S$_N$2 reaction of a sulfonate ester in the presence of alkyltriphenylphosphonium bromides and mixed cationic-cationic systems

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ABSTRACT: The effects of alkyltriphenylphosphonium bromides (C$_n$TPB, $n = 10$, 12, 14, 16) on the rates of S$_N$2 reactions of methyl 4-nitrobenzenesulfonate and bromide ion have been studied. Observed first-order rate constants are significantly higher than those found for other cationic surfactants for the same reaction. The results have been analyzed by the pseudophase model of micellar kinetics and show true micellar catalysis in the sense that second-order micellar rate constants are higher than the second-order rate constants in water. An attempt has also been made to investigate mixed cationic–cationic surfactant systems with respect to observed rates and pseudophase regression parameters. In addition, modeling of some cationic head groups has illustrated possible differences in head group charges and counterion interactions that may prove kinetically relevant. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: S$_N$2 reaction; kinetic parameters; micellar catalysis; pseudophase model alkyl phosphonium surfactants; mixed micelles

INTRODUCTION

The use of novel surfactants in assisting a variety of organic reactions is highly promising for basic and applied research.[1–5] The application of quantitative analysis of kinetic data to micellar mediated reactions and the implications of different models describing such reactions are also topics of continuing interest.[6–11]

The majority of fundamental studies on micellar mediated S$_N$2 reactions have been conducted in the presence of cationic micelles of quaternary ammonium surfactants such as those with trialkylammonium, pyridinium, and quinuclidinium bromides and chlorides.[12–14] In the present investigation, the kinetics of the reaction of methyl 4-nitrobenzenesulfonate (MNBS) with bromide ion (Scheme 1) in alkyltriphenylphosphonium bromide (C$_n$TPB) surfactants (Scheme 2) has been studied.

These surfactants offer head groups that are significantly bulkier than those which have been investigated previously and also possess aromatic moieties at the micellar surface. Recently, the self-aggregation properties and thermodynamics of micellization for this series of surfactants and their binary mixtures have been studied by our group.[15,16] Surprisingly, however, the body of chemical investigations on C$_n$TPB surfactants is rather limited, and there appear to be no systematic studies of this series with respect to its effects on the kinetics of S$_N$2 reactions. One report has considered the use of derivatized hexadecyltriphenylphosphonium surfactants in an ester cleavage reaction,[17] highlighting a further use of these surfactants in their ability to be functionalized to different degrees.

Mixed micelles have recently expanded into a wide area of research,[18,19] and the body of knowledge on effects of mixed surfactant systems on rates of hydrolysis,[4,20–23] nucleophilic substitution,[19,24,25] and other reactions,[26] continues to grow. Very few studies have been carried out on the effects of cationic–cationic mixed surfactants on the enhancement of rate constants. In the present work, we have cursorily studied three such systems: C$_{14}$TPB and hexadecyltrimethylammonium (CTAB) bromides, C$_{14}$TPB and hexadecyldiethylethanolammonium bromide (C$_{16}$DEEA), and C$_{16}$TPB and C$_{10}$TPB. Molecular modeling technique of selective head groups interacting with bromide ion was carried out in the present study, to evaluate structures and charge distribution that may be kinetically relevant.[27,28]

RESULTS AND DISCUSSION

The reaction of MNBS and bromide ion was investigated in the presence of C$_n$TPB surfactants for chain lengths

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$$O_2N-\underset{}{\bigcirc}-SO_3-CH_3 + Br^- \longrightarrow O_2N-\underset{}{\bigcirc}-SO_3^- + CH_3Br$$
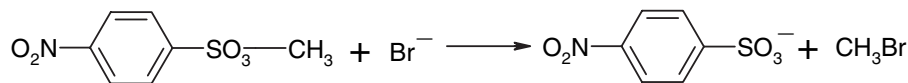
Scheme 1

C_{10}, C_{12}, C_{14}, and C_{16}. The range of concentrations over which these surfactants were studied was limited somewhat by their solubility in water. Rate-surfactant profiles were determined for each surfactant at 298.2 K and are shown in Fig. 1 with theoretical regression fits (discussed later). As in the case with other quaternary nitrogen based cationic surfactant systems (TABS), an increase in rate enhancement with increased surfactant concentration is observed. In addition, for a given head group, this enhancement is pronounced with an increase in hydrophobic chain length of the surfactant. This has been observed previously for all other cationic systems for similar anionic bimolecular reactions. The distinguishing characteristic in these rate-surfactant profiles, however, is the magnitude of increase in the pseudo first-order rate constant (k_{obs}) values as compared to other quaternary ammonium bromide surfactants of similar chain length.[29–33] The values of the second order rater constant ($10^3 K_2^m/V_m$) to other quaternary ammonium bromide surfactants of similar chain length[31] are presented in Table 1.

A rate-surfactant profile at 298.2 K (Fig. 2) was also determined for the surfactant, hexadecyltributylphosphonium bromide (C_{16}TBuB), in order to investigate the extent of rate increase due to its bulky alkyl head group and to compare this with the aryl substituted head group.[34–36] The observed rates were significantly lower than those of C_{16}TPB, though still higher than the corresponding quaternary ammonium bromide surfactants. Previous work.[13,17] with trialkylammonium head groups and S_N2 reactions of similar substrates shows a modest increase in the observed rate for hexadecyltributylammonium over trimethyl, triethyl, and tripropyl head groups. If the case was similar for quaternary phosphonium head groups (i.e., that a hexadecyltrimethylphosphonium bromide surfactant would only show a slightly lower observed rate), it would indicate greater rate enhancement for the phosphorous center than for nitrogen centers.

