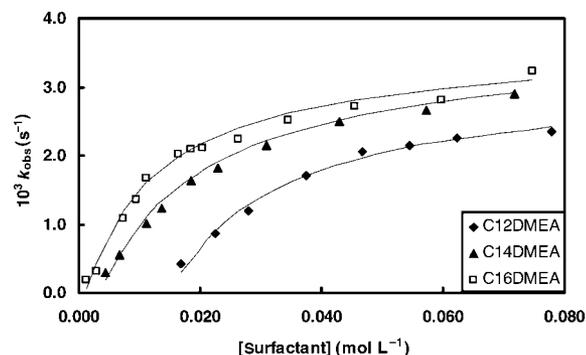
Figure 2   Influence of C$_n$DMEA concentrations on the observed rate constant for the reaction of MNBS + Br$^-$. Solid lines are according to regression fits described in the text.
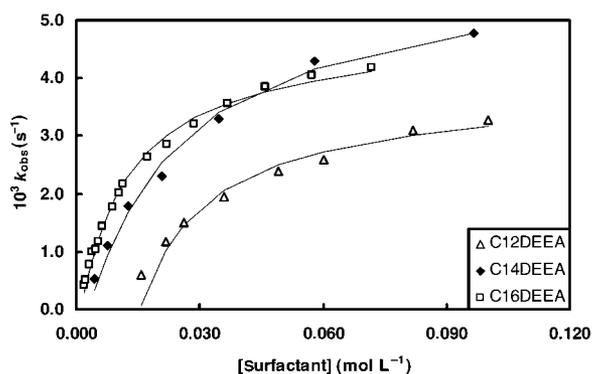
Figure 3   Influence of C_nDEEA concentrations on the observed rate constant for the reaction of MNBS + Br⁻. Solid lines are according to regression fits described in the text.

C_nDMEA and C_nDEEA, respectively. The observed rate constants increased progressively with the rise in surfactant concentrations. In both cases, the observed reactivity increases with increasing hydrophobic chain length of the surfactant. Two factors involved in the catalysis of the reaction by the micellar aggregates, i.e., the electrophilic interaction of the head group and disruption of the hydration shell of the bromide ion in the formation of 4-nitrobenzenesulfonate ion [9–12]. This second factor is probably the more important because reactions of nucleophilic anions are strongly inhibited by anionic solvation, and disruption of this solvation is a major part of the energy barrier to the reaction [7]. Methyl 4-nitrobenzenesulfonate molecules have a nitro group responsible for an increase in reactivity with Br⁻ with respect to methyl benzenesulfonate. The strong electron withdrawal by the 4-nitro group increases charge dispersion in the transition state, favoring the reaction in water as well as in micelles.

Quantitative Treatment of the Data

Each rate-surfactant profile was fitted to a regression according to the pseudophase model (PPM). The overall rate of reaction is the sum of the rates in each micellar and aqueous pseudophases and is given by the following equation [7,13]:

$$\frac{-d[S_{\text{tot}}]}{dt} = k_{\text{obs}}[S_{\text{tot}}] = k_2^w[S_w][X_w] + k_2^m[S_m]X_m$$

(1)

In Eq. (1), k_2^w and k_2^m refer to the second-order rate constants of the reaction, $[S_w]$ and $[S_m]$ refer to substrate concentrations, and $[X_w]$ and X_m refer to nucleophile concentrations in the aqueous (w) and micellar (m) pseudophases, respectively. For the nucleophile concentrations, $[X_w]$ is the solution concentration of

nucleophile in the bulk water while X_m, which corresponds to the interfacial concentration of nucleophile in the micellar pseudophase, is given by

$$X_m = \frac{[X_m]}{V_m[D_n]}$$

(2)

where V_m is the molar volume of the interfacial reaction region and $[X_m]$ is the *solution* concentration of the nucleophile in the micellar pseudophase. The value of V_m is usually assumed to be in the range of $0.14\text{ M}^{-1} < V_m < 0.37\text{ M}^{-1}$, according to Stigter's model of micellar structure [6,7]. Solving for k_{obs} in Eq. (1), substituting X_m according to Eq. (2), and incorporating an equilibrium substrate binding constant (K_S) yields the following overall relationship:

