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**MOLECULAR INTERACTIONS IN MIXTURES
CONTAINING SURFACTANTS WITH TWO HYDROPHILIC AND TWO
OR THREE HYDROPHOBIC GROUPS**

**by
LETIAN LIU**

**A dissertation submitted to the Graduate Faculty in Chemistry in
partial fulfillment of the requirements for the degree of Doctor of
Philosophy, The City University of New York**

1997

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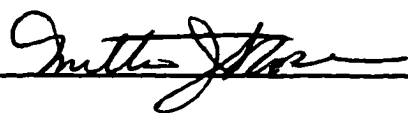
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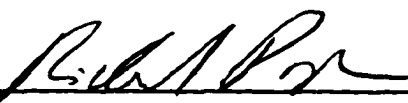
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ABSTRACT

Molecular Interactions in Mixtures Containing Surfactants with Two Hydrophilic and Two or Three Hydrophobic Groups

by Letian Liu

Advisor: Professor Milton J. Rosen

A series of novel cationic gemini surfactants, butane 2,3-diol- α , ω -bis(dimethylalkylammonium) bromide (alkyl chain length = 8,10,12,14,16,18), and two series of novel anionic gemini surfactants, 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dialkyl hexane (alkyl chain length = 6, 8, 10 12) and 2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dialkyldiphenyl methane (alkyl chain length =9, 12), were synthesized. Surface properties of these gemini surfactants were investigated by means of surface tension measurements in H₂O and in 0.1 M salt solution at 25 °C. The interactions of these geminis with conventional surfactants of different charge type were extensively studied.

It was found that these gemini surfactants had unusually higher surface activities, such as much lower C₂₀, cmc values and more closely packed surfactant molecules at the interface, compared to comparable conventional surfactants. However, in

contrast to conventional surfactants, the gemini surfactants all showed decreased surface activity at a certain critical chain length. It was proposed that formation of a small, soluble non-surface-active aggregates below the cmc accounts for the above observation. Quantitative calculation of the equilibrium constants for forming these small aggregates below the cmc for longer chain gemini surfactants above the critical chain length then demonstrated that the non-surface active small aggregates are primarily small oligomers of the gemini surfactant.

In a study of the interaction of the gemini surfactants with conventional surfactants of different charge type, it was found that for the geminis having the shorter alkyl chains, strong synergistic interaction occurred in the mixed binary surfactant solutions. However, no synergistic interactions were observed for gemini surfactants having alkyl chain lengths exceeding the critical chain length. The critical chain length for no synergistic interaction depends on the structure of the both gemini and conventional surfactants. The abnormal interaction is attributed to the formation of small, soluble, non-surface active, non-micellar aggregates. Calculations of equilibrium constants for the formation of these aggregates indicated that the two surfactants are present in a 1:1 molar ratio in the aggregate in most of cases.

DEDICATION

To my husband, Dr. Shaoxiang Lu; my daughter, Meilin Lu; my son, Jeffrey Lu who arrived during my study and my parents.

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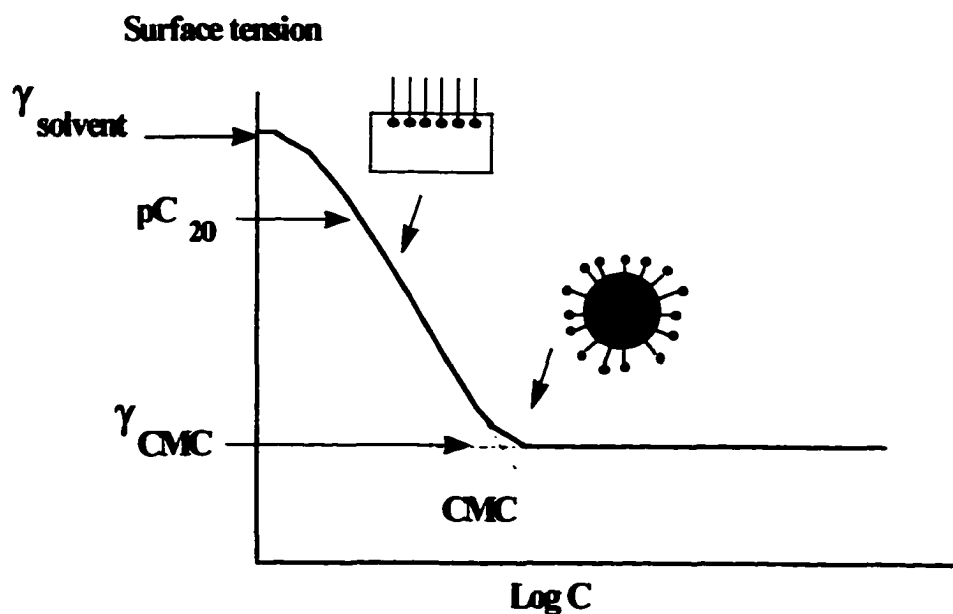
CHAPTER I INTRODUCTION

I-1. General Aspects of Surfactants

Conventional surfactants are molecules consisting of one hydrophilic and one hydrophobic tail groups in a single molecule. Surfactant molecules in aqueous media at very low concentration have a tendency to adsorb at interfaces^{1,2} which results in a marked decrease in surface tension, and subsequently to form micelles³⁻⁶ as the concentration of the surfactant increases. Both adsorption and micellization reduce the free energy of the system by removing hydrophobic groups from contact with the aqueous phase. These important characteristics of surfactant molecules give them a wide variety of applications ranging from home laundry detergents⁷⁻⁹ to high-tech ink printings¹⁰⁻¹². The general characteristic features of a surfactant in water can be described by a plot of the surface tension (γ) against the logarithm of surfactant molar concentration ($\log C$). A typical plot of γ — $\log C$ for a surfactant solution is illustrated in Scheme I-1. At low concentrations of surfactant in the solution phase, due to the adsorption of surfactant at the interface, surface tension is reduced (only monomeric surfactant molecules contribute to the surface tension reduction). The surface tension continues to decrease

as the concentration of the surfactant increases in the solution phase and the interface becomes gradually saturated with surfactant molecules, and finally surfactant molecules aggregate into clusters to form micelles. The concentration at which micelle formation is achieved is defined as the critical micelle concentration (cmc), as illustrated by the break point in Scheme I-1. The cmc value is a measure of the micellization ability of a surfactant. The smaller the cmc value is, the easier it is for a surfactant to form micelles in solution.

Scheme I-1. A typical surface tension (γ)-log C plot of a dilute surfactant solution



Other quantitative measures of surface properties of a surfactant solution are:

pC_{20} measures the efficiency of the adsorption of a surfactant (it is the negative logarithm of the concentration of surfactant in the bulk phase required to producing a 20 dyn/cm reduction in the surface or interfacial tension of the solvent)¹³ or $-\log C_{(-\Delta\gamma=20)} \equiv pC_{20}$.

Π_{cmc} : the maximum reduction of the surface tension of the solvent by a surfactant at its cmc (this is often the maximum reduction attainable).¹⁴ It is the difference between the surface tension of the solvent and the surface tension at cmc of the surfactant solution. It measures the effectiveness of a surfactant in reduction of surface tension.

Γ_{max} : is the surface excess concentration of a surfactant at surface saturation, it is the maximum value which adsorption can attain at surface saturation. It is a useful measure of the effectiveness of adsorption of the surfactant at the interface.

A_{min} : the minimum area per surfactant at the interface;⁴⁸ the smaller the A_{min} values, the more closely packed the surfactant molecule at the interface.

One of the most important properties of the surfactant in applications is solubilization,⁴⁸ which is defined as the spontaneous

dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized materials. Solubilization into aqueous media is of major practical importance in the formulation of products containing water-insoluble ingredients. It can replace the use of organic solvent or co-solvents. In detergency, solubilization is believed to be one of the major mechanisms involved in the removal of oily soil. Solubilization into nonaqueous media is of major importance in dry cleaning. The solubilization of materials in biological systems can describe the mechanism of the interaction of drugs and other pharmaceutical materials with lipid bilayer and membranes.