$R = C_{10}$, C_{12}, C_{14} and C_{16}
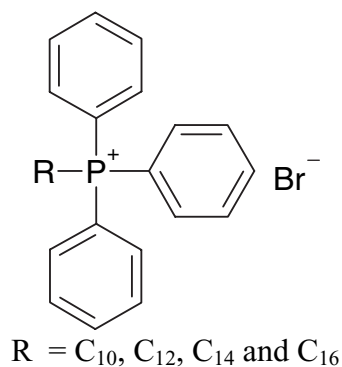
Scheme 2

Quantitative treatment of the data

Each rate-surfactant profile was fitted to a regression according to the pseudophase model (PPM). For a second-order reaction between a substrate (*S*) and a nucleophile (*X*), the reaction can be assumed to occur in either the micellar or aqueous pseudophases so that the overall rate of reaction is the sum of the rates in each pseudophase and is given by the following equation.[30,38]

$$\frac{-d[S_{tot}]}{dt} = k_{obs}[S_{tot}] = k_2^w[S_w][X_w] + k_2^m[S_m]X_m \quad (1)$$

In Eqn (1), k_2^m 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:

$$X_m = \frac{[X_m]}{V_m[D_n]} \quad (2)$$

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 $0.14\,M^{-1} < V_m < 0.37\,M^{-1}$, according to Stigter's model of micellar structure.[29,30] Solving for k_{obs} in Eqn (1), substituting X_m according to Eqn (2), and incorporating an equilibrium substrate binding constant (K_S) yields the following overall relationship:

$$k_{obs} = \frac{k_2^w[Br_w^-] + \left(\frac{k_2^m}{V_m}\right)[Br_m^-]K_s}{1 + K_S[D_n]} \quad (3)$$

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. 1 and 2 are regression fits of the data according to Eqn (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:

$$K_{Br} = \frac{[Br_m]}{[Br_w]([D_n] - [Br_m])} \quad (4)$$

In Eqn (4), K_{Br} is the equilibrium constant that describes binding of bromide ion to the cationic micelle,
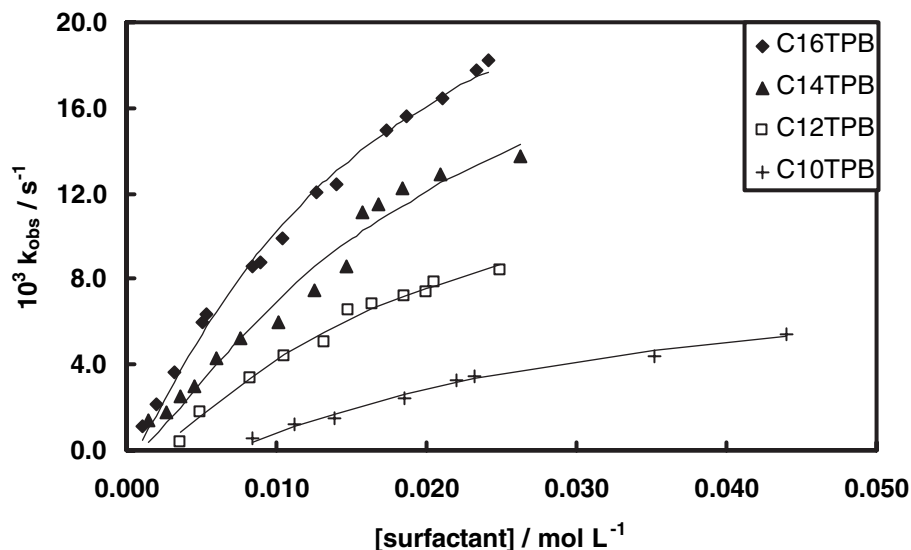
Figure 1. Influence of C$_n$TPB concentrations on the observed rate constant for the reaction of MNBS + Br$^-$ at 298.2 K. Solid lines are theoretical regression fits according to equations described in the text

[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$_{tot}$]) and the concentration of monomeric surfactant, with the latter usually assumed to be equal to the cmc.[39–44]

$$D_n = [D_{tot}] - \text{cmc} \qquad (5)$$

By taking into account the mass and charge balance, Eqn (4) (the Langmuir equation that describes bromide binding) can be transformed to the following quadratic form[30]:

$$K_{Br}[Br_m^-]^2 - (K_{Br}[D_n] + K_{Br}[Br_{tot}^-] + 1)[Br_m^-] + K_{Br}[D_n][Br_{tot}^-] = 0 \qquad (6)$$

where the values of bromide ion concentrations in each pseudophase can be found by solving the quadratic

Table 1. PPM regression parameters for C$_n$TPB and C$_{16}$TBuB surfactants at 298.2 K

|	K_{Br} M^{-1}	$10^3 k_2^m/V_m$ s^{-1}	K_S M^{-1}
C$_{16}$TPB	100 (1000)*	40.2 (5.87)	200 (76)
	2000	38.4	49
C$_{14}$TPB	100 (1000)	35.3 (4.13)	109 (71)
	2000	38.4	30
C$_{12}$TPB	100 (1000)	21.1 (9.92)	126 (39)
	2000	19.7	42
C$_{10}$TPB	100	11.5	61 (39)
	2000	10.3	32
C$_{16}$TbuB	100	17.5	273
	2000	15.6	63

*Bracketed terms are the corresponding values for alkyl trimethyl ammonium bromides (Ref. 31)

equation at each concentration of surfactant investigated for a given bromide binding constant (K_{Br}).