$$k_{\text{obs}} = \frac{k_2^w[Br_w^-] + (k_2^m/V_m)[Br_m^-]K_S}{1 + K_S[D_n]}$$

(3)

where the nucleophile (X) for these investigations has been identified as bromide ion. This relates k_{obs} to changing concentrations of surfactant and bromide ion. The theoretical lines in Figs. 2 and 3 are regression fits of the data according to Eq. (3).

Most commonly for bimolecular reactions in ionic surfactant systems, such as in this investigation, the concentration of micellized counterion has been assumed to follow a Langmuir form equation as given below:

$$K_{\text{Br}} = \frac{[Br_m]}{[Br_w]([D_n] - Br_m)}$$

(4)

In Eq. (4), K_{Br} is the equilibrium constant that describes binding of bromide ion to the cationic micelle, $[Br_m]$ and $[Br_w]$ are concentrations of bromide ion in the micellar pseudophase and bulk water phase, respectively, and $[D_n]$ is the solution concentration of surfactant present in micelles. The value of $[D_n]$ is equal to the difference between the total surfactant concentration ($[D_{\text{tot}}]$) and the concentration of monomeric surfactant, with the latter usually assumed to be equal to the critical micelle concentration (cmc) [9–12,14]:

$$[D_n] = [D_{\text{tot}}] - \text{cmc}$$

(5)

By taking into account the mass and charge balance, Eq. (1) (the Langmuir equation that describes bromide binding) can be transformed to the following quadratic form [7]:

$$K_{\text{Br}}[Br_m^-]^2 - (K_{\text{Br}}[D_n] + K_{\text{Br}}[Br_{\text{tot}}^-] + 1)[Br_m^-]$$
$$+ K_{\text{Br}}[D_n][Br_{\text{tot}}^-] = 0$$

(6)

where the values of bromide ion concentrations in each pseudophase can be found by solving the quadratic equation at each concentration of surfactant investigated for a given bromide-binding constant (K_{Br}). Bromide-binding constants were estimated based on comparison of the literature values of fractional micellar ionization (α) with other quaternary ammonium bromide surfactants as well as by examination of the fits, and they were assumed to be constant with hydrophobic tail length for a given head group as has been reported in the previous work [1,7,15–19]. This assumption has been shown to be valid as the value of the bromide-binding constant can be varied significantly without markedly changing the fit or the adjustable parameter values. A value of 8.5×10^{-4} M^{-1}s^{-1} at 298.2 K was used for the second-order rate constant in water ($k_2{}^w$); this value was obtained experimentally in this study and agreed with the previous work [7]. In all cases, the regression correlation coefficients (r^2) were greater than 0.97.

The parameters determined from the regression are given in Table I with corresponding error values estimated based on the quality of the fit, the dependency on variation of other parameters, and the precision of the experimentally determined rate constants. The corresponding values for cetyltrimethylammonium bromide (CTAB) from the literature are shown for comparison [7,19].

The rate constant in the micellar pseudophase has been presented as an effective first-order rate constant that is equal to the ratio of the second-order rate constant ($k_2{}^m$) to the molar volume of the reaction region at the micellar surface (V_m). Relative second-order rate constants with water are shown in Table II.

As with all results for similar reactions studied in cationic micelles, there is a decrease in the observed rate with a decrease in hydrophobic chain length for the same surfactant head group. This trend is reflected

Table II Relative Second-Order Rate Constants in C$_n$DMEA and C$_n$DEEA Surfactants^{a,b}

	$k_2{}^m/k_2{}^w$
C$_{16}$DMEA	0.6
C$_{14}$DMEA	0.7
C$_{12}$DMEA	0.6
C$_{16}$DEEA	0.9
C$_{14}$DEEA	1.1
C$_{12}$DEEA	0.8
CTAB^c	1.0