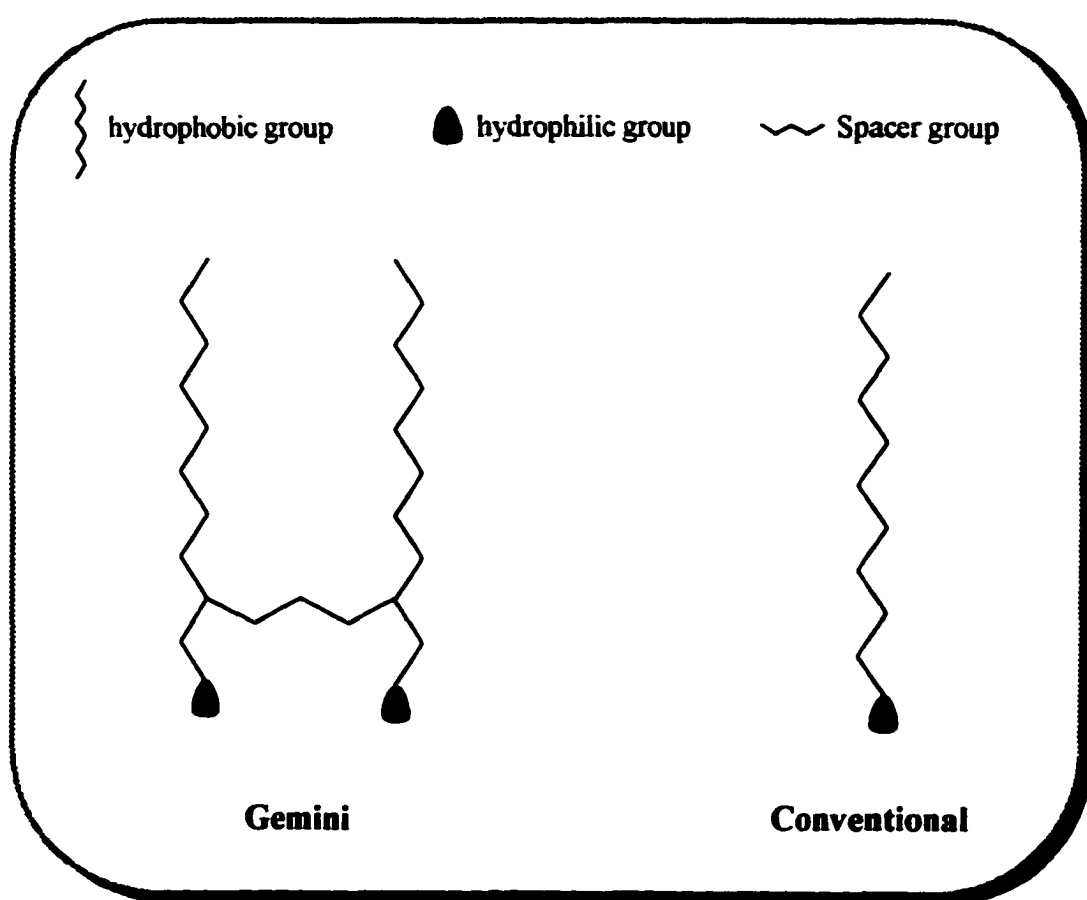
Solubilization happens only when the concentration of the surfactant solution is greater than its cmc value.

I-2. Gemini Surfactants

As early as 1974, a new class of surfactants with two hydrophobic chains and two hydrophilic head groups connected by a spacer was synthesized.¹⁵ These surfactants,¹⁶⁻²⁴ which were later termed gemini or dimeric surfactants,^{25-33,51} have unusual properties,

such as a very low critical micelle concentration and a high efficiency in reducing surface tension in comparison with the conventional single-chain surfactants (Scheme I-2).

Scheme I-2. Schematic comparison of molecular structure of Gemini and Conventional Surfactants

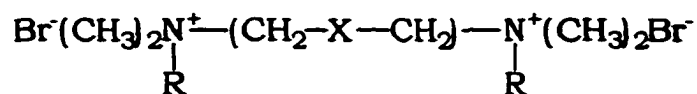


The greater surface activity of gemini surfactants can be important both economically and environmentally. Surfactants with much greater surface activity can be used at much lower concentrations in formulations and therefore greatly reduce the environmental impact of surfactants. Furthermore, at these lower concentrations less raw material is needed to manufacture the required amount of surfactant and fewer manufacturing by-products have to be treated for disposal.³⁴

I-2a. Cationic Gemini Surfactants

In an effort to find high antimicrobial activity compounds, Devinsky, etc.³⁵⁻³⁷ reported the synthesis of *N,N'*-bis(alkyldimethyl)-3-X-1,5-pentanediammonium dibromides (Scheme I-3) and found that these diquatery ammonium salts have very low cmc values in comparison with the analogous conventional monoquatery ammonium salts.

**Scheme I-3. *N,N'*-bis(alkyldimethyl)-3-X-1,5-
pentanediammonium dibromides**



R = C₆, C₈, C₁₀, C₁₂, C₁₄, C₁₆ and C₁₈

X = CH₂, NCH₃, O or S

Recently, Zana et al.^{38,39} studied the effect of the alkyl side chain length and the spacer chain length on the cmc and micelle ionization degree of the surfactants [RN⁺(CH₃)₂-(CH₂)_mN⁺(CH₃)₂R•2Br⁻] in aqueous solution. The changes of cmc and micelle ionization with alkyl side chain length were similar to those found for monoquaternary ammonium salt surfactants, namely, cmc values decreased with an increase in alkyl chain length and the degree of micelle ionization increased with an increase of alkyl chain length. However, the changes of cmc values with spacer chain length were quite complicated. A small maximum of cmc at about 5 carbon units was found along with a continued decrease in cmc values with increasing spacer chain length. Further studies of the self-association behavior of the diquaternary ammonium salt surfactants by means of time-resolved fluorescence

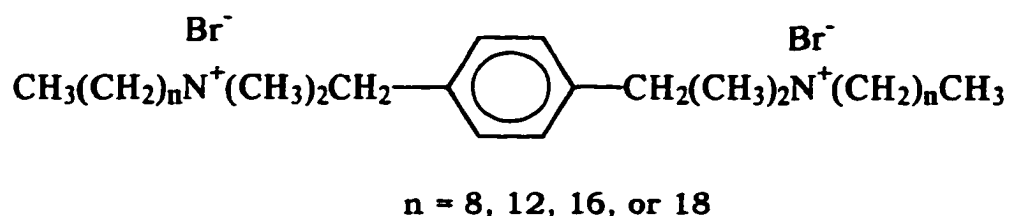
quenching and cryogenic transmission electron microscopy revealed that the surfactants with short spacers had a much stronger tendency for micellar growth and the formation of aggregates of lower curvature compared to analogous monoquatarnary ammonium salt surfactant.

Speculation on the effect of the spacers on the surface activities of diquatarnary ammonium salts with respect to monoquatarnary ammonium salts was offered. In a mixture of water and single-chain surfactants, the system tries to minimize its free energy by forming micelles in which the hydrophobic chains are brought together to minimize the contact with water. The hydrophilic head groups are kept near the water and away from each other as a result of electrostatic repulsion. In gemini surfactants, the two head groups are chemically linked by a hydrophobic spacer; as a consequence, a compromise has to be found for the location of the spacer depending on its length and flexibility and on the degree of repulsion between the two similarly charged head groups. For example, when the spacer length is shorter than the equilibrium distance between two-charged head groups, the spacer will be fully extended to minimize the repulsion between the head groups. This positioning leads to a large unfavorable contact of the spacer with water. In cases where the spacer is longer than the

equilibrium distance between two charged head groups, the spacer will not be fully extended and will try to minimize its contact with the water. This reaction will, of course, depend to a large extent on the flexibility of the spacer. Therefore, characteristics such as the spacer's characteristics (hydrophobicity or hydrophilicity), length and flexibility are essential in determining the aggregation and surface properties.