A wide range of values for the bromide binding constant (K_{Br}) were employed in the regressions in order to examine the variance of the rate constant (k_2^m/V_m) and substrate binding constant (K_S) values. Conductometric studies have shown that counterion binding in triphenyl-phosphonium bromides is lower (0.13 for C$_{10}$, 0.40 for C$_{12}$, 0.44 for C$_{14}$ and 0.31 for C$_{16}$ TPBs respectively) than that found for other cationic micelles (i.e., quaternary ammonium bromides).[15] This has been attributed to a decrease in effective micellar surface charge density in TPB head groups (as is the case with hexadecylpyridinium bromide) as compared to other non-aromatic head groups, and this may be due to the significantly lower aggregation numbers for C$_n$TPB micelles that are afforded by a head group of such bulkiness. Aggregation numbers as determined by fluorescence quenching for CTAB and C$_{16}$TPB are 61 and 15, respectively.[15]

The focus in the present study was not so much on bromide binding in these surfactants as it was an attempt to investigate the nature of the reaction of MNBS and Br$^-$ and the binding of the substrate to the surface of TPB micelles. Therefore, results of the PPM regression fits have been presented in Table 1 in terms of the range of bromide binding constants (K_{Br}) used in order to examine k_2^m/V_m and K_S values. A value of 4.5×10^{-4} M^{-1} s^{-1} at 298.2 K was used for the second-order rate constant in water (k_2^w).[33,37] The regression parameters for C$_{16}$TBuB are similarly included in Table 1. In all cases, the regression correlation coefficients (r^2) were greater than 0.97.

As with results for similar reactions studied in cationic micelles,[12] the decrease in the observed rate with a decrease in hydrophobic chain length for the same surfactant head group is reflected in the PPM regression
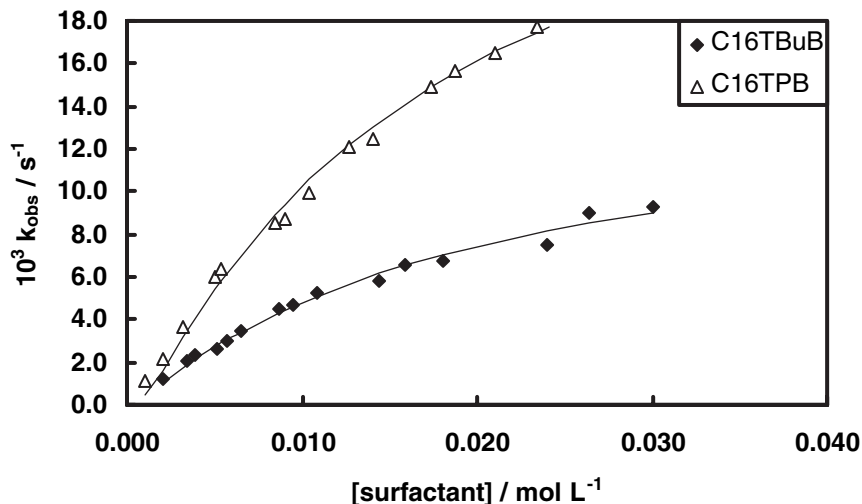
Figure 2. Influence of C_{16}TBuB concentration on the observed rate constant for the reaction of MNBS $+$ Br$^-$ at 298.2 K. The rate-surfactant profile for C_{16}TPB is shown for comparison. Solid lines are theoretical regression fits according to equations described in the text

parameters primarily in a decrease in the substrate binding constant (K_S), assuming constant K_{Br} values with varying chain length. 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.

One interesting point to note from the kinetic parameters is that K_S values are nearly comparable to those found for quaternary ammonium bromides while k_2^m/V_m values are 3–8 times higher for phosphonium bromide surfactants than their quaternary ammonium surfactants. Although there is considerable deviation in the values for substrate binding with a change in the bromide binding constant, micellar rate constant values differ only slightly (well within an estimated experimental error of 15%) with a wide variation in counterion binding. The increase in k_2^m/V_m values would be even more pronounced for strict second-order rate constants (k_2^m) if one were to consider that the molar volume of the interfacial region of TPB surfactants is much greater than that for quaternary ammonium head groups. It is likely that the enhancement of the second-order rate constants as a function of surfactant concentration can be attributed to increased micellar and effective bromide ion concentrations at the micellar surface.

The parameters obtained for C_{16}TBuB also a show an enhancement in the second-order rate constant in the micellar pseudophase over water and other surfactants (depending on precise values for V_m) as opposed to a simply greater concentration of the reactants at the interfacial region. However, the extent of this enhancement is not as high as for the TPB series.

Possible sources for the rate enhancement at the TPB micellar interface may include an increase in disruption of the hydration of the attacking bromide ion that

corresponds to such a bulky head group. In this case, the mechanism of rate enhancement in these surfactants would simply be an extension of what is believed to be observed with the trialkylammonium surfactant series[13] and would therefore also be observed with C_{16}TBuB. The difference in k_2^m/V_m values between C_{16}TPB and C_{16}TBuB would then be due to the greater head group bulk of the former. The effect would correspond to a general decrease in the polarity of the head group region that would therefore increase the rate of an S_N2 reaction.[37] Another possible explanation would be the steric effects by the phenyl rings in the head group region that would activate the bound MNBS substrate towards substitution.

