

Characterization of micelle formation of dodecyldimethyl-*N*-2-phenoxyethylammonium bromide in aqueous solution

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Abstract

Aggregation behavior of dodecyldimethyl-*N*-2-phenoxyethylammonium bromide commonly called domiphen bromide (DB) was studied in aqueous solution. The Krafft temperature of the surfactant was measured. The surfactant has been shown to form micellar structures in a wide concentration range. The critical micelle concentration was determined by surface tension, conductivity, and fluorescence methods. The conductivity data were also employed to determine the degree of surfactant counterion dissociation. The changes in Gibbs's free energy, enthalpy, and entropy of the micellization process were determined at different temperature. The steady-state fluorescence quenching measurements with pyrene and *N*-phenyl-1-naphthylamine as fluorescence probes were performed to obtain micellar aggregation number. The results were compared with those of dodecyltrimethylammonium bromide (DTAB) surfactant. The micelle formation is energetically more favored in DB compared to that in DTAB. The ¹H-NMR spectra were used to show that the 2-phenoxyethyl group, which folds back onto the micellar surface facilitates aggregate formation in DB.

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Keywords: Domiphen bromide; Krafft temperature; CMC; Gibbs free energy; Enthalpy; Entropy

1. Introduction

Quaternary ammonium salts have antimicrobial and antibacterial activities, which depend upon the lipophilicity of these compounds [1]. The critical micelle concentration (CMC) is one of the important parameters that describe lipophilicity of a compound. The nature of interactions between amphiphilic molecules and proteins and bacterial cells is strongly related to the CMC value. It has been found that the highest antibacterial activity is observed at amphiphile concentrations below CMC. This means that the molecular form of the amphiphile is responsible for antibacterial and antimicrobial activity [2,3]. Dodecyldimethyl-*N*-2-phenoxyethylammonium bromide also called domiphen bromide (DB) is a quaternary ammonium salt, which is used in hygiene mouthspray formulation that reduces oral bacteria and is effective against dental plaque, gingivitis and oral malodor [4]. Like cetylpyridinium chloride (CPC), de-

qualinium chloride DB acts as a bactericidal agent. Also, DB has inhibitory action on adherent water-insoluble glucan (WIG) synthesis by glucosyltransferases [5]. Therefore, aggregation properties of DB are very important. However, there is no report available in the literature on the detailed aggregation properties of the surfactant, except the CMC values in aqueous buffered solutions [6].

Recently, we have studied the aggregation behavior of (–)-*N*-dodecyl-*N*-methylephedrinium bromide, DMEB, in aqueous medium [7]. The DMEB surfactant was found to form vesicular aggregates above room temperature (~28 °C). This observation is very unusual for a relatively short and single-chain surfactant. Both DB and DMEB are structurally similar to dodecyltrimethylammonium bromide (DTAB) surfactant (see Chart 1 for structures). DB and DMEB are obtained when 2-phenoxyethyl group and 1-methyl-2-hydroxy-2-phenylethyl group, respectively, substitute one of the methyl groups of the surfactant headgroup of DTAB. Although this structural modification produces interesting consequences in the case of DMEB, the effects of variation of the structure of the surfactant headgroup on micellar properties have been much less studied. For

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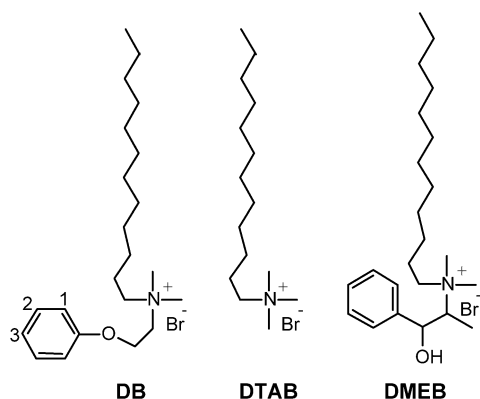


Chart 1. Chemical structures of DB, DTAB and DMEB.