In order to eliminate the possible chain/chain association within a single molecule of a gemini surfactant (possible with a flexible or short spacer), Menger and Littau synthesized a series of diammonium bromide gemini surfactants^{25,26} (Scheme I-4). They reported an anomalous trend in cmc values of these geminis with respect to the alkyl chain length (measured at 50°C due to the limited solubility of these geminis in water). The gemini with 18 carbon alkyl chains has a cmc value of 3.7×10^{-4} M significantly higher than that of the gemini with 16 carbon alkyl chains (6.7×10^{-5} M), as measured by surface tension measurements. This anomalous behavior was attributed to the unique structure of these geminis (discussed later in the anionic gemini surfactant section below). A monolayer study by film-balance methods indicated that this gemini with 18 carbon units lies absolutely flat upon the water surface.

Scheme I-4. Cationic Gemini Surfactants with a rigid spacer reported by Menger and Littau



I-2b. Anionic Gemini Surfactants

Okahara and his colleagues reported^{1821,40-44} the synthesis and unusual surface activities of a series of anionic gemini surfactants. The structure of these anionic sulfate and sulfonate gemini surfactants are shown in Scheme I-5. The surface properties of these gemini surfactants are listed in Table I-1 along with closely related conventional analogous surfactants. For the convenience of direct comparison, 12 carbon atoms were used in comparison because carbon atoms between two hydrophilic groups are equivalent to half a carbon atom in a straight alkyl chain in surface tension reduction and micellization effects. As seen from Table I-1, these anionic gemini surfactants are about three orders of magnitude more efficient at reducing the surface tension (C_{20}) and somewhat more than two orders

of magnitude more efficient at forming micelles (cmc) than are conventional ionic surfactants.

Scheme I-5. Anionic sulfate and sulfonate gemini surfactants reported by Okahara, et al.

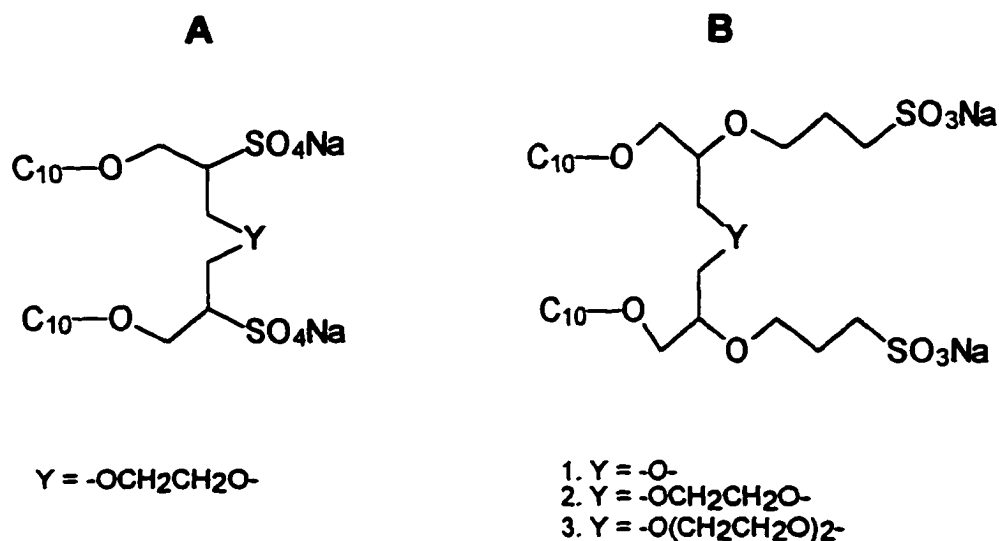


Table I-1. Comparison of the properties of gemini and closely related conventional surfactants

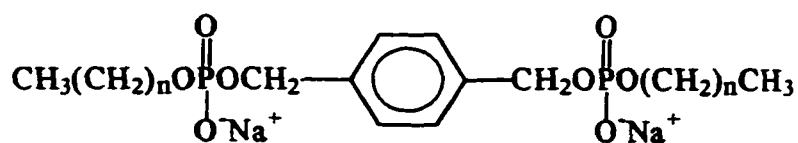
Type	Y	cmc(mM)	C ₂₀ (mM)	cmc/C ₂₀
A	-OCH ₂ CH ₂ O-	0.013	0.0010	13.0
C ₁₂ H ₂₅ SO ₄ Na	-----	8.2	3.1	2.6
B	-O-	0.033	0.008	4.1
B	-OCH ₂ CH ₂ O-	0.032	0.0065	4.9
B	-O(CH ₂ CH ₂ O) ₂ -	0.060	0.0010	6.0
C ₁₂ H ₂₅ SO ₃ Na	-----	9.8	4.4	2.2

The values of cmc/C_{20} ratios of these gemini surfactants are greater than the values generally observed for conventional surfactants, which have a typical cmc/C_{20} value of about 3 in water. The larger the cmc/C_{20} ratio is, the greater the tendency of the surfactant to adsorb at the surface (relative to its tendency to form micelles).⁴⁸ The larger cmc/C_{20} ratio probably reflects the difficulty of packing two hydrophobic groups per molecule into the micelle.²⁶ Gemini surfactants therefore are more likely than conventional surfactants to adsorb at the aqueous solution surface rather than to form micelles. The cmc/C_{20} ratio also measures how far the surface tension of water can be reduced by the presence of the surfactant.⁴⁸ The larger the cmc/C_{20} ratio, the larger the Π_{cmc} values (the reduction of the surface tension of the solvent by surfactant molecule).

Menger and Littau also reported some phosphate-containing anionic gemini surfactants with rigid spacers²⁶ (Scheme I-6). Beside their very low cmc values and high efficiency in reducing surface tension, they found that the geminis with longer alkyl chains had relatively higher cmc values as determined from surface tension measurements (as mentioned in previous section). To rationalize this non-classical behavior of the geminis, a spectroscopy study using a dye, pinacyanol chloride, was employed. The experimental results

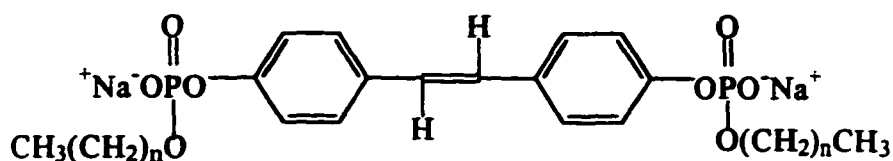
showed that the dye gave a color change at a value lower than the cmc value obtained by surface tension method and the spectral features of the geminis with dye generated characteristic micelle-like spectra. This suggested that geminis with longer chains might form some pre-aggregates (pre or sub-micelle) which was not detectable by conventional surface tension methods due to very low concentrations.

Scheme I-6. Anionic gemini surfactants with rigid spacers
reported by Menger and Littau



$n = 8, 12, \text{ or } 16$

A

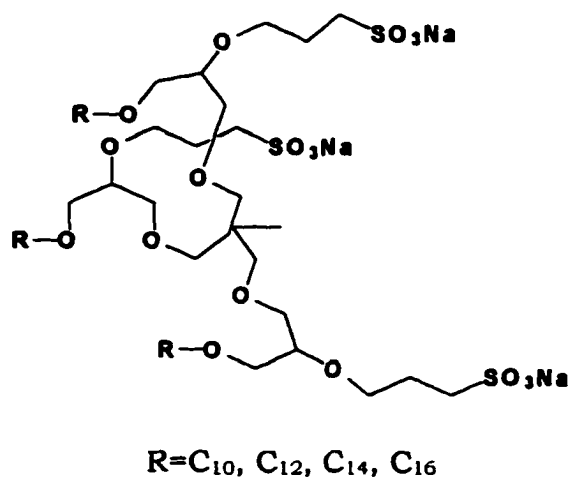


$n = 12, 16 \text{ or } 20$

B

Similar results were also found for triple-chain trisulfonates⁴⁵ (Scheme I-7) by Masuyama, et al. The cmc values increased with an increase of alkyl chain length in the order of $C_{10} < C_{12} < C_{14}$. Ultraviolet (UV) spectra measurements of the aqueous solution of this series of compounds at various concentration (with 5×10^{-7} mol/dm³ of pinacyanol chloride as a dye probe) suggested that these compounds could form "pre-micelles" (molecular aggregates at lower concentrations than indicated by their cmc values as measured by the surface tension measurement). The cmc value increase for the longer chain gemini surfactants for both anionic and cationic (mentioned in above section) geminis are all considered evidence for the "pre-micellar" molecular aggregates at lower concentrations than the cmc values.