Mixed micellar systems

The rates of reaction of MNBS $+$ Br$^-$ were also determined for mixed cationic–cationic systems of C_{14}TPB-CTAB and C_{14}TPB-C_{16}DEEA at varying concentrations and compositions in an attempt to correlate the observed rates and determined parameters with system properties. Rate-surfactant profiles (Fig. 3) were found for both systems at varying solution mole fraction of C_{14}TPB ($\alpha_{C_{14}}$) and at constant total surfactant concentration (25 mM, respectively). Both plots exhibit curves that negatively deviate from a straight line of ideality. In order to confirm that a straight line relationship between the observed rate constant (k_{obs}) and the solution mole fraction exists for an ideal system, rate experiments were also carried out for the mixed C_{16}TPB-C_{10}TPB system showing a linear relationship of rate constant with mole fraction; the profile for this system is shown in Fig. 4. This system has been shown to behave ideally with respect to other micellar properties[16]
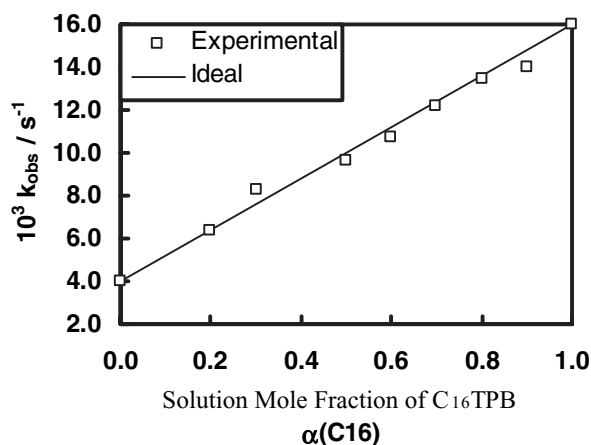
A

B
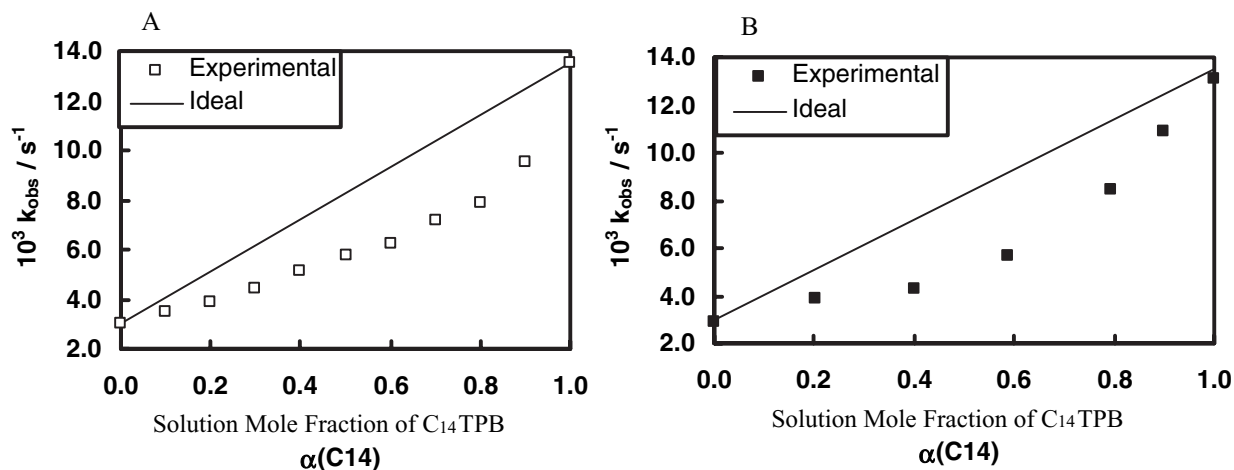
Figure 3. Influence of solution composition (solution mole fraction of C$_{14}$TPB) on the observed rate constant for the reaction of MNBS + Br$^-$ for A. C$_{14}$TPB-C$_{16}$DEEA and B. C$_{14}$TPB-CTAB mixed surfactant systems at 298.2 K with total surfactant concentrations of 25 mM

(e.g., cmc, counterion binding, enthalpy of micellization, etc.), so it is not surprising that it also behaves ideally from a kinetic viewpoint. One would certainly expect that for a reaction such as this, (which is believed to occur preferentially at the micellar surface[6]), therefore a system employing surfactants with the same head group would offer an approximate picture of ideality. It is interesting to note that for the inhibition of both this and similar S$_N$2 reactions in the presence of cationic micelles by nonionic surfactant additives, a comparable straight-line relationship also exists between the observed rate constant and the mole fraction of the additive.[19].

In this light, the observed results for C$_{14}$TPB-CTAB and C$_{14}$TPB-C$_{16}$DEEA systems indicate that the mixed micelles that are formed result in a lower observed rate of reaction than would occur if the surfactants were independent of each other. A possible explanation for

the observed results may lie, at least partly, in the relationship between the compositions of surfactants in the micelle with their overall solution compositions. According to Rubingh's approach, deviation from ideal behavior is due to differing compositions of surfactant monomers as compared to the bulk solution.[45] From conductivity studies and the use of the regular solution approximation, the mole fraction of a surfactant in the mixed micelle can be determined for its particular solution concentration.[46] In the case of C$_{14}$TPB-C$_{16}$DEEA, for example, a conductivity study was performed previously by our group,[47] and the resulting micellar composition plot is presented here in Fig. 5. The straight line relationship represents the situation where the mixed micelle composition is equal to the composition in the bulk solution, that is, $x(C_{14}) = \alpha(C_{14})$ in the ideal case. According to this plot, there is more C$_{14}$TPB