^{a} $k_2{}^m$ values have been estimated using $V_m = 0.14$ M^{-1}.
^{b} $k_2{}^m = 8.5 \times 10^{-4}$ M^{-1} s^{-1} according to [7].
^{c} From [19].

in the PPM regression parameters primarily in the marked decrease in the substrate-binding constant (K_S) with decreases in the hydrophobic chain length for C$_n$DMEA and C$_n$DEEA surfactants. This may be due to decreased room for accommodation of the substrate at the micellar surface, and therefore would be a reflection of the decrease in micellar size with a decrease in the hydrophobic chain length. Similarly, there is an observed increase in K_S in going from CTAB to C$_{16}$DMEA to C$_{16}$DEEA that may be due to an increase in polar head group area and therefore more room for the substrate to bind to the cationic head group.

There is a definite increase in the rate constants ($k_2{}^m / V_m$) in the micellar reaction volumes with the increase in head group bulk from C$_n$DMEA to C$_n$DEEA surfactants that appears to mimic the trend observed in trialkylammonium bromide surfactants of constant chain length for similar anionic bimolecular reactions [1]. In those studies, the observed effect was attributed to greater disruption of the hydration shell of reactive bromide ion with an increase in head group bulk. This would be consistent with a decrease in bromide ion solvation due to the decrease in polarity of the interfacial region. Similarly, one can envision a greater disturbance of the hydration shell of bromide ion for the C$_n$DEEA head group over that of C$_n$DMEA that would result in the increase in rate constants in the interfacial region for the former. Even if the change that is observed for $k_2{}^m/V_m$ values (rather than for the strict second-order rate constant, $k_2{}^m$) is due to any significant change in interfacial molar volume, an increase in head group bulk would increase V_m, and this would make even more pronounced the increase in $k_2{}^m$ from C$_n$DMEA to C$_n$DEEA.

The higher values of bromide binding (K_{Br}) for CTAB, as compared to the C$_n$DMEA and C$_n$DEEA surfactants, may reflect the greater ability of the positive ammonium center in CTAB to bind bromide ion.

Table I PPM Regression Parameters for C$_n$DMEA and C$_n$DEEA Surfactants at 298 K

	K_{Br} (M^{-1})	$\times 10^3 k_2{}^m/V_m{}^a$ (s^{-1})	$K_S{}^b$ (M^{-1})
C$_{16}$DMEA	750	3.9	116
C$_{14}$DMEA	750	4.0	68
C$_{12}$DMEA	750	3.4	49
C$_{16}$DEEA	450	5.3	153
C$_{14}$DEEA	450	6.5	60
C$_{12}$DEEA	450	4.1	61
CTAB^c	1000	5.9	72

^{a} Error estimated at $\pm 15\%$.
^{b} Error estimated at ± 10 M^{-1}.
^{c} From [19].

That is, the ethanol moiety in C_nDMEA and C_nDEEA may serve to sterically shield the head group's positive charge and/or to withdraw electron density and stabilize the charge through an inductive effect. The increase in head group bulk may result in a decrease in head group–head group repulsions and therefore a decrease in the requirement of bromide counterion to be accommodated at the interfacial region. This would be consistent with values of counterion binding (β) as determined by conductometric method [8]. Similar decreases in counterion binding with increasing head group bulk for the trialkylammonium bromide series have been observed previously [1]. This can also be expected in going from the C_nDMEA to the C_nDEEA series.

The rather high value of k_2^m/V_m for CTAB as compared to C_nDMEA may be a reflection of (a) an ion–dipole interaction between the ethanol moiety in C_nDMEA (and C_nDEEA) that decreases the rate of bromide ion attack much in the same way as hydration does and is not present for CTAB and/or (b) a significant decrease in interfacial reaction volume for CTAB as compared to C_nDMEA.