Scheme I-7. Triple-chain trisulfonates reported by Masuyama, et al.



Worthy of mention is that these anionic gemini surfactants have relatively lower Krafft points (the temperature at which the solubility equals the cmc value) than analogous conventional surfactants and therefore relatively high solubility for these gemini surfactants is expected. The high solubility of surfactants means greater convenience when geminis are used in product formulations.

Molecular dynamics simulations by Karaborni etc.¹⁶ indicated that gemini surfactants form structures and have dynamic properties that are drastically different from those of single-chain surfactants. At the same weight fraction (16 wt.%), single-chain surfactants form spherical micelles whereas gemini surfactants form thread-like micelles. Simulations at different surfactant concentrations revealed the formation of different structures for the gemini surfactants. Although the simulations were performed at relatively high concentrations, they still provided with some useful information concerning the morphologies and dynamics of aggregate formation by gemini surfactants.

1-3. Mixtures of Surfactants Containing a Gemini Surfactant

In most practical applications, mixtures of surfactants, rather than individual surfactants, are used^{46,47}. When different types of surfactants

are purposely mixed and give properties greater than would have been expected on the basis of the sum of their individual activities, this is called synergism.⁴⁸ Although the existence of synergistic relations between certain types of conventional surfactants has been known and utilized for many years, the investigation of synergism in quantitative terms is a very recent development based upon a simple, convenient method for measuring molecular interactions between surfactants (see Chapter II-3). Only a few papers, by Rosen et al^{49,50}, dealing with synergism in mixtures containing anionic gemini surfactants, have been published.

Extensive studies of molecular interactions in mixed surfactant solutions have been carried out by Rosen's group for conventional surfactants and, most recently, for interactions of gemini-type disulfonates with conventional cationic surfactants.^{50,51} They found that the interaction of gemini type surfactants has much stronger synergistic interactions with conventional surfactants (compared to the mono-sulfonate conventional surfactants) in the water/air interface (The strength of the attractive interaction in mixed monolayers increases in the order: monoalkyl monosulfonate < monoalkyl disulfonate < dialkyl disulfonate). This is true since molecular interactions between surfactants of different charge type are generally dominated by the electrostatic forces between their head groups,⁵²

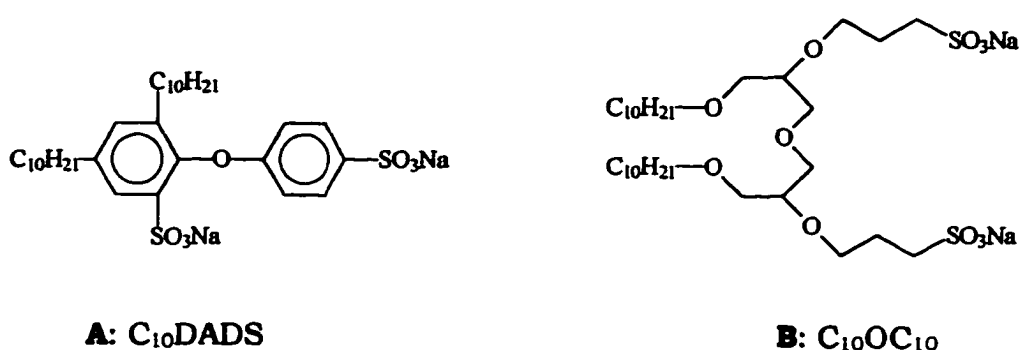
therefore, such interaction would be stronger for surfactants having two ionic groups. Somewhat weaker interactions occur in the mixed micelle (This is attributed to the difficulty of incorporating a surfactant with multiple hydrophobic groups into a micelle.^{50, 51}). Because of the stronger interaction in the mixed monolayer at the water/air interface and the weaker interaction in the mixed micelle formation, the gemini-type dialkyl disulfonate structure has a greater probability of exhibiting synergism in both surface tension reduction efficiency and effectiveness than the corresponding monoalkyl monosulfonate or monoalkyl disulfonate, but a lower probability of showing synergism in mixed micelle formation.

The interactions of some anionic gemini surfactants having different spacer chain lengths (scheme I-8) with conventional surfactants have also been studied.⁵¹

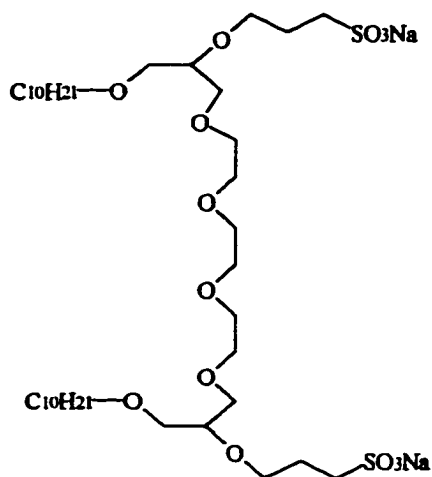
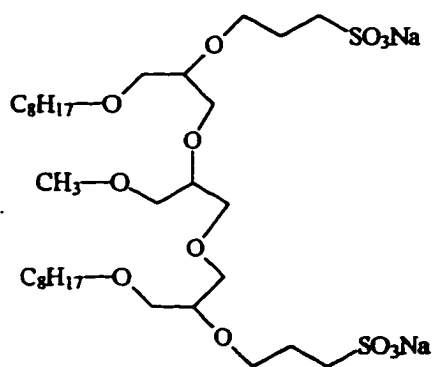
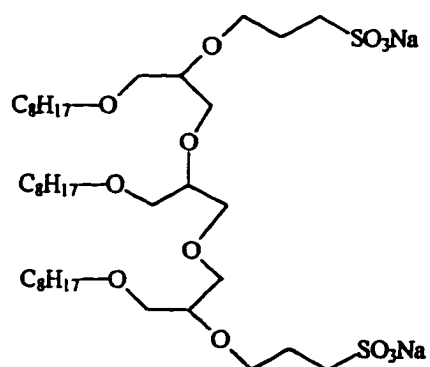
It was found that the strength of interaction of the gemini surfactants ($C_{10}DADS$, $C_{10}OC_{10}$, $C_8C_1C_8$, $C_{10}E_3C_{10}$, $C_8C_8C_8$) with the zwitterionic surfactant (N,N -dimethyl-1-tetradecanamine oxide) decreases with increase in the minimum area per sulfonate group of the gemini surfactant at the air/water interface. The interaction with the zwitterionic surfactant or the polyoxyethylenated non-ionic

surfactant ($C_{12}H_{25}(OC_2H_4)_7OH$ or $C_{12}H_{25}(OC_2H_4)_8OH$) is also weakened by the presence of multiple ether linkages in the hydrophilic group of the gemini surfactant. The latter surfactants with these linkages show a smaller increase in the strength of interaction, compared with the gemini surfactant upon reduction of the pH of the solution. They also show an increase with this change in their area per molecule at the air/water interface and an increase in their interactions with an alkanesulfonate surfactant ($C_{12}H_{25}SO_3Na$). There is no increase in the strength of interaction when neither surfactant has multiple ether linkages in the molecule. It has been suggested that the relative ease of protonation of the multiple rather oxygen atoms in the doubly charged anionic gemini molecule accounts for these observations.