cationic surfactants having general structure $R'N^+(R)_3Br^-$, it has been observed that for a given R' , an increase in the length of R results in a decrease in the CMC and mean aggregation number (N_{agg}) values and an increase in degree of counterion dissociation, α [8]. Therefore, we have undertaken this study in order to investigate whether DB also self-organizes in water to form vesicular aggregates like DMEB surfactant. The major objective is to study the thermodynamics of micelle formation of DB. A number of methods, such as surface tension, conductivity, and fluorescence, were used for characterization of the surfactant solution. The surface properties of DB at the air–water interface were investigated. An effort is made to measure Krafft temperature (T_K), CMC, and α of the surfactant molecule. N_{agg} , and hydrodynamic radius, R_h , of the aggregates formed by DB molecules were also estimated. The results will be compared with those of DTAB surfactant.

2. Experimental

2.1. Materials

Domiphen bromide (DB), cetylpyridinium chloride (CPC), pyrene, and *N*-phenyl-1-naphthylamine (NPN) obtained from Aldrich were recrystallized either from pure acetone or from acetone–ethanol mixture at least three times before use. $CDCl_3$ and D_2O were also purchased from Aldrich. All solvents used in this work were commercial reagents. The solvents were purified and distilled whenever required.

2.2. Measurements and calculations

2.2.1. Surface tension

Surface tensions of aqueous solutions were measured at room temperature ($\sim 30^\circ C$) with a Du Nöuy tensiometer (Hurdson & Co., Kolkata) by ring detachment method. Before each experiment, the instrument was calibrated and checked by measuring the surface tension of distilled water. A stock solution of DB was made in double distilled water. Aliquot of this solution was transferred to a beaker containing known volume of water. The solution was gently stirred magnetically and allowed to stand for about 5 min and then surface tension was measured. Measurements were repeated until three successive

readings gave γ values within $\pm 0.1 \text{ mN m}^{-1}$ difference. The CMC was obtained from the breakpoint of plot of surface tension (γ) versus $\ln C$. From the slope of the linear decrease of γ , the maximum surface excess concentration, Γ_{max} , and minimum surface area per surfactant headgroup, A_{min} , were calculated from the following equations, as described elsewhere [9]:

$$\Gamma_{max} = -\frac{1}{2RT} \left[\frac{d\gamma}{d \ln C} \right], \quad (1)$$

$$A_{min} = \frac{1}{N_A \Gamma_{max}}, \quad (2)$$

where R is gas constant, T is absolute temperature, N_A is Avogadro number, and C is surfactant concentration in mol L^{-1} .

2.2.2. Conductivity

All conductivity measurements were performed with a Thermo Orion digital conductivity meter (Model 150 A+) using a conductivity cell having cell constant 0.467 cm^{-1} . Conductivity (κ) of aqueous surfactant solutions was measured in a water-jacketed beaker by successive dilution method. After each dilution, the surfactant solution was thermostated for 5 min before conductivity was measured. The temperature of the beaker was controlled by a Thermo Neslab (Model: RTE 7) circulating bath.

2.2.3. Steady-state fluorescence

The steady-state fluorescence spectra were measured on a Perkin–Elmer LS-55 luminescence spectrometer equipped with filter polarizers that uses the L-format configuration. The temperature of the water-jacketed cell holder was controlled by a Thermo Neslab (RTE 7) circulating bath. Saturated solutions of the fluorescence probes, pyrene, and NPN were made in double distilled water. The pyrene and NPN solutions were excited at 335 and 340 nm, respectively. The excitation and emission slit widths were respectively 2.5 and 5 nm. Each spectrum was blank-subtracted.

2.2.4. Calculation of thermodynamic parameters

The CMC values determined at various temperatures from conductivity measurements were used to calculate the thermodynamic parameters of micellization according to the following equations [10,11]:

$$\Delta G_{mic}^0 = (1 + \beta)RT \ln \frac{CMC}{C_r}, \quad (3)$$

$$\Delta H_{mic}^0 = -(1 + \beta)RT^2 \left[\frac{d \ln(CMC)}{dT} \right], \quad (4)$$

$$\Delta S_{mic}^0 = \frac{\Delta H_{mic}^0 - \Delta G_{mic}^0}{T}, \quad (5)$$

where ΔG_{mic}^0 , ΔH_{mic}^0 , and ΔS_{mic}^0 are the change of Gibbs free energy, enthalpy, and entropy of micellization, respectively, $\beta (= 1 - \alpha)$ is a degree of counterion binding, and $C_r (= 1 \text{ mol L}^{-1})$ is the reference concentration.