Activation Parameters

The rates of the MNBS + Br⁻ reaction were determined for a range of C_nDMEA and C_nDEEA surfactant concentrations at 303 and 308 K in an attempt to determine activation parameters of the reaction at the micellar interface. Rate-surfactant profiles at 298, 303, and 308 K were generated for each surfactant along with PPM theoretical regression fits according to Eqs. (3) and (6). For an example, the rate-surfactant profiles for C_{16}DEEA at different temperatures are shown in Fig. 4. As bromide-binding constants were assumed to be relatively constant with varying hy-

Table III PPM Regression Parameters for DMEA and DEEA at 303 and 308 K

	T (K)	K_{Br} (M^{-1})	$\times 10^3 k_2^m/V_m{}^a$ (s^{-1})	$K_S{}^b$ (M^{-1})
C_{16}DMEA	303	750	5.0	169
C_{16}DMEA	308	750	6.5	202
C_{14}DMEA	303	750	6.9	61
C_{14}DMEA	308	750	9.4	68
C_{12}DMEA	303	750	5.6	51
C_{12}DMEA	308	750	8.1	51
C_{16}DEEA	303	450	9.4	124
C_{16}DEEA	308	450	13.2	106
C_{14}DEEA	303	450	9.0	76
C_{14}DEEA	308	450	13.7	62

^{a} Error estimated at $\pm 15\%$.
^{b} Error estimated at ± 10 M^{-1}.

drophobic chain length, K_{Br} was also assumed not to vary significantly within the temperature range used for the same surfactant. The kinetic regression parameters for each surfactant are listed in Table III. In general, wide variation (from 100 to 2000 M^{-1}) of the bromide-binding fitting parameter induced rather significant changes in K_S values but had only a minor effect on k_2^m/V_m values, and thus did not allow for an examination of a trend in substrate binding although there were certain increases in k_2^m/V_m values with temperature.

The activation parameters that were estimated from the regressions for C_{16}DEEA, C_{16}DMEA, and in 0.1 M NaBr$_{(aq)}$ are given in Table IV; for the same head group, minimal variation was observed in the parameters. All Eyring and Arrhenius plots showed linear correlation coefficients (r^2) greater than 0.96. The standard state for the thermodynamic activation parameters was taken to be 1 M.

The $\Delta G^{\ddagger}$ values for all of the surfactant systems investigated are nearly constant. The $\Delta S^{\ddagger}$ values provide an estimate in the change in order in going from reactants to the transition state of the rate-limiting elementary process of a reaction [20]: negative $\Delta S^{\ddagger}$ values would be consistent with a mechanism of bond formation and increased order in the transition state. This would certainly be expected for a bimolecular substitution (S_N2) in which the nucleophile attacks the carbon center as the substituted group begins to leave resulting in a transition state with higher coordination number on the carbon center. The positive value obtained for $\Delta S^{\ddagger}$ in the absence of surfactant (that is, in 0.1 M NaBr$_{(aq)}$) perhaps indicates that there is a significant loss in order due to loss of bromide hydration on obtaining the transition state. Entropy of activation ($\Delta S^{\ddagger}$) values in the presence of surfactant are

Figure 4 Influence of C_{16}DEEA concentration on the observed rate constant for the reaction of MNBS + Br⁻ at 298, 303, and 308 K. Solid lines are according to regression fits described in the text.

Table IV   Activation Parameters for $C_{16}DMEA$ and $C_{16}DEEA$ Surfactants

	E_a (kJ mol^{-1})	log (A)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})s
$C_{16}DMEA$	43	4.3	40	−160	91
$C_{16}DEEA$	77	10.9	75	−50	90
0.1 M NaBr	108 ± 10	16 ± 2	105 ± 10	89 ± 1	90 ± 1

negative and vary considerably between surfactant systems. However, there is a very strong dependency of k_2^m/V_m values on determination of $\Delta S^{\ddagger}$ such that variations of ±15% in the former induce changes in $\Delta S^{\ddagger}$ of up to 100 J mol^{-1} K^{-1}. Thus, it was not possible to precisely determine relative enthalpic and entropic contributions to the reaction rate in the micellar pseudophase for comparison to water as several assumptions have been made in the determination of activation parameters from the second-order rate constants determined by the PPM.

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