Surface Activity and Premicellar Aggregation of Some Novel Diquaternary Gemini Surfactants

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ABSTRACT: A series of novel cationic gemini surfactants, $C_nH_{2n+1}N^+(CH_3)_2CH_2CHOHCHOHCH_2N^+(CH_3)_2\ C_nH_{2n+1} \cdot 2Br^-$, have been synthesized, and their surface properties were investigated in water, 0.1 N NaCl, and 0.1 N NaBr at 25°C. From surface tension-log molar concentration plots, the pC_{20}, critical micelle concentration (CMC), and γ_{CMC} values have been determined, and the area/molecule at the aqueous solution/air interface was calculated. When the number of carbon atoms in the alkyl (hydrophobic) chains is above a certain number, which depends upon the molecular environment, the surface activity of the compounds is less than expected. This appears to be due to formation of small, soluble aggregates below the CMC. Equilibrium constants calculated for this aggregation indicate that a series of oligomers are formed.
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KEY WORDS: A_{min}, CMC, cationic surfactants, γ_{CMC}, gemini surfactants, pC_{20}, premicellar aggregates, quaternary ammonium, surface tension.

Surfactants with two hydrophilic and two hydrophobic groups in the molecule, called "gemini" surfactants, have evoked considerable interest (1–12) since it became evident that compounds of this type can have much greater surface activity than comparable conventional surfactants with one hydrophilic group and one hydrophobic group in the molecule. Because of their novelty, structure/property relationships for these surfactants are still not well understood.

Several papers have been published on the surface properties and micellization of diquaternary ammonium halide gemini surfactants of the type $RN^+(CH_3)_2(CH_2)_mN^+(CH_3)_2R \cdot 2\ Br^-$ (13,14), symbolized as $(C_nN)_2(CH_2)_2$, and $RN^+(CH_3)_2CH_2C_6H_4CH_2N^+(CH_3)_2R \cdot 2\ Br^-$, symbolized as $(C_nN)_2Ar$ (11,15). In the former type, the linkage between the two quaternary ammonium groups (the "spacer") is a flexible hydrophobic group; in the latter it is rigid and hydrophobic. Some of the latter showed poor surface activity.

Anionic gemini surfactants, studied previously (9,10,16–22), with a hydrophilic flexible spacer between the two hydrophilic groups all show high surface activities. To learn whether this phenomenon applies also to cationic gemini, a series of cationic gemini surfactants with a flexible hydrophilic spacer between the two hydrophilic groups, $[C_nH_{2n+1}N^+(CH_3)_2CH_2CHOH]_2 \cdot 2Br^-$, symbolized $(C_nN)_2(OH)_2$, were synthesized, and their interfacial properties were studied *via* surface tension measurement. Properties studied include determination of the critical micelle concentration (CMC), pC_{20} (negative log of the surfactant molar concentration required to reduce the surface tension of the solvent by 20 mN/m), γ_{CMC} (the surface tension at the CMC), Γ_{max} (the maximum surface excess concentration at the air/aqueous solution interface), and A_{min} (the minimum area per surfactant molecule at the air/aqueous solution interface).

EXPERIMENTAL PROCEDURES

Materials. The diquaternary gemini surfactants were synthesized by the reaction of 1,4-dibromo-2,3-butanediol with the appropriate *N,N*-dimethylalkylamine in *n*-propanol solvent under reflux at about 95°C for 48 h in the presence of a 20% excess of amine to ensure complete diquaternization. (The excess dimethylalkylamine was titrated with HCl to monitor the completion of the reaction.) Excess dimethylalkylamine and *n*-propanol were removed in a rotary evaporator under reduced pressure.