3. Results and discussion

3.1. Krafft temperature

For the determination of T_K , a clear aqueous solution of DB (100 mM) was prepared in a water-jacketed beaker at room temperature. The solution was placed in a refrigerator at 5 °C for 48 h, where the precipitation of hydrated crystals occurred. The temperature of the precipitated solution was gradually raised by a water circulating cooling bath under constant stirring. At regular intervals of temperature, κ was measured using the digital conductivity meter. The solution was equilibrated at every temperature for 5 min and then κ was recorded. The T_K value was taken as the temperature where the κ vs T plot (not shown) showed an abrupt change in slope. At this temperature, the hydrated solid surfactant completely dissolved (by visual judgment) in water. The T_K value thus obtained should not be confused with the Krafft point (K_P), which is defined as the temperature at which the solubility is equal to the CMC of the surfactant [12]. The T_K value of DB is included in Table 1. It can be observed that the T_K value of DB is much higher than that of DTAB but less than that of DMEB (~ 28 °C) [7]. The rise in T_K is obviously due to the larger headgroup in the former surfactant. Davey et al. [13], however, have reported a decrease of T_K due to substitution of a triethyl group for a trimethyl group in alkyltrimethylammonium bromide surfactant. On the other hand, a further increase in the headgroup size for alkyltriethylammonium bromide from ethyl to propyl leads to a slight increase in the T_K value. The change in T_K can be due to a change in monomer solubility. Substitution of one of the methyl groups of DTAB by 2-phenoxyethyl group decreases CMC, which is

Table 1

Krafft temperature (T_K), critical micelle concentration (CMC), surface tension (γ_{cmc}) and surface pressure (π_{cmc}) at CMC, surface excess concentration (Γ_{max}), surface area/headgroup (A_{min}), average aggregation number (N_{agg}), hydrodynamic radius (R_h), and micropolarity (I_1/I_3) of DB and DTAB surfactants at 303 K

Properties	Surfactant	
	DB	DTAB ^a
T_K (K)	287.3	<273
CMC (mM)		
Surface tension	1.78	14.45
Fluorescence	1.79 ^b , 1.94 ^c	—
Conductivity	1.86	15.80
γ_{cmc} (mN m ⁻¹)	36.5	33.2 ^d
π_{cmc} (mN m ⁻¹)	34.7	39.0
$\Gamma_{max} \times 10^6$ (mole m ⁻²)	1.21	1.40
A_{min} (nm ² molecule ⁻¹)	1.37	1.18
α	0.392	0.234
N_{agg}	52.0 ^b $\pm$ 4.0	48.0
	51.0 ^c	
R_h (nm)	1.39	1.389 ^e
I_1/I_3	1.25	1.42

^a Data taken from [22].

^b Using pyrene probe.

^c Using NPN probe.

^d Calculated from values of γ_{H_2O} (72.2 mN m⁻¹) and π_{cmc} .

^e Taken from [27].

indicative of decreased monomer affinity for the solvent. A decrease in headgroup hydration as a result of the bulky headgroup prevents water contact with the charged nitrogen atom. The van der Waals interactions between 2-phenoxyethyl groups may also increase the crystal stability.

3.2. Critical micelle concentration

The CMC of DB was mainly obtained from conductivity measurements. The conductivity was measured by successive dilution of a concentrated solution of the surfactant by water. The CMC was obtained from the intersection point of the straight lines of pre- and post-micellar concentration range. The plots of κ vs [DB] at various temperatures are shown in Fig. 1. In order to check accuracy of the conductivity measurement, we have also employed fluorescence probe method using NPN and pyrene as a probe molecules to determine CMC of DB surfactant. NPN is a very sensitive probe whose fluorescence intensity increases with the decrease of solvent polarity [14]. Since NPN is a hydrophobic molecule, it gets solubilized in the palisade layer of micelles as indicated by the increase of fluorescence intensity and shift of the emission maximum to shorter wavelengths [15]. Therefore, steady-state fluorescence spectra of NPN were measured in aqueous solutions in the presence of different concentrations of DB. The change of relative fluorescence intensity of the probe as a function of surfactant concentration is shown in Fig. 2. The concentration corresponding to the inflection point was taken as the CMC.