Figure 4. Influence of solution composition (solution mole fraction of C$_{14}$TPB) on the observed rate constant for the reaction of MNBS + Br$^-$ for C$_{16}$TPB-C$_{10}$TPB mixed surfactant system at 298.2 K with a total surfactant concentration of 20 mM
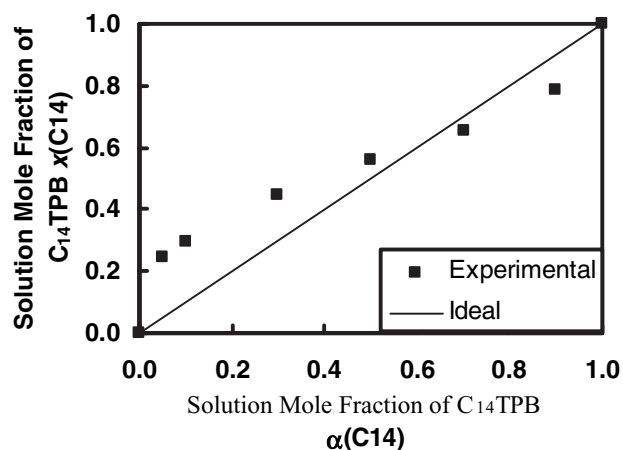
Figure 5. Mixed micelle composition plot as determined by conductivity using Rubingh's model for the C$_{14}$TPB-C$_{16}$DEEA system at 298.2 K
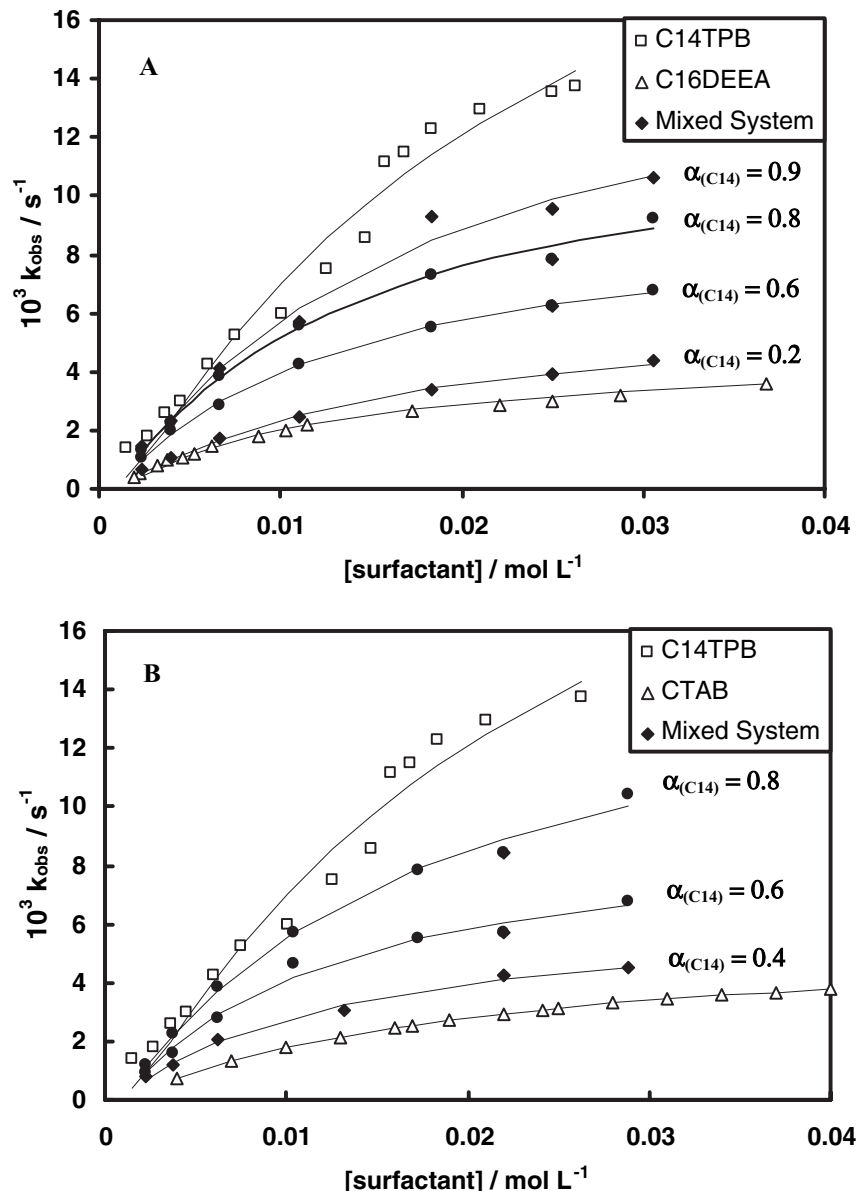
Figure 6. Rate-surfactant profiles for A. $C_{14}TPB$-$C_{16}DEEA$ and B. $C_{14}TPB$-CTAB mixed surfactant systems at 298.2 K and varying total surfactant concentrations for select compositions. Solid lines are theoretical regression fits according to equations described in the text using a sample value of $K_{Br} = 450 \, M^{-1}$

than is predicted by the solution concentration ($\alpha(C_{14})$) at low amounts of $C_{14}TPB$ until a mole fraction of about 0.6 after which there is a greater amount of $C_{16}DEEA$ in the mixed micelles than given according to its solution concentration. Therefore, the region of the largest negative deviation from ideality of the observed rate occurs at higher amounts of $C_{14}TPB$ in the solution composition which corresponds to less $C_{14}TPB$ in the micelles. This would suggest that with more $C_{16}DEEA$ (the surfactant whose k_{obs} value in the pure micelle is much lower), there is a greater deviation from ideality in the rate constant. Also, additional $C_{14}TPB$ (as the mole fraction is increased to unity) is more effective in increasing the observed rate. As for the source of the

negative deviation in general across the whole composition range, this remains unclear.