The crude gemini surfactant was dissolved in a minimum amount of ethanol and recrystallized from tetrahydrofuran three times. A white solid product was obtained (yield > 80%). The purity of the material was checked by two-phase dye transfer titration with sodium dodecanesulfonate solution of known concentration and a mixed indicator (23,24). The purity of the product reached a constant value >99.0%. The structures also were checked by ^1H nuclear magnetic resonance (NMR) spectrum in a Varian EM-390 90-MHz NMR instrument (Palo Alto, CA). Elemental analysis for $(C_{10}N)_2(OH)_2$ monohydrate; theory: C, 52.82; H, 10.13; N, 4.40; found: C, 53.15; H, 9.81; N, 4.29; for $(C_{12}N)_2(OH)_2$ monohydrate: theory: C, 55.48; H, 10.48; N, 4.05; found: C, 55.86; H, 10.34; N, 3.98; for $(C_{14}N)_2(OH)_2$ monohydrate: theory: C, 57.74; H, 10.76; N, 3.74; found: C, 58.06; H, 10.77; N, 3.68.

Before being used for surface tension measurement, aqueous solutions of the diquat surfactant (in quartz-condensed water) were further purified by repeated passage (25) through mini-columns (Sep-Pak C18 Cartridge; Waters Associates, Milford, MA) of octadecyl-silanized silica gel to remove any

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traces of impurities that are more surface-active than the parent compound. The concentration of diquat in the effluent from these columns was determined by the mixed-indicator two-phase dye transfer titration.

Sodium bromide and sodium chloride used to increase the ionic strength of solutions were reagent-grade materials that were then baked for several hours in a porcelain casserole at red heat to remove traces of organic compounds. The surface tension of aqueous solutions of the baked salts was measured to ensure the absence of traces of surface-active impurities.

Surface tension measurements. Measurements were made by the Wilhelmy plate technique. The Wilhelmy plate (sand-blasted platinum, *ca.* 5-cm perimeter) was hung from the arm of a Bethlehem dial-type torsion balance. The solutions were immersed in a constant temperature bath at the desired temperature ±0.02°C. The instrument was calibrated against the quartz-condensed water each day that measurements were made. Sets of measurements were taken at 30-min intervals until no significant change occurred.

RESULTS AND DISCUSSION

Solubility. The presence of a flexible hydrophilic group, $-CH_2CHOHCHOHCH_2-$, between the two quaternary ammonium groups in the series $(C_nN)_2(OH)_2$ results in much higher solubility compared to compounds with the rigid hydrophobic spacer in the $(C_nN)_2Ar$ series, between the two quaternary ammonium groups. $(C_8N)_2(OH)_2$ is easily dissolved at 20 g/L, while the C_{10}, C_{12}, and C_{14} homologs have solubilities of about 2, 1.5, and 0.3 g/L, respectively. As a result, surface tensions easily can be measured at 25°C, whereas measurement for the members of the $(C_nN)_2Ar$ series with chainlengths of 14 or more carbon atoms could only be taken at 50°C or higher (11,15).

Interfacial properties. The surface tension vs. log molar concentration (logC) curves for $(C_{10}N)_2(OH)_2$, $(C_{12}N)_2(OH)_2$, $(C_{14}N)_2(OH)_2$, and $(C_{16}N)_2(OH)_2$ in H_2O at 25°C are shown in Figure 1. The C_8, C_{10}, C_{12}, and C_{14} members of this series in 0.1 M NaBr at 25°C are shown in Figure 2; C_{10}, C_{12} and C_{14} members in 0.1 M NaCl at 25°C are shown in Figure 3. From the curves, pC_{20}, CMC, γ_{CMC}, Γ_{max}, and A_{min} values can be determined (26–28). Values are listed in Table 1, along with data on the $(C_nN)_2Ar$ series and on reference compounds that contain one alkyl chain and one quaternary ammonium group.

pC_{20} values. The pC_{20} value measures the efficiency of adsorption of the surfactant at the interface. pC_{20} values of members of the $(C_nN)_2(OH)_2$ series are listed in Table 1. Table 1 shows that the pC_{20} values increase with increasing number of carbon atoms in the hydrophobic chain (*n*). The longer the chainlength of the surfactant, the larger the pC_{20} value and the smaller the bulk liquid phase concentrations required to attain either saturation adsorption or surface tension reduction of 20 dynes/cm (mN/m). Figure 4 shows the linear relation between pC_{20} ($-\log C_{20}$) and *n* for these geminis in H_2O and in 0.1 M NaBr. The higher homologs deviate from the linear plots (see below).