The CMC of DB was also obtained from fluorescence studies using pyrene as a probe molecule. Pyrene is a well-known fluorescence probe for the micropolarity studies of its solubilization site in micellar interior [16,17]. The intensity ratio I_1/I_3 of the first (372 nm) and the third (384 nm) vibronic peaks of the pyrene fluorescence spectrum is very sensitive to solvent polarity [18] and therefore has been widely used as a measure of the polarity of the microenvironment of the probe [16,17] and CMC of surfactants. Normally, high value of I_1/I_3 indicates polar environment whereas low value indicates nonpolar environment. Therefore, the polarity ratio, I_1/I_3 , was measured

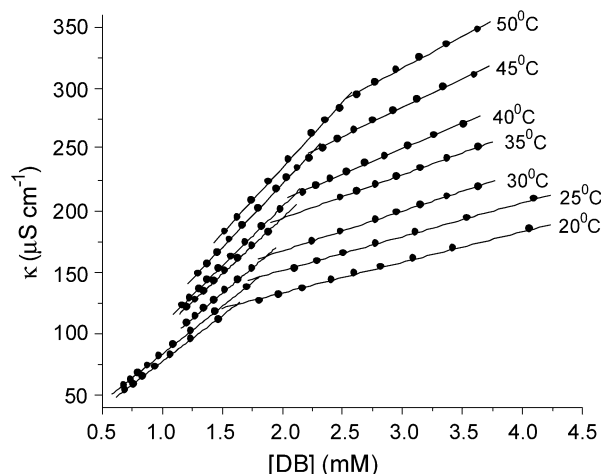


Fig. 1. Conductivity (κ) vs [DB] plots at various temperatures.

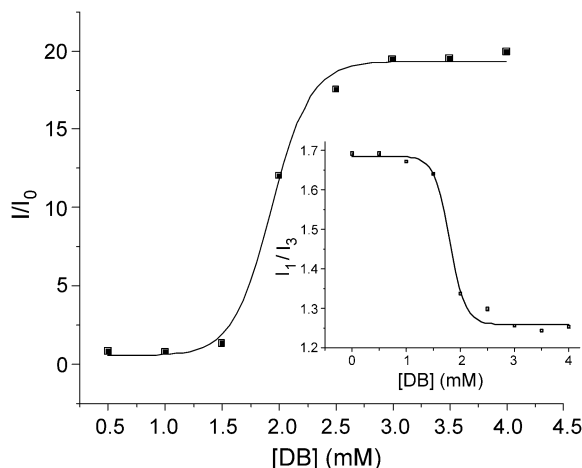


Fig. 2. Plot of relative fluorescence intensity (I/I_0) of NPN against [DB]; inset: Plot of intensity ratio, I_1/I_3 , of pyrene as a function of [DB]; saturated solutions of pyrene and NPN were used for the measurements.

in the presence of varying concentration of DB. The polarity ratio decreased with the increase of [DB] as shown in the inset of Fig. 2. The inflection point gave the CMC value. The CMC values (Table 1) obtained by conductivity and fluorescence methods are equal within the range of common error of different experimental methods. The lower value of CMC of DB compared to that of DTAB surfactant suggests its strong tendency to form micelles. The low CMC might be due to the bulky surfactant headgroup, which reduces electrostatic repulsion among ionic headgroups.

The polarity ratios for both types of aggregates are also included in Table 1. The I_1/I_3 ratio in all the surfactant micelles is much less than that in water (1.69). This indicates that the probe molecule is solubilized within the hydrophobic domains of spherical aggregates. The I_1/I_3 ratio for the micelles of DB is less than that of DTAB. This suggests more ordering at the interface of the former surfactant micelles than that in the latter. The ordering of the aggregate interface reduces the degree of water penetration in the hydrocarbon layer in accordance with the reduction observed in micropolarity sensed by the probe molecules.