Scheme I-8. Gemini surfactants used in the study of interactions with conventional surfactants



Scheme I-8 continued

**C:** $\text{C}_{10}\text{E}_3\text{C}_{10}$ **D:** $\text{C}_8\text{C}_1\text{C}_8$ **E:** $\text{C}_8\text{C}_8\text{C}_8$

Chapter II THEORY

II-1. Surface Concentrations at the Interface Γ_1

For surface-active solutes, the surface excess concentration, Γ_1 , can be considered to be equal to the actual surface concentration without significant error. The concentration of surfactant at the interface may therefore be calculated from surface or interfacial tension data by use of the appropriate Gibbs equation⁵³. Thus, for a dilute solution of a nonionic surfactant, or a 1:1 ionic conventional surfactant in the presence of a swamping amount of electrolyte containing a common non-surfactant ion, surface concentration can be expressed as:⁴⁸

$$\Gamma_1 = -\frac{1}{2.303RT} \left(\frac{\partial \gamma}{\partial \log a_1} \right)_T \quad [\text{II-1}]$$

where R is the gas constant; T is the absolute temperature; γ is the surface tension and a_1 is the surfactant molar activity. When the solution is very dilute, a_1 can be replaced by C_1 , the surfactant molar concentration. Γ_1 can be obtained by plotting γ against $\log C_1$, or $(\log C_1 + \log f_1)$ when the activity coefficient f_1 is taken into account.

For solutions of 1:1 ionic surfactant in the absence of any other solutes, in similar fashion,

$$\Gamma_1 = -\frac{1}{4.606RT} \left(\frac{\partial \gamma}{\partial \log C_1} \right)_T \quad [\text{II-2}]$$

II-2. Area Per Molecule of Surfactant at the Interface

The area per molecule at the interface gives us information regarding the packing and the orientation of the adsorbed surfactant molecule, when compared with sizes as obtained by use of molecular models. From the surface excess concentration, the area per molecule at the interface a_1^{s48} , in square angstroms, is calculated from the following relation

$$a_1' = \frac{10^{16}}{N\Gamma} \quad [\text{II-3}]$$

where N is Avogadro's constant and Γ_2 is the surface concentration of the surfactant in moles/cm².

II-3. Mixtures of Surfactants

The interfacial and colloid properties of a solution of two or more surfactants can be quite different from those of a solution of the individual components. Therefore, studies of surfactant interactions have great significance in both theory and practice. A large number of investigations have been directed towards understanding these

interactions in mixtures of surfactants.⁵⁴⁻⁶² When a solution of the mixed surfactants shows greater surface activity (e.g., lower surface tension) than that attainable with any of the individual surfactants of the mixture at the same concentration, then the mixture is said to exhibit synergism. On the other hand, when a solution of the mixed surfactants shows lower surface activity than the individual ones, then the mixture is said to show antagonism. For conventional surfactants, synergism interactions may be exhibited if the two surfactants attract each other sufficiently, either through mutual electrostatic attraction of opposite charged hydrophilic groups or through van der Waals attraction of their hydrophobic groups.

In the early 1960s the ideal mixing model was developed and widely used for ideal surfactant systems.⁶³⁻⁶⁹ In 1979, Rubingh⁷⁰ developed a method to treat mixed micelle formation in nonideal mixtures based on a regular solution model. A surfactant interaction parameter for mixed micelle formation (β^M) in binary mixtures of surfactants was calculated, based upon this treatment. This method has been extended and applied to a wide range of investigations.⁷¹⁻⁷⁶

Later, Rosen et al⁷⁷⁻⁸³ extended the nonideal treatment to mixed monolayer formation and to investigate the molecular interactions and

synergism in binary mixtures of nonionic-nonionic, nonionic-anionic, anionic-anionic, zwitterionic-nonionic, zwitterionic-anionic and cationic-anionic surfactants at various interfaces and in micelles.⁸⁴⁻⁹⁶

The nature and the strength of the interactions between the two surfactants can be determined by calculating ⁴⁸ the values of their β parameters (which are a measure of their interactions), from the surface tension (γ)-concentration (C) plots of aqueous solutions of the individual surfactants and their mixtures with other individual surfactants. The interaction parameter for mixed monolayer formation at the aqueous solution/air interface, β^σ , is calculated by using Equations.[II-4] and [II-5]

$$\frac{X_1^2 \ln(\alpha_1 C_{12} / X_1 C_1^0)}{(1 - X_1)^2 \ln[(1 - \alpha_1) C_{12} (1 - X_1) C_2^0]} = 1 \quad \text{[II-4]}$$

$$\beta^\sigma = \frac{\ln(\alpha_1 C_{12} / X_1 C_1^0)}{(1 - X_1)^2} \quad \text{[II-5]}$$

where X_1 is the mole fraction of surfactant 1 in the total mixed monolayer (on a surfactant-only basis); C_1^0 , C_2^0 , and C_{12} are the molar concentrations in the solution phase of surfactant 1, surfactant 2, and their mixture at the mole ratio α_1 (on a surfactant-only basis), required to produce a given γ value. Equation [II-4] is solved numerically for X_1 , which is then substituted into Equations. [II-5] to calculate β^σ .

The value of β^m , the interaction parameter for mixed micelle formation in an aqueous medium, is calculated from analogous Equations [II-6] and [II-7].

$$\frac{(X_1^m)^2 \ln(\alpha_1 C_{12}^m / X_1^m C_1^m)}{(1 - X_1^m)^2 \ln[(1 - \alpha_1) C_{12}^m (1 - X_1^m) C_2^m]} = 1 \quad [\text{II-6}]$$

$$\beta^m = \frac{\ln(\alpha_1 C_{12}^m / X_1^m C_1^m)}{(1 - X_1^m)^2}, \quad [\text{II-7}]$$

where X_1^m is the mole fraction of surfactant 1 in the total surfactant in the mixed micelle and C_1^m , C_2^m , and C_{12}^m are the critical micelle concentrations (cmc) for surfactant 1, surfactant 2, and their mixture at mole fraction α_1 , respectively.

For strong interactions (when $|\beta^s|$ is ≥ 6), β^s is calculated⁹ from equations [II-8] and [II-9], related to equations [II-4] and [II-5], but which take into consideration the change in the area (A) per molecule at the interface upon mixing:

$$\frac{X_1^2}{(1 - X_1)^2} \times \frac{\ln \frac{C_{12} \alpha_1}{C_1^0 X_1} - \frac{\gamma A_1^0}{RT} \left[1 - \frac{A_{AF}}{X_1 A_1^0 + (1 - X_1) A_2^0} \right]}{\ln \frac{C_{12} (1 - \alpha_1)}{C_2^0 (1 - X_1)} - \frac{\gamma A_2^0}{RT} \left[1 - \frac{A_{AF}}{X_1 A_1^0 + (1 - X_1) A_2^0} \right]} = 1 \quad [\text{II-8}]$$

$$\beta^\sigma = \frac{\ln \frac{C_{12}a_1}{C_1^\circ X_1} - \frac{A_1^\circ}{RT} \left[1 - \frac{A_{AV}}{X_1 A_1^\circ + (1 - X_1) A_2^\circ} \right]}{(1 - X_1)^2} \quad [\text{II-9}]$$

An attractive interaction yields a negative β value; a repulsive interaction generates a positive value. The larger the negative β value, the stronger the attractive interaction between the two surfactants.

II-4. Synergism

The existence of synergism in mixtures containing two surfactants has been shown to depend not only on the strength of the interaction between them (measured by the value of the β parameter), but also on the relevant properties of the individual surfactant components in the mixture.⁹⁷ Thus, the conditions for synergism in surface tension reduction efficiency (when the total concentration of mixed surfactant required to reduce the surface tension of the solvent to a given value is less than that of either surfactant) are: 1), β^σ is negative; 2), $|\beta^\sigma| > |\ln(C_1^\circ/C_2^\circ)|$, where C_1° , C_2° are the molar concentrations of surfactants 1 and 2, respectively, required to achieve that same surface tension value.