Rates of MNBS + Br^{-} reaction were measured at several concentrations for select compositions for both $C_{14}TPB$-CTAB and $C_{14}TPB$-$C_{16}DEEA$ systems. The resulting rate-surfactant profiles are presented in Fig. 6 with theoretical lines representing regression fits according to Eqn (3), and the determined parameters are shown in Table 2. Again, a range of bromide binding values were used in order to confirm that k_2^m/V_m values do not vary significantly, and for constant K_{Br} values, the relationship of k_2^m/V_m with solution composition proved to be similar in nature to that of k_{obs}. That is, there was a negative deviation from ideality for k_2^m/V_m values for both mixed

Table 2. PPM regression parameters for select compositions of mixed C$_{14}$TPB-C$_{16}$DEEA and C$_{14}$TPB-CTAB mixed surfactant systems at 298.2 K

C$_{14}$TPB-C$_{16}$DEEA	$\alpha_{C_{14}}$	K_{Br} M^{-1}	$10^3 k_2^m / V_m$ s^{-1}	K_S M^{-1}
	0	100	6.17	536
		2000	5.11	96
	0.2	100	8.23	311
		2000	7.12	70
	0.6	100	12.6	470
		2000	10.3	93
	0.8	100	16.9	394
		2000	14.1	84
	0.9	100	21.1	257
		2000	18.4	65
	1	100	35.3	109
		2000	38.4	30
C$_{14}$TPB-CTAB	0	100	6.77	233
		2000	5.85	64
	0.4	100	8.59	537
		2000	6.97	99
	0.6	100	12.8	474
		2000	10.2	99
	0.8	100	20.0	287
		2000	17.6	66
	1	100	35.3	109
		2000	38.4	30

systems. Because K_m values depend more strongly on bromide binding, no relationship with system composition could be found for this parameter.

Molecular modeling

Molecular modeling along with *ab initio* study of selected head groups interacting with bromide counterion were performed in order to elucidate structures and charge distribution which might be kinetically relevant. The alkyl side chains of all the surfactants were simplified to ethyl groups as the effect of added methylene groups on electronic structure becomes negligible.[27] In light of low aggregation number of 15 reported earlier[15] for C$_{16}$TPB and the low value of 25 for C$_{16}$TBuB determined by our group using steady state fluorescence quenching,[48] the examination at molecular level is relevant. Simple modeling of a micelle of C$_{16}$TPB using GaussView03 visualization program[49] (structure is not reported due to complexity) depicted a significant distance (over 14 Å) between surfactant head groups. Therefore, the computational analysis of interaction of a surfactant monomer head group with counter ion was carried out in the gas phase as a crude model of catalysis at the micellar interface.

All computations were performed using Gaussian03[50] program suite. Hartree-Fock (HF) *ab initio* method with doubly-split 3-21G, 3-21G*, and 6-31 + G* basis sets was employed for geometry optimization as well as for Mulliken and natural population atomic (NPA)[51–54]

charges as implemented in Gaussian03. Figure 7 shows optimized structures along with Mulliken and NPA charges summed to the heavy atoms for the following head groups: trimethylammonium (TMA), dimethylethanolammonium (DMEA), diethylethanolammonium (DEEA), trimethylphosphonium (TMP), triphenylphosphonium (TPP), and tributylphosphonium (TBP) cations.

According to Mulliken and NPA analyses, the positive charge of the quaternary ammonium head groups (TMA, DMEA, and DEEA) is distributed over the substituent groups (essentially on hydrogen atoms); nitrogen atom adopts a negative charge. In contrast, for the quaternary phosphonium cations, the phosphorus center bears highly positive charge. The NPA values are of +1.59, +1.73, and + 1.74 for TMP, TPP, and TBP, respectively. Thus, the total charge of the substituent groups is slightly negative albeit hydrogen atoms are positively charged (values are not shown). Although it is not a scope of present theoretical study, one might suppose that the difference in charge distribution may cause the difference in the structure of solvent shells that in turn may result in different behavior of nitrogen- and phosphorus-containing head groups in counterion binding and/or the kinetics of S$_N$2 reactions in condensed phase.

The highly positive charge on phosphorus atom allows suggesting that it may coordinate directly with the bromide counterion. This suggestion however was not supported by our computational results shown in Fig. 8. The binding of bromide anion on phosphorus center of TMP leads to the formation of Br-TMP, with Br interacting with three hydrogen atoms of three methyl groups. The TMA and TBP head groups form similar systems. Comparison of Br-TMA and Br-TMP reveals only minor differences in geometries and charge distribution. For Br-TMP, bromide interacts with hydrogen atoms at somewhat longer distances and bears slightly less negative charge. The TPP head group interacts with bromide differently. Due to steric effect of bulky phenyl groups, Br interacts with only two of three *ortho* phenyl hydrogens with the third phenyl ring oriented away from the Br. This may suggest that the improved performance of TPP as a catalyst for S$_N$2 attack may be due to steric effects of phenyl substituents. However it is not possible to point out whether the increased activity is due to the charge on the phosphorus atom or π–π interactions between the phenyl groups and the substrate or to the steric effects due to the phenyl moieties in the head group region. Further investigations in this direction may throw light on this matter.