CMC. It is clear that the CMC values of this series decrease as the length of the alkyl chain increases from 8–14 carbon atoms in salt solution, from 10–14 carbon atoms in H_2O. Plots of log CMC vs. *n*, for members of the $(C_nN)_2(OH)_2$ series in H_2O and 0.1 N NaBr, are shown in Figure 5. Here, the C_{14} homolog in 0.1 N NaBr and the C_{16} homolog in H_2O deviate from the linear plots. This deviation is believed to indicate aggregation of the monomeric gemini to small aggregates with little or no surface activity (see below).

The CMC values of the members (*n* = 10–14) of the

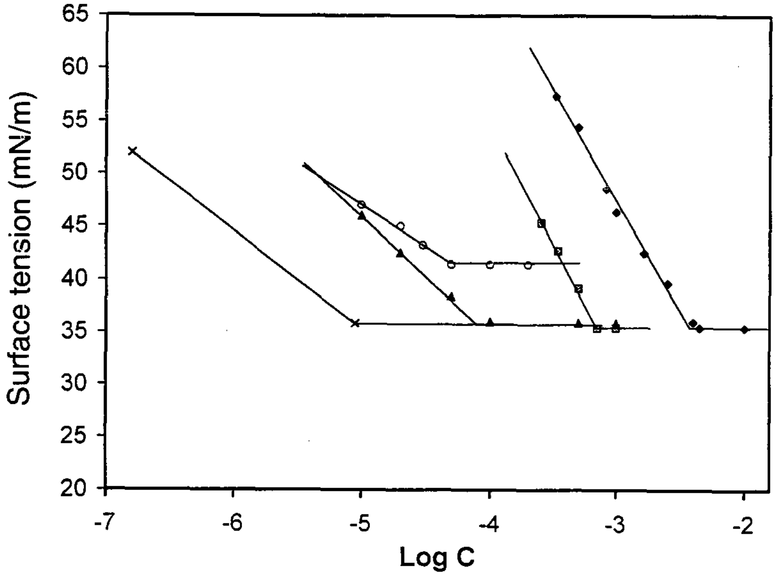

FIG. 1. Surface tension vs. log C plots of $(C_nN)_2(OH)_2$ in H_2O at 25°C: ◆, C_{10}; ■, C_{12}; ▲, C_{14}; ○, C_{16}, experimental; ×. C_{16}, calculated for no premicellar aggregation.

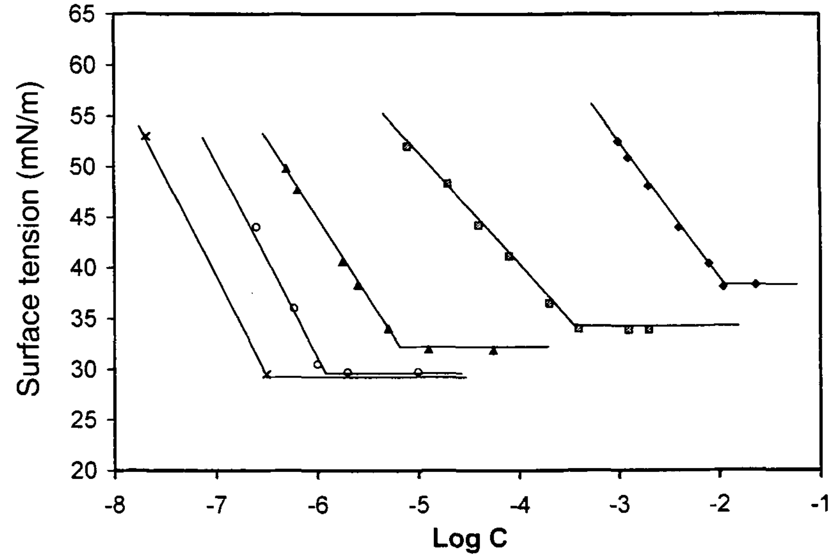

FIG. 2. Surface tension vs. log C plot of $(C_nN)_2(OH)_2$ in 0.1 M NaBr at 25°C: ◆, C_8; ■, C_{10}; ▲, C_{12}; ○, C_{14}, experimental; ×, C_{14}, calculated for no premicellar aggregation.