3.3. Interfacial properties

Surface tension (γ) of water in the presence of DB surfactant was measured to investigate its surface properties at the air–water interface. The breakpoint of the plot of γ versus $\ln C$ (not shown) gives the CMC of the surfactant. The CMC value (Table 1) is very close to those obtained by conductivity and fluorescence methods. Table 1 lists the values of surface tension (γ_{cmc}) and surface pressure, π_{cmc} ($= \gamma_{\text{water}} - \gamma_{\text{cmc}}$) at CMC, surface excess concentration, Γ_{max} , and surface area per surfactant headgroup, A_{min} , for DB surfactant. The corresponding data for DTAB surfactant are also included in the table. The low γ_{cmc} value suggests that the amphiphile is a very good surface-active agent. However, surface activity of DB is less than that of DTAB surfactant. The hydrophobic 2-phenoxyethyl group at the surfactant headgroup of DB perhaps decreases its tendency

Table 2

Critical micelle concentration (CMC), degree of counterion binding (β), and standard Gibbs free energy (ΔG_{mic}^0), standard enthalpy (ΔH_{mic}^0) and standard entropy (ΔS_{mic}^0) of micellization of DB surfactant at different temperatures

Temperature (± 0.1 K)	CMC (mM)	β	ΔG_{mic}^0 (kJ mol $^{-1}$)	ΔH_{mic}^0 (kJ mol $^{-1}$)	ΔS_{mic}^0 (J K $^{-1}$ mol $^{-1}$)
293.0	1.62	0.667	−26.09	−16.38	33.14
298.0	1.80	0.645	−25.76	−16.72	30.33
303.0	1.86	0.608	−25.48	−16.90	28.32
308.0	1.96	0.592	−25.40	−17.29	26.33
313.0	2.12	0.570	−25.15	−17.61	24.09
318.0	2.26	0.541	−24.82	−17.84	21.95
323.0	2.53	0.509	−24.23	−18.02	19.23

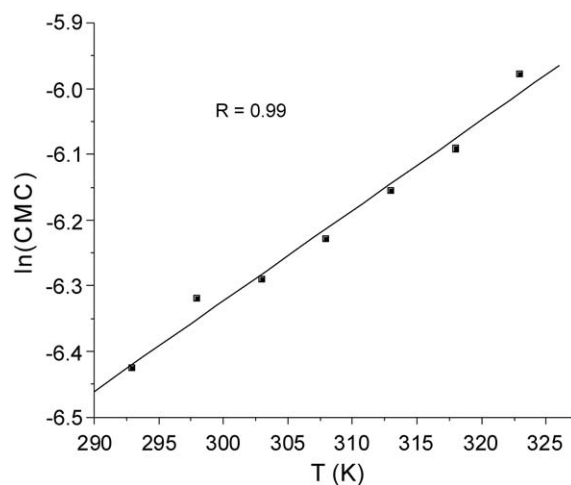


Fig. 3. Plot of $\ln(\text{CMC})$ as a function of temperature.

to adsorb at the interface because the bulky headgroup prevents water contact with the charged nitrogen atom. The lower π_{cmc} and Γ_{max} values for DB surfactant compared to that of DTAB substantiate this conclusion. Consequently, the surface area per surfactant headgroup, A_{min} , is higher for DB surfactant. The large A_{min} value is consistent with the bulky surfactant headgroup compared to that of DTAB. At room temperature, the A_{min} value (1.37 nm 2) is > 1.0 nm 2 , which suggests formation of micellar structures [19].