EXPERIMENTAL

Materials

MNBS, Hexadecyltributylphosphonium bromide (C$_{16}$TBuB) Hexadecyltrimethylammonium bromide
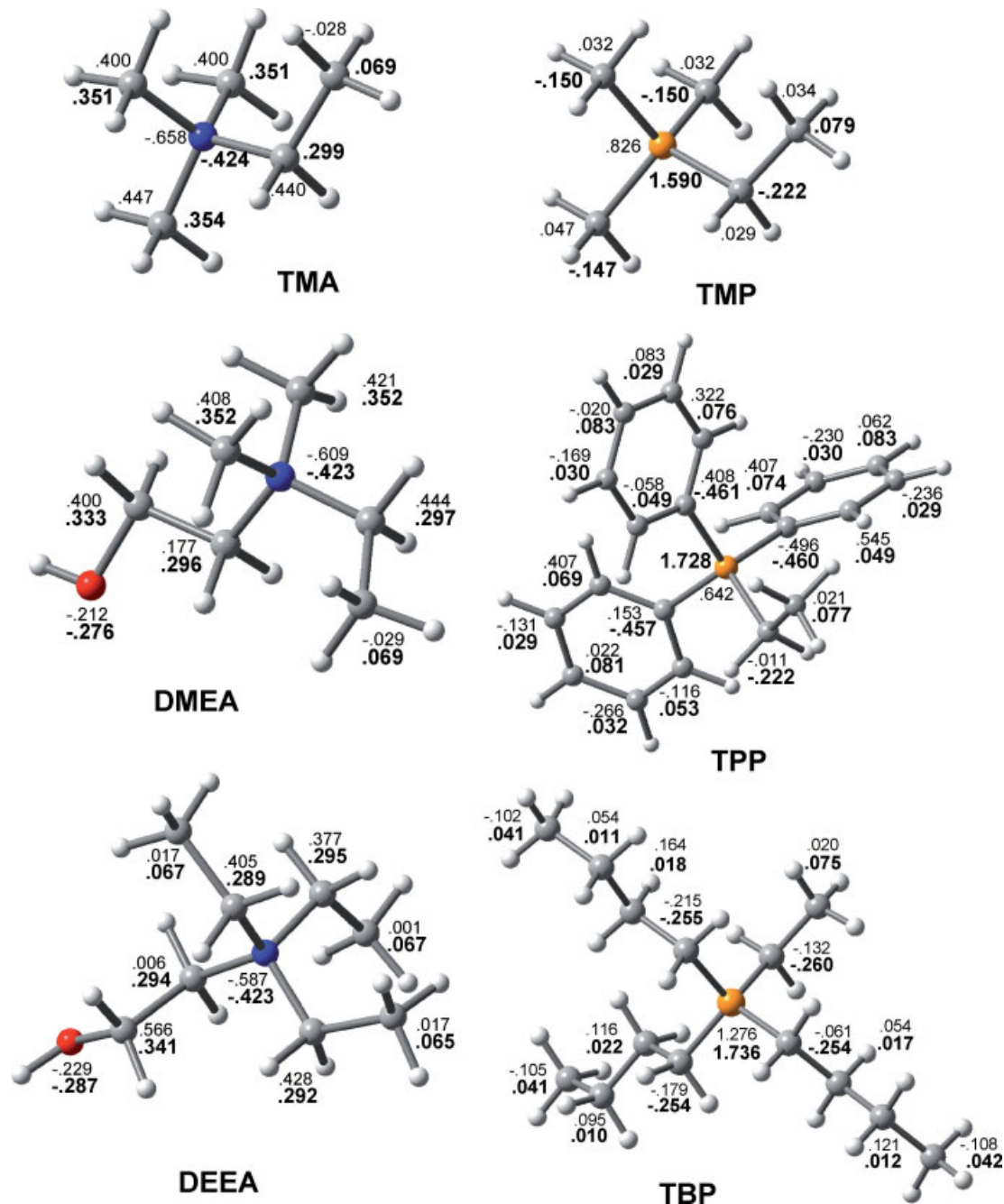
Figure 7. Structures of the TMA, DMEA, DEEA, TMP, TPP, and TBP cationic head groups (with ethyl side chains) optimized at the HF/3-21G level. Mulliken and NPA (in bold) charges with hydrogens summed to heavier atoms predicted with the HF/6-31 + G* method are shown

(CTAB) were obtained from Sigma-Aldrich, the alkyl-triphenylphosphonium bromide (C_nTPB) surfactants were obtained from Lancaster Synthesis and used as received. Hexadecyldiethylethanolammonium bromide ($C_{16}DEEA$) was synthesized[28] (>99.2% pure) with starting materials Dimethyl ethanol amine and diethyl ethanol amine, *n*-bromododecane, *n*-bromotetradecane, and *n*-bromohexadecane obtained from Sigma-Aldrich. All surfactant solutions were prepared freshly in doubly distilled deionized water before use.