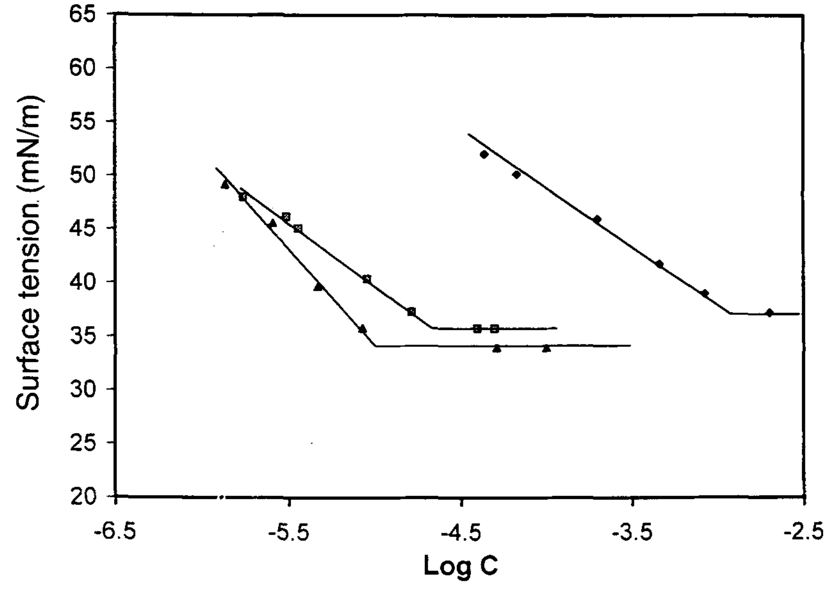

FIG. 3. Surface tension vs. log C plots of $(C_nN)_2(OH)_2$ in 0.1 M NaCl at 25°C: ◆, C_{10}; ■, C_{12}; ▲, C_{14}.

$(C_nN)_2(OH)_2$ series in H_2O are all about 1.5 orders of magnitude smaller than the comparable conventional surfactants (with one hydrophobic group of the same carbonlength and one quaternary ammonium group). This indicates much better micelle-forming ability than the comparable single-chain surfactant. The CMC values of these geminis with a hydrophilic flexible space are also smaller than comparable ones with a hydrophobic flexible spacer $(C_nN)_2(CH_2)_2$ or a hydrophobic rigid spacer, $(C_nN)_2Ar$. This is possibly because the two -OH groups form H-bonds with H_2O molecules in and thus facilitate bending of the spacer toward the aqueous phase, to form the convex micelle surface. For the $[RN(CH_3)_2CH_2CH_2]_2^{2+}2Br$ gemini, the spacer is hydrophobic and would tend to bend away from the aqueous solution together with the two long hydrophobic groups, which would make it more difficult to form micelles. For the $(C_nN)_2Ar$ compounds, with a rigid hydrophobic spacer, micellization would be even more difficult because it would

TABLE 1
Physical Properties of $(C_nN)_2(OH)_2$ Gemini Surfactants and Related Compounds at 25°C[a]