3.4. Thermodynamics of micelle formation

The thermodynamic parameters ΔG_{mic}^0 , ΔH_{mic}^0 , and ΔS_{mic}^0 of micelle formation were calculated from CMC and β values obtained by conductivity measurements at various temperatures using Eqs. (3)–(5). The data are listed in Table 2. The plots of κ vs [DB] at various temperatures (20–50 °C) are shown in Fig. 1. The plots exhibit two straight lines intersecting at the CMC. Values of α at different temperatures were calculated as the ratio of the slope of the line above the CMC to the slope of the line below the CMC following Evan's method [20]. The data in Table 2 suggest that the degree of counterion binding, β , decreases continuously with the increase of temperature. On the other hand, the plot in Fig. 3 shows that $\ln(\text{CMC})$ increases linearly with temperature. Both ΔG_{mic}^0 and ΔH_{mic}^0 are negative at all temperatures and change very little over the tem-

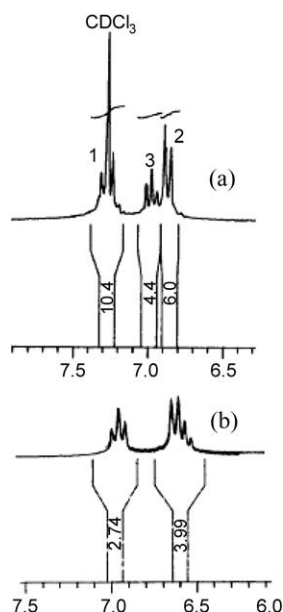


Fig. 4. ^1H -NMR spectra of 50 mM DB in (a) CDCl_3 and (b) D_2O solvents; only truncated spectra are shown here to save space.

perature range. The negative values of ΔH_{mic}^0 suggest that the process of micellization of DB is exothermic. This means that the major attractive force for micellization of DB molecules is hydrophobic interaction [21]. On the other hand, the entropy change, ΔS_{mic}^0 , is positive and has a decreasing tendency with the increase in temperature, indicating formation of more disordered aggregates. Similar results were also reported by others for DTAB surfactant. However, it is observed that in the case of DTAB, magnitudes of ΔH_{mic}^0 ($-1.77 \text{ kJ mol}^{-1}$) and ΔG_{mic}^0 ($-18.4 \text{ kJ mol}^{-1}$) [22] are smaller than those of DB micelles. The magnitudes of ΔG_{mic}^0 for DB and DTAB surfactants clearly suggest that micelle formation is energetically as well as entropically more favorable in the former than in the latter surfactant. This is perhaps because the hydrophobic hydration is more in the case of DTAB, which results in a more hydrated, i.e., more polar, interface and hence a smaller ΔG_{mic}^0 value. This suggests increased contact of the phenoxyethyl group with water molecules. This is possible only if the phenoxyethyl group folds back onto the micelle surface. This is substantiated by the ^1H -NMR spectra (see Fig. 4), which exhibit sharp peaks due to the aromatic protons in CDCl_3 as well as in D_2O solvent. This leads to increased interaction between the 2-phenoxyethyl group and the quaternary ammonium ion, which screens ammonium ions and thus reduces charge repulsion. Consequently, the CMC value decreased. The increase in surfactant headgroup volume also leads to an increase in α and A_{min} values. Indeed, the α and A_{min} values of DB surfactant are higher than the respective values of DTAB surfactant (see Table 1). El Seoud and coworkers [23] have also suggested that the 2-phenylethyl group in cetyldimethyl-*N*-2-phenylammonium chloride surfactant lies more or less parallel to the micelle surface. The driving force for this is the interaction between the aromatic ring and ammonium ion. However, in the case of DMEB surfactant, the phenylethyl group as already reported by us is bent toward the

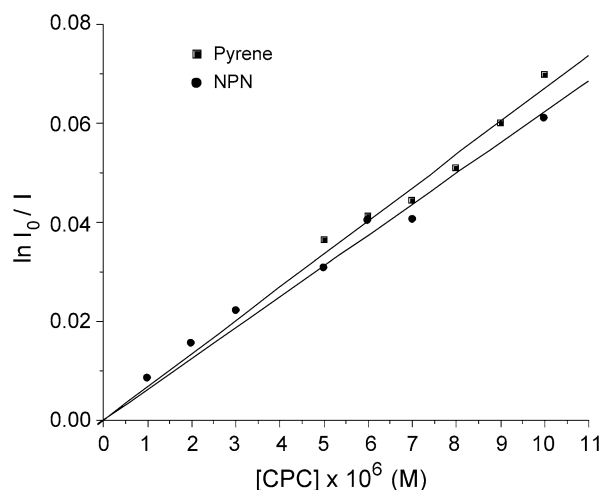


Fig. 5. Plot of $\ln(I_0/I)$ vs [CPC] in 10 mM DB at 303 K for pyrene, and NPN probes; saturated solutions of pyrene and NPN were used for the measurements.

micelle interior [7]. The difference in orientation of the aromatic moiety and hence in aggregation behavior of the surfactants is perhaps due to the ether linkage that allows easy rotation of phenoxyethyl group in DB molecule.