Kinetic measurements

The reaction rates were followed spectrophotometrically using a Hewlett Packard 8452A diode array single beam spectrophotometer. The substrate (MNBS) was added to the reaction cell as 25 μL of stock solution in acetonitrile 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
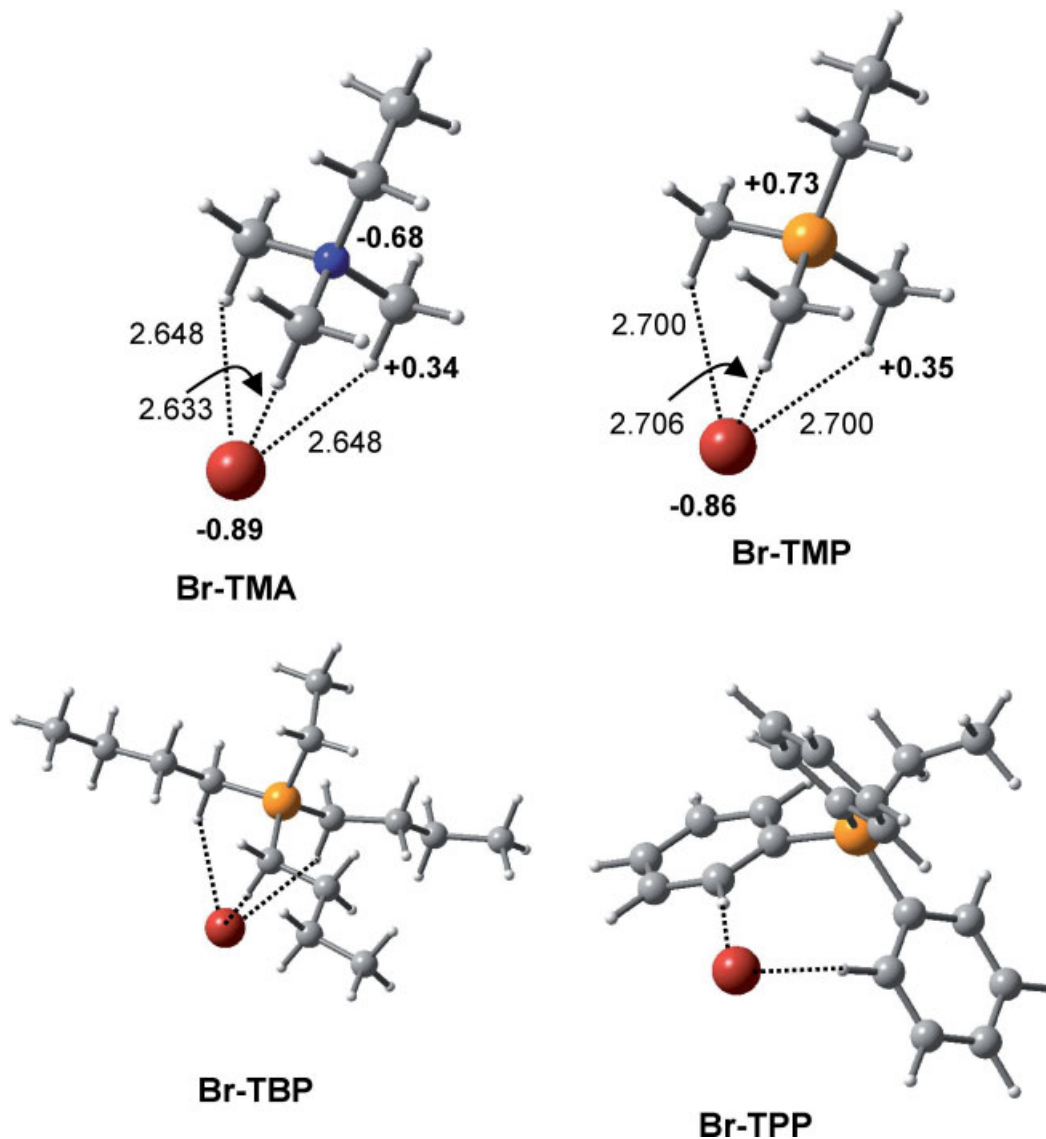
Figure 8. Structures, selected geometries (in Å), and selected NPA charges (in bold) predicted for bromide interacting with TMA and TMP head groups (Br-TMA and Br-TMP) using the HF/6-31 + G* method. Structures of bromide interacting with TBP and TPP head groups, Br-TBP and Br-TPP, predicted with the HF/3-21G* level are reported

solution. Due to interference from the UV absorption of the phenyl rings in the C$_n$TPB surfactants with respect to MNBS absorbance, measurements for kinetic data were taken at 290 nm for the phosphonium bromide surfactants and for C$_{16}$TBuB, absorbance was measured at 280 nm. The temperature for all kinetic runs was maintained at 298.2 K using a thermostated Haake DC-3 water bath and water-jacketed cell compartment.

Observed pseudo first-order rate constants (k_{obs}) were obtained from the slopes of plots of $\ln((A_\infty - A_0)/(A_\infty - A_t))$ versus time, where A_∞, A_t, and A_0 are absorbencies 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 two to three times to show that rate constants were reproducible within a precision of 5% or better.

CONCLUSIONS

1. Three to eight fold rate increases have been observed for the C$_n$TPB surfactant series for the reaction of MNBS with bromide ion over those found for other cationic surfactants investigated for this and other very similar reactions. The pseudophase model shows that the rate enhancement is due to catalysis at the micellar surface.
2. The rate enhancement in the presence of C$_{16}$TBuB is significantly higher than found for CTAB and, given

the relationship between observed rates for trialky-lammonium surfactants in an analogous reaction, suggests a possible rate enhancement due to the phosphorus center.

3. Mixed $C_{14}TPB$-$C_{16}DEEA$ and $C_{14}TPB$-CTAB surfactant systems have shown a negative deviation from ideality in both observed rate constants and determined k_2^m/V_m parameters with solution composition, while the mixed $C_{16}TPB$-$C_{10}TPB$ system exhibited near ideality.

4. Mulliken and NPA analyses have shown significant differences in charge distribution for the nitrogen- and phosphorus-containing head groups, which may result in any observed differences in kinetics between ammonium and phosphonium surfactants.

5. Theoretical study at HF level has shown that for TPB, bromide interacts only with two phenyl substituents while for other head groups three substituents are involved in the interaction. That allows more room for substrate binding in C_nTPB surfactants.

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