The degree of synergism in surface tension reduction efficiency that is possible in a mixture is measured by the maximum decrease in

the molar concentration of (mixed) a surfactant needed to produce a given surface tension value relative to that required of the more efficient of the two individual surfactants by itself; i.e., $(C_1^0 - C_{12,\min})/C_1^0$ or $1-(C_{12,\min}/C_1^0)$, where $C_{12,\min}$ is the minimum concentration of mixed surfactants that can produce this surface tension and C_1^0 is the concentration required of the more efficient surfactant. The ratio, $C_{12,\min}/C_1^0$ is given by the relationship:^{101,102}

$$C_{12,\min} / C_1^0 = \exp \left\{ \frac{[\beta^\sigma - \ln(C_1^0 / C_2^0)]^2}{4\beta^\sigma} \right\} \quad [\text{II-10}]$$

Synergism in mixed micelle formation exists when the cmc of the mixture is less than that of either surfactant in the mixture. The conditions for this to exist in a mixture of two surfactants^{48,97} are: 1), β^m is negative; 2), $|\beta^m| > |\ln(C_1^m/C_2^m)|$, where C_1^m , C_2^m are the critical micellar concentrations (cmc) of surfactants 1 and 2, respectively. The degree of synergism possible in mixed micelle formation in a mixture is measured by the maximum decrease in the cmc of the two individual surfactants comprising the mixture; i.e., $(C_1^m - C_{12,\min}^m)/C_1^m$ or $1-(C_{12,\min}^m/C_1^m)$, where $C_{12,\min}^m$ is the lowest possible cmc of the mixed surfactant system and C_1^m is the lower cmc of the two surfactants constituting the mixture. The ratio, $C_{12,\min}/C_1^0$, is given by the relationship:

$$C_{12,\min}^m / C_1^m = \exp \left\{ \frac{[\beta^m - \ln(C_1^m / C_2^m)]^2}{4\beta^m} \right\} \quad [\text{II-11}]$$

The greater the value of $1 - (C_{12,\min}^m / C_1^m)$ (maximum=1), the greater the degree of synergism.

Synergism in surface tension reduction effectiveness (when the surface tension of the mixture at its cmc is lower than that of either of the individual surfactants at their respective cmc's) depends on the values of both β^σ and β^m , in addition to the C_1^σ , C_2^σ , C_1^m and C_2^m values of the two surfactants.^{48,97} The conditions for this type of synergism to exist are :1), $\beta^\sigma - \beta^m$ must be negative; 2). $|\beta^\sigma - \beta^m| > |\ln(C_1^\sigma C_2^m / C_2^\sigma C_1^m)|$.

II-5. Gemini Surfactant Solutions

The theory we described in the preceding sections can be applied to gemini surfactant solutions. The pC_{20} values and cmc values are obtained by the same method as in the case of conventional surfactants. But when we apply the Gibbs' ⁵³ equation to the surfactant solution, we made the following modifications:

For gemini surfactants, which are 1:2 electrolytes of the type, $A^{2+}2B^-$, as the only solute

$$d\gamma = -3RT\Gamma d\ln C_1$$

$$=-6.909RT\Gamma d\log C_1 \quad [\text{II-12}]$$

without significant error.

For dilute solutions of a completely dissociated surface-active 1:1 electrolyte in the presence of a swamping, constant amount of electrolyte containing a common nonsurfactant counterion,

$$\begin{aligned} d\gamma &= -RT\Gamma_1 d\ln C_1 \\ &= -2.303RT\Gamma_1 d\log C_1 \end{aligned} \quad [\text{II-13}]$$

The above equation is also suitable for dilute solutions of a completely dissociated ionic gemini surfactant of the 1:2- or even 1:3- electrolyte type in the presence of a swamping, constant amount of electrolyte containing a common nonsurfactant counterion.

For mixed two-surfactant systems, in the presence of a swamping, constant amount of electrolyte containing a common nonsurfactant counterion,

$$d\gamma = -RT\Gamma_1 d\ln C_1 - RT\Gamma_2 d\ln C_2 = -RT(\Gamma_1 d\ln C_1 + \Gamma_2 d\ln C_2) \quad [\text{II-14}]$$

Chapter III OBJECTIVE OF RESEARCH PROJECT

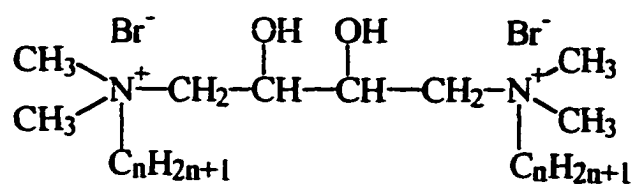
Since gemini surfactants have dramatically improved surface and micellization properties compared to analogous conventional surfactants, gemini surfactants have evoked considerable research interest since their unusual properties were first recognized a few years ago. However, only a few papers dealing with a limited number of novel gemini surfactants have been published, and considerable information on the structure - property relationships of gemini surfactants is still lacking.

My research project was to design and synthesize a variety of novel cationic and anionic gemini surfactants, study the surface properties, identify structure - property relationships, and most importantly, the interactions and synergism of these gemini surfactants with conventional surfactants.

The novel gemini surfactants studied in this dissertation are listed below:

1. **Bisquaternary ammonium bromide cationic gemini surfactants:**

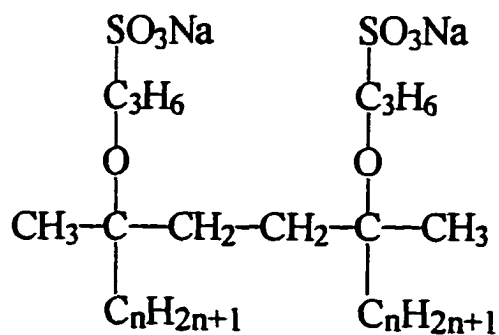
Butanediol- α - ω -bis(dimethylalkylammonium bromide)



$n = 8, 10, 12, 14, 16 \text{ and } 18$

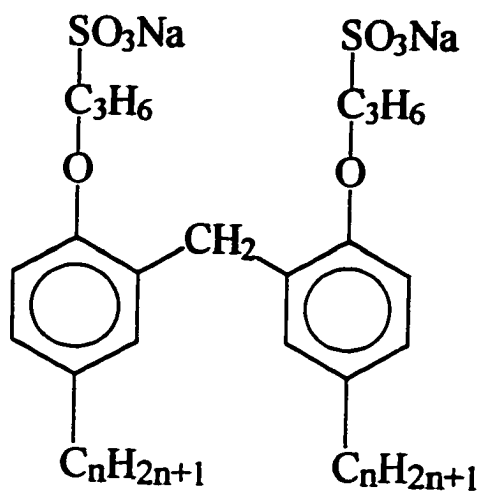
2. Anionic sulfonate gemini surfactants:

2a. 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dialkyl hexane



$n = 6, 8, 10 \text{ and } 12$

2b. 2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dialkyldiphenyl methane



$n = 9$ and 12 (branched chain)

CHAPTER IV EXPERIMENTAL

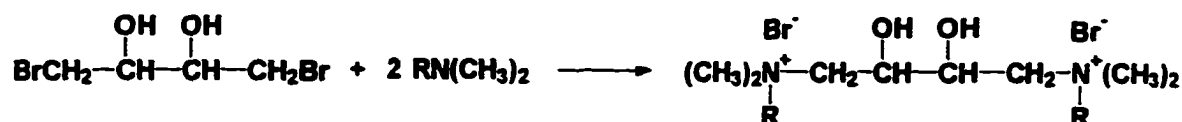
IV-1. Synthesis of A Series of Diquaternary Ammonium Bromide Cationic Gemini Surfactants



Symbol $(C_nN)_2(OH)_2$, where $n = 8, 10, 12, 14, 16$ and 18

The synthesis of 2,3-butanediol- α - ω -di(dimethylalkylammonium bromide) was carried out by refluxing the mixture containing appropriate amounts of 1,4-dibromo-2,3-butanediol and N,N-dimethylalkylammonium in n-propanol for over 48 hours (Scheme IV-1). The obtained crude product was then recrystallized from THF.