3.5. Aggregation number of DB micelles

The mean aggregation number was determined by fluorescence quenching method using pyrene as fluorescent probe and cetylpyridinium chloride (CPC) as quencher molecule. N_{agg} value of the amphiphile was calculated from the slope of the plot of $\ln(I_0/I)$ versus [Q] according to the equation [24,25]:

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_{\text{agg}}[Q]}{(C - \text{CMC})}, \quad (6)$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, C is the total surfactant concentration, and $[Q]$ is quencher concentration. The highest CPC concentration was much below its CMC ($\sim 10^{-4} \text{ M}$). The concentration of pyrene ($\sim 3 \times 10^{-7} \text{ M}$) was much less than the micelle concentration so that Poisson distribution is maintained. This ensures quenching of the fluorescence of pyrene molecules that are solubilized in the micelles. This is indicated by the high value of the Stern–Volmer constant, K_{SV} ($= 6960 \text{ M}^{-1}$), obtained from the plot (not shown here) of Stern–Volmer equation ($I_0/I = 1 + K_{\text{SV}}[Q]$) [26]. It should be noted here that in the absence of micelles, the fluorescence quenching of pyrene is mainly dynamic (collisional) in nature. The plot of $\ln(I_0/I)$ vs [CPC] for 10 mM DB is shown in Fig. 5. The N_{agg} value as obtained from the slope of the straight line is listed in Table 1. As a cross check, similar quenching studies were performed using NPN and CPC as fluorophore and quencher, respectively. The corresponding plot is included in Fig. 5. As in the case of pyrene, the Stern–Volmer constant is very high (6040 M^{-1}). A closely similar value of N_{agg} was obtained for DB micelles. The aggregation number of DB micelles is very close to that of DTAB micelles.

3.6. Hydrodynamic radius of micelles

Wettig et al. [27] developed a calibration curve for the determination of molecular weight (MW) of micelles from the experimentally determined R_h values and molecular weights calculated from aggregation numbers of *n*-alkyltrimethylammonium bromide surfactants determined using fluorescence quenching method. The equation can be written as

$$\text{MW} = -9.855R_h^2 + 50.79R_h - 30.04, \quad (7)$$

where the molecular weight is in kilodaltons (kDa) and R_h is in nanometers. Equation (7) has also been successfully used to estimate aggregation number of cationic gemini surfactants [27]. Since DB is structurally similar to DTAB, we employed the above equation to calculate the R_h of DB micelles. The molar mass of DB molecule is $414.46 \text{ g mol}^{-1}$ and the N_{agg} value is 52.0. Therefore, the molecular weight of the DB micelles formed at 30°C is 21.55 kDa. The acceptable value of R_h (1.39 nm) thus calculated by the use of Eq. (7) is included in Table 1. The R_h value suggests presence of micellar structure in surfactant solutions containing 10 mM DB. It is interesting to note that both DB and DTAB micelles have almost equal R_h values. This is because both surfactants have closely similar N_{agg} values.

4. Conclusions

Aggregation behavior of domiphen bromide (DB) surfactant was studied in water. Unlike DMEB surfactant, DB forms micellar structures in aqueous solutions. This is because the 2-phenoxyethyl group of the surfactant head of DB folds back on to the micelle surface. The adsorption efficiency of DB at the air–water interface is less compared to that of DTAB. On the other hand, micelle formation is energetically more favored in DB than in DTAB surfactant. The Krafft temperature of DB is higher than that of DTAB surfactant. However, CMC and degree of counterion binding of DB is much less than that of DTAB surfactant. This has been attributed to the bulky surfactant headgroup of DB compared to that of DTAB. The mean aggregation number and hydrodynamic radius of DB and DTAB micelles are almost equal in magnitude.

Acknowledgments

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