Compound	Medium (25°C)	pC_{20}	CMC (mol/dm^3)	γ_{CMC} (mNm^{-1})	Γ_{max} (mol/cm^2 × 10^{10})	A_{min} (nm^2 × 10^2)
$(C_{10}N)_2(OH)_2$	H_2O	3.24	3.7E-3	35.5		
$C_{10}H_{21}N(CH_3)_3Br$	H_2O		6.8E-2			
$(C_{12}N)_2(OH)_2$	H_2O	3.89	7.0E-4	35.4		
$(C_{12}N)_2(CH_2)_2$	H_2O		1.2E-3			
$(C_{12}N)_2Ar$	H_2O (50°C)	1.3E-3	39.0			
$C_{12}H_{25}N(CH_3)_3Br$	H_2O	1.6E-2				
$(C_{14}N)_2(OH)_2$	H_2O	5.50	8.5E-5	36.0		
$C_{14}H_{29}N(CH_3)_3Br$	H_2O		3.6E-3			
$(C_{16}N)_2(OH)_2$	H_2O	5.50	5.0E-5	41.4		
$(C_{16}N)_2Ar$	H_2O (50°C)		8.0E-5	40.0		
$C_{16}H_{33}N(CH_3)_3Br$	H_2O		2.7E-5			
$(C_8N)_2(OH)_2$	0.1M NaBr	3.05	1.1E-2	38.3	2.3	79
$(C_{10}N)_2(OH)_2$	0.1M NaBr	5.17	3.3E-4	33.8	2.0	75
$(C_{10}N)_2(OH)_2$	0.1M NaCl	4.40	1.0E-3	37.2	1.8	95
$(C_{12}N)_2(OH)_2$	0.1M NaBr	6.47	6.0E-6	31.8	2.8	64
$(C_{12}N)_2(OH)_2$	0.1M NaCl	6.03	2.1E-5	35.8	2.1	84
$(C_{12}N)_2Ar$	0.1M NaCl		8.0E-5	38.0		111
$(C_{14}N)_2(OH)_2$	0.1M NaBr	6.90	1.0E-6	29.7	3.9	42

[a] CMC, critical micelle concentration; pC_{20}, negative log of the surfactant molar concentration required to reduce the surface tension of the solvent by 20 mN/mk; Γ_{max}, the maximum surface excess concentration at the air/aqueous solution interface; A_{min}, the minimum area per surfactant molecule at the air/aqueous solution interface; γ_{CMC}, the surface tension at the CMC.

not remove the hydrophobic spacer from contact with the aqueous phase.

As expected for these doubly-charged compounds, the CMC decreases sharply with increase in the ionic strength of the solution and with increased binding of the counterion to the quaternary *N*. Thus, the CMC decreases with solvent in the following order: H_2O > 0.1 N NaCl > 0.1 N NaBr.

Γ_{max}, A_{min}, and γ_{CMC}. Γ_{max} and A_{min} values were calculated only in solutions that contained swamping amounts of counterion to avoid any ambiguity in the value of the coefficient in the Gibbs adsorption equation (26), used to calculate these values. This is particularly important for these double-charged compounds. The Γ_{max} values are greater (and the A_{min} are smaller) in 0.1 N NaBr than in 0.1 M NaCl, reflecting the tighter binding of the Br^- than the Cl^- to the quaternary *N*. The Γ_{max} values also increase (and the A_{min} values decrease) with increase in the alkyl chainlength. This indicates that the molecules are more tightly packed in the

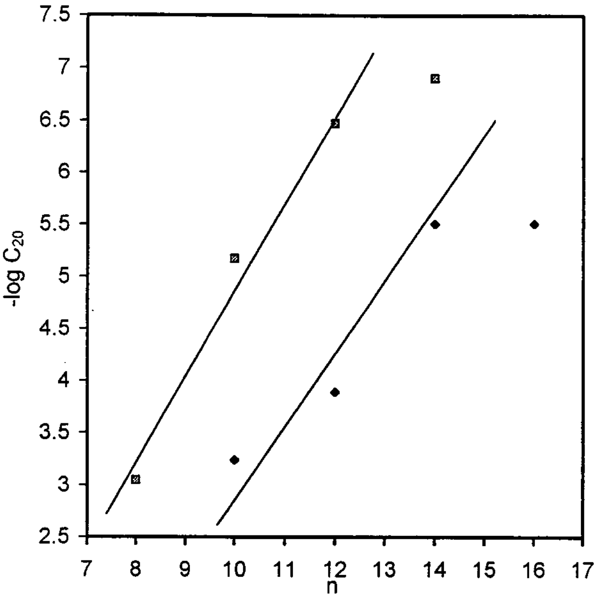

FIG. 4. -Log C_{20} vs. n plots of $(C_nN)_2(OH)_2$ at 25°C: ◆, in H_2O; ■, in 0.1 M NaBr.