Scheme IV-1. Synthesis of 2,3-butanediol- α - ω -di(dimethylalkyl-
ammonium bromide)



1. $R = C_8H_{17}$
2. $R = C_{10}H_{21}$
3. $R = C_{12}H_{25}$
4. $R = C_{14}H_{29}$
5. $R = C_{16}H_{33}$
6. $R = C_{18}H_{37}$

Materials: 1,4-dibromo-2,3-butanediol (95%) was purchased from Aldrich Chemical Co.. N,N-Dimethyloctylamine (99% purity),

dimethyldecylamine (99% purity), N,N-dimethyldodecylamine (99% purity), N,N-dimethyltetradecylamine (99% purity), N,N-dimethylhexadecylamine (98% purity) and N,N-dimethyloctadecylamine (96% purity) were courtesy of Albemarle Chemical Co.. All chemicals were used as received.

Synthesis of 2,3-butanediol- α - ω -bis(dimethyloctylammonium bromide) [symbol: (C₈N)₂(OH)₂]: To a 250 ml round-bottom flask equipped with a condenser, 0.01 mol (2.479 g) of 1,4-dibromo-2,3-butanediol, 0.024 mol (3.768 g) of N,N-dimethyloctylamine and 75 ml of n-propanol were charged. The reaction mixture was heated to reflux at about 95°C for 48 hours. The completion of reaction was monitored by titration of the reaction mixture with a standard HCl solution. After reaction was finished, n-propanol and excess amount dimethyloctylamine were removed under reduced pressure. The residue was re-crystallized from 60 ml THF. The recrystallization processes were repeated three more times. The obtained final white solid was dried under vacuum in a desiccator to constant weight. Yield: 52%. ¹HNMR (CDCl₃) results are listed in table IV-1.

Synthesis of 2,3-butanediol- α - ω -bis(dimethyldecylammonium bromide)[symbol: (C₁₀N)₂(OH)₂]: By a similar procedure, the analogous bisdecyl derivative was prepared in 62% yield. ¹HNMR

(CDCl₃) results are listed in table IV-1. Elemental analysis: monohydrate: theory: C, 52.82; H, 10.13; N, 4.40. found: C, 53.15; H, 9.81; N, 4.29.

Synthesis of 2,3-butanediol- α - ω -bis(dimethyldodecylammonium bromide) [symbol: (C₁₂N)₂(OH)₂]: By a similar procedure, the analogous bisdodecyl derivative was prepared in 80% yield. ¹HNMR (CDCl₃) results are listed in table IV-1. Elemental analysis: monohydrate: theory: C, 55.48; H, 10.48; N, 4.05. found: C, 55.86; H, 10.34; N, 3.98.

Synthesize of 2,3-butanediol- α - ω -bis(dimethyltetradecylammonium bromide)[symbol: (C₁₄N)₂(OH)₂]:

By a similar procedure, the analogous bistetradecyl derivative was prepared in 90% yield¹HNMR (CDCl₃) results are listed in table IV-1. Elemental analysis: monohydrate: theory: C, 57.74; H, 10.76; N, 3.74. found: C, 58.06; H, 10.77; N, 3.68.

Synthesis of 2,3-butanediol- α - ω -bis(dimethylhexadecylammonium bromide) [symbol: (C₁₆N)₂(OH)₂]: By a similar procedure, the analogous bishexadecyl derivative was prepared in 92% yield. ¹HNMR (CDCl₃) results are listed in table IV-1.

Synthesis of 2,3-butanediol- α - ω -bis(dimethyloctadecylammonium bromide) [symbol: (C₁₈N)₂(OH)₂]: By a similar procedure, the

analogous bisoctadecyl derivative was prepared in 96% yield. ^1H NMR (CDCl_3) results are listed in table IV-1.

The representative ^1H NMR spectra of the synthesized 2,3-butanediol- α - ω -di(dimethylalkylammonium bromide) with alkyl chain length of 10 is shown in Figure IV -1.

Elemental analysis of carbon, hydrogen and nitrogen confirmed that the synthesized surfactants have a purity > 99 %.

The results are summarized in Table IV-1.

Table IV-1. Summary of the synthesis of 2,3-butanediol- α - ω -di(dimethylalkylammonium bromide)

Compound	Yield(%)	^1H NMR(CDCl_3)
$(\text{C}_8\text{N})_2(\text{OH})_2$	52	4.8~4.5 (2H, m), 4.0~3.7 (2H, m), 3.7~3.0 (12H, s), 2.1~1.6 (4H, m), 1.5~1.0 (28H, s) and 1.0~0.7 (6H, m).
$(\text{C}_{10}\text{N})_2(\text{OH})_2$	62	4.8~4.5 (2H, m), 4.0~3.7 (2H, m), 3.7~3.0 (12H, s), 2.1~1.6 (4H, m), 1.5~1.0 (36H, s) and 1.0~0.7 (6H, m). The relative peak area (mm) is 2:2:12:4.5:31.5:8 (H is in the order listed above). Total area = 60 mm
$(\text{C}_{12}\text{N})_2(\text{OH})_2$	80	4.8~4.5 (2H, m), 4.0~3.7 (2H, m), 3.7~3.0 (12H, s), 2.1~1.6 (4H, m), 1.5~1.0 (44H, s) and 1.0~0.7 (6H, m).
$(\text{C}_{14}\text{N})_2(\text{OH})_2$	90	4.8~4.5 (2H, m), 4.0~3.7 (2H, m), 3.7~3.0 (12H, s), 2.1~1.6 (4H, m), 1.5~1.0 (52H, s) and 1.0~0.7 (6H, m).

Table IV-1 continued

$(C_{16}N)_2(OH)_2$	92	4.8~4.5 (2H, m), 4.0~3.7 (2H, m), 3.7~3.0 (12H, s), 2.1~1.6 (4H, m), 1.5~1.0 (60H, s) and 1.0~0.7 (6H, m).
$(C_{18}N)_2(OH)_2$	96	4.8~4.5 (2H, m), 4.0~3.7 (2H, m), 3.7~3.0 (12H, s), 2.1~1.6 (4H, m), 1.5~1.0 (68H, s) and 1.0~0.7 (6H, m).



Figure IV-1. ¹H NMR spectrum of 2,3-butanediol- α - ω -di(dimethyldecylammonium bromide)) in

CDCl₃. The relative peak area is 1:1:6:2:18:3 (H is in the order listed above).

IV-1-1. Determination of Cationic Gemini Surfactant Concentration By Two Phase Titration

The surface tension-log C plots of the C₈ C₁₀ C₁₂ surfactant homologs in 0.1 M NaBr solution were measured for the raw compounds. The results are listed in Table IV-2.

Table IV -2. Surface tension and CMC values of C₈, C₁₀ and C₁₂ in 0.1 M NaBr solution*

	(C ₈ N) ₂ (OH) ₂	(C ₁₀ N) ₂ (OH) ₂	(C ₁₂ N) ₂ (OH) ₂
CMC*	2.0×10 ⁻³	3.5×10 ⁻⁴	5.5×10 ⁻⁶
γ _{cmc} (mN/m)	29.4	33.8	31.7

* at 25 °C.

Upon examining the values for the CMC and γ_{cmc}, we found that the CMC and γ_{cmc} of C₈ were too small compared to those of C₁₀ and C₁₂. Since the reactant N,N-dimethyloctylamine used for the synthesis of C₈ may contain some N,N-dimethylalkylamine with chain length greater than 8, it is possible that C₈ may contain some longer chain segments (C₁₀ or C₁₂) which are more interfacially active than C₈. It is well known that a surfactant with a longer chain length has greater surface activity than that with a shorter one. Even a trace amount of a

longer chain component may have significant contribution to the surface activity of a shorter homolog. To eliminate possible interference of longer chain components, the surfactant solutions were passed through high-density chromatographic columns of octadecylsilarized silica gel (SEP-PAK C₁₈ Cartridge). Any trace amount of components that are more interfacially active than the parent compound are removed. Since the surfactant concentration is changed after passing through SEP-PAK, a method to determine the concentration of the cationic gemini surfactants by two-phase titration^{98,99} with standard C₁₂SO₃Na anionic surfactant solution had to be established. The general procedure and results are described as follow:

General procedure: We first made the cationic gemini surfactant with a certain concentration (see Table IV-3: prepared surfactant concentration) by using the solid materials. The fixed concentration of anionic surfactant C₁₂SO₃Na was titrated with these cationic gemini surfactant solutions. Five ml of 3.8328×10^{-3} M C₁₂SO₃Na aqueous solution, 15 ml of chloroform, 10 ml of H₂O and 10 ml of acidic mixed indicator (see below) were mixed in a capped graduate cylinder. Cationic gemini surfactant solution was added dropwise with good agitation to the above mixed solution. The end point was recorded when the indicator turns from pink to blue. The concentration of

cationic gemini surfactants was then calculated from the concentration of $C_{12}SO_3Na$. The results are listed in Table IV -3.