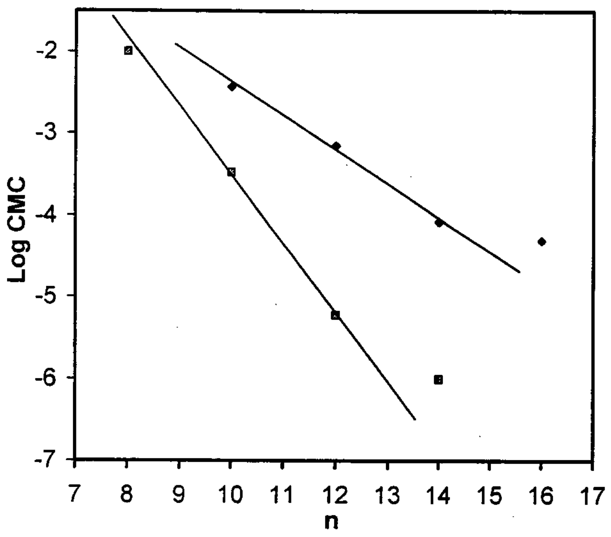

FIG. 5. Log critical micelle concentration (CMC) vs. n plots of $(C_nN)_2(OH)_2$ at 25°C: ◆, in H_2O; ■, in 0.1 M NaBr.

water–air interface for the longer-alkyl surfactants. With increase in the value of Γ_{max}, the value of γ_{CMC} decreases (28). Thus, the γ_{CMC} of these compounds are all lower in 0.1 N NaBr than in 0.1 N NaCl solution, due to the stronger binding of Br^- and N^+ than Cl^- and N^+, making the compounds more closely packed in 0.1 N NaBr than 0.1 N NaCl.

Premicellar aggregation. Plots of -log C_{20} (pC_{20}) and log CMC vs. n (Figs. 4 and 5, respectively) show the deviation of the values of log C_{20} and log CMC from the linear plots of the lower homologs when the value of n increases above a certain value. The direction of the deviation indicates a decrease in surface activity, compared to that expected. Menger and Littau (11,15) have observed an increase in the CMC with increase in chainlength in the $(C_nN)_2Ar$ series of diquaternary geminis, with a rigid hydrophobic spacer, and submitted evidence for the formation of small premicellar aggregates.

If we assume that the decreased surface activity, compared to the expected, that we observe in these plots of -log C_{20} and log CMC vs. n is due to the formation of small, premicellar soluble aggregates, we can formulate the formation of these aggregates as follows:

$$xS \Leftrightarrow S_x \qquad [1]$$

where S is the monomeric gemini and x the number of monomers involved in forming the soluble aggregate. The equilibrium constant, K_{eq}, for this aggregate is then

$$K_{eq} = [S_x]/[S]^x \qquad [2]$$

where $[S_x]$ is the activity of the aggregate S_x, and $[S]$ the activity of the monomeric gemini. In these dilute solutions, we can use molar concentrations for activities.

Because the presence of these premicellar aggregates causes the solution to have less surface activity than expected, it can be assumed that these aggregates have little or no surface activity. Therefore, the observed surface tension of the solution can be assumed to be due only to the monomeric surfactant present. To determine its concentration, we constructed the expected γ-log C plot of the compound in the absence of any premicellar aggregation from the linear plots of log C_{20} and log CMC, estimating the value of γ_{CMC} from the γ_{CMC} values of the lower homologs that show no deviation from these plots. This gives us two points on the γ-log C plot (the C_{20} point and the CMC), and because the plot is linear between these two points, we can draw the plot between these two points. Figures 1 and 2 show the plots for $(C_{16}N)_2(OH)_2$ and H_2O and $(C_{14}N)_2(OH)_2$ in 0.1 N NaBr, respectively, as expected in the absence of any premicellar aggregation, calculated in this fashion. The quantities for use in Equation 2 can then be evaluated from the experimental and calculated γ-log C plots (Fig. 2). Thus, for any experimental value of γ for $(C_{14}N)_2(OH)_2$ in 0.1 M NaBr (Fig. 2), we can determine the value of $[S]$ at that value of γ from the calculated γ-log C plot because only nonaggregated S causes the observed value of γ. The value of $[S_x]$ is then the actual molar concentration of $(C_{14}N)_2(OH)_2$ (on the experimental curve) at that γ value minus $[S]$ at that value of γ, divided by x. We now assume small integral values for x (= 2, 3, 4), substitute $[S]$ and $[S_x]$ values into Equation 2 for different γ values of $(C_{14}N)_2(OH)_2$, and calculate sets of K_{eq} values at particular values of x. K_{eq} values calculated in this fashion are listed in Table 2 for values of x = 2, 3, and 4. As the K_{eq} units for x = 2 are $(mol/L)^{-1}$, for x = 3 $(mol/L)^{-2}$, and for x = 4 $(mol/L)^{-3}$, to compare these values for constancy we have used $(K_{eq})^{1/2}$ and $(K_{eq})^{1/3}$ for the latter two x values, respectively. It is apparent that the values, compared in this manner, have about the same degree of constancy, indicating that a series of oligomers are formed.

TABLE 2
Equilibrium Constants of Premicellar Aggregation

		$(C_{14}N)_2(OH)_2$ in 0.1 M NaBr				
	γ	$x = 2$	$x = 3$		$x = 4$	
		K_{eq}	K_{eq}	$(K_{eq})^{1/2}$	K_{eq}	$(K_{eq})^{1/3}$
	45	$1.98 \times 10^{+7}$	$2.09 \times 10^{+14}$	$1.44 \times 10^{+7}$	$2.49 \times 10^{+21}$	$1.35 \times 10^{+7}$
	40	$1.25 \times 10^{+7}$	$8.33 \times 10^{+13}$	$9.14 \times 10^{+6}$	$6.25 \times 10^{+20}$	$8.55 \times 10^{+6}$
	35	$9.77 \times 10^{+6}$	$4.07 \times 10^{+13}$	$6.38 \times 10^{+6}$	$1.91 \times 10^{+20}$	$5.76 \times 10^{+6}$
	37	$9.82 \times 10^{+6}$	$4.68 \times 10^{+13}$	$6.84 \times 10^{+6}$	$2.51 \times 10^{+20}$	$6.31 \times 10^{+6}$
	43	$1.90 \times 10^{+7}$	$1.84 \times 10^{+14}$	$1.35 \times 10^{+7}$	$2.00 \times 10^{+20}$	$5.85 \times 10^{+6}$
Range		$(0.98–1.25) \times 10^7$	$(0.41–2.1) \times 10^{14}$	$(0.64–1.44) \times 10^7$	$(0.19–2.5) \times 10^{21}$	$(0.58–1.35) \times 10^7$
		$(C_{16}N)_2(OH)_2$ in H_2O				
	γ	$x = 2$	$x = 3$		$x = 4$	
		K_{eq}	K_{eq}	$(K_{eq})^{1/2}$	K_{eq}	$(K_{eq})^{1/3}$
	42	$7.00 \times 10^{+6}$	$1.67 \times 10^{+12}$	$1.29 \times 10^{+6}$	$6.25 \times 10^{+17}$	$8.55 \times 10^{+5}$
	44	$8.26 \times 10^{+6}$	$4.59 \times 10^{+12}$	$2.14 \times 10^{+6}$	$2.87 \times 10^{+18}$	$1.42 \times 10^{+6}$
	47	$9.78 \times 10^{+6}$	$8.25 \times 10^{+12}$	$2.87 \times 10^{+6}$	$7.84 \times 10^{+18}$	$1.99 \times 10^{+6}$
	43	$6.69 \times 10^{+6}$	$2.97 \times 10^{+12}$	$1.72 \times 10^{+6}$	$1.49 \times 10^{+18}$	$1.14 \times 10^{+6}$
	45	$9.70 \times 10^{+6}$	$6.53 \times 10^{+12}$	$2.56 \times 10^{+6}$	$4.95 \times 10^{+18}$	$1.70 \times 10^{+6}$
Range		$(7.00–9.78) \times 10^6$	$(1.67–8.23) \times 10^{13}$	$(1.29–2.87) \times 10^6$	$(0.63–7.8) \times 10^{18}$	$(0.86–1.99) \times 10^6$

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