Table IV -3. Comparison of the surfactant by two phase titration

surfactant	concentration (M)	concentration (M)
	(prepared)	(calculated)
$(C_8N)_2(OH)_2$	2.50×10^{-3}	2.50×10^{-3}
$(C_{10}N)_2(OH)_2$	4.00×10^{-4}	4.04×10^{-4}
$(C_{12}N)_2(OH)_2$	1.00×10^{-3}	1.00×10^{-3}

It is obvious that the concentrations determined by two-phase titration are same as those prepared from the solid material. Therefore, we concluded that the two-phase titration method is effective in determine the concentration of these cationic gemini surfactants.

Once the method to determine these cationic gemini surfactants was established, further purification of the surfactants can be applied to these surfactant solution by sending them through the SEP-PAK.

The surface tension-log C plots for C_{10} , C_{12} were same before and after passing through the SEP-PAK. However, the surface tension-log C plots of C_8 were quite different (to be discussed below), which indicated that the C_8 gemini contained some trace amount of more interfacial active species which were removed by passage through the SEP-PAK.

The acidic mixed indicator was made from dimidium bromide (Burroughs Wellcome Co., Ltd., London, England) and Erioglaucine (also called Disulphine Blue V) (BDH Chemical Ltd., Poole, England)^{104,100}. Weigh $0.5 \pm 0.005\text{g}$ of dimidium bromide into a 50 ml beaker and weigh Disulphine Blue V, $0.25 \pm 0.005\text{ g.}$ into another 50 ml beaker. Add 25 ml of 10% (volume) hot ethanol in water to each beaker. Stir the solutions to dissolve the dye, then transfer them to a 250 ml volumetric flask and dilute to the mark with the hot 10% ethanol solution. This solution was saved as stock solution in a brown bottle. Transfer 20 ml of the above stock solution, 200 ml of deionized distilled water and 20 ml of 2.5 M sulfuric acid into a 500 ml graduated flask and shake it well, then dilute to 500 ml with distilled water.

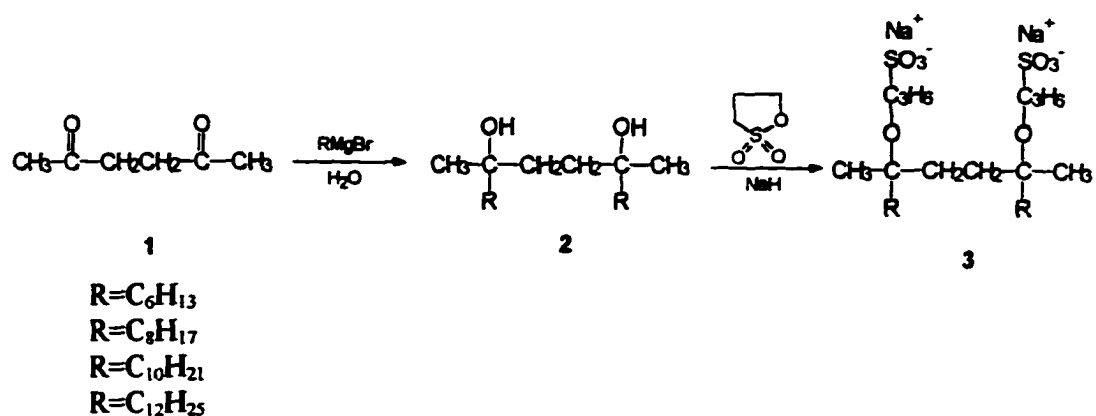
IV-2. Synthesis of a Series of Anionic Sulfonate Gemini Surfactants

IV-2a. Synthesis of 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dialkyl hexane: $[(\text{C}_n\text{SO}_3\text{Na})_2(\text{CH}_2)_2]$.

Symbol: $(\text{C}_n\text{SO}_3\text{Na})_2(\text{CH}_2)_2$, where $n = 6, 8, 10$ and 12

The synthesis of 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dialkyl hexane (3) was carried out by reacting 2,5-dialkyl-2,5-hexanediol (2) with 1,3-propanesultone in the presence of sodium hydride in anhydrous THF (Scheme IV-2). 2,5-dialkyl-2,5-hexanediol (2) was synthesized from the corresponding n-alkyl magnesium bromide and 2,5-hexanedione (1). The obtained 2,5-dialkyl-2,5-hexanediol (2) was used in preparing 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dialkyl hexane (3) without further purification. The synthetic procedures described in the experimental part do not represent the optimized synthetic and purification procedures.

Scheme IV -2. Synthesis of 2,5-di(sodium 3-oxypropane-sulfonate)-2,5-dialkyl hexane



Materials: 1-Bromooctane (99% purity), 1-bromodecane (98% purity), 1-bromododecane (98% purity), 2,5-hexanedione, magnesium turnings, 1,3-propane sultone, 37 % formaldehyde solution, sodium hydroxide and anhydrous THF were purchased from Aldrich Chemical Co. All chemicals were used as received unless otherwise specified in the text.

Synthesis of 2,5-dioctyl-2,5-hexanediol: 5.0 g (0.2 mole) Magnesium turnings and 50 ml anhydrous tetrahydrofuran (THF) were charged into a 500 ml three-necked round-bottom flask which was equipped with a nitrogen gas inlet tube, a pressure-equalized addition funnel and a condenser with a guard tube filled with Drierite. About 5 ml solution of 1-bromooctane (19.3 g, 0.1 mole) in 25 ml anhydrous THF was introduced initially with good agitation under a nitrogen atmosphere. After the temperature of reaction mixture was raised to about 50 °C, the rest of 1-bromooctane solution was added dropwise in about 30 minutes. The reaction mixture was gently refluxed for additional 40 minutes and then cooled to room temperature. 4.6 g (0.04 mole) 2,5-hexanedione in 25 ml anhydrous THF was added dropwise in about 20 minutes. The reaction mixture was heated to reflux for 2 hours. After the reaction

mixture was cooled with an ice-water bath, 50 ml ice-water was added followed by an addition of 50 % ammonium chloride solution until the mixture turned clear. The mixture was then filtered, washed with 10 % sodium hydrogen carbonate and water, successively. The solution was finally dried with sodium sulfate overnight. The sodium sulfate was removed by filtration and the solvent removed under reduced pressure, 12.6 g of 2,5-dioctyl-2,5-hexanediol was obtained (yield: 92%). ¹HNMR (CDCl₃) results are listed in table IV-4.

Synthesis of 2,5-didecyl-2,5-hexanediol: By a similar procedure, 2,5-didecyl-2,5-hexanediol was obtained in 91% yield. ¹HNMR (CDCl₃) results are listed in table IV-4.

Synthesis of 2,5-didodecyl-2,5-hexanediol: By using a similar procedure, 2,5-didodecyl-2,5-hexanediol was obtained in 93 % yield. ¹HNMR (CDCl₃) results are listed in table IV-4.

Synthesis of 2,5-dihexyl-2,5-hexanediol: By using a similar procedure, 2,5-dihexyl-2,5-hexanediol was obtained in 90 % yield.

Synthesis of 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dioctyl hexane: To 9.25 g (27 mmole) 2,5-dioctyl-2,5-hexanediol in 250 ml anhydrous THF, 2.0 g (81 mmole) sodium hydride and 9.9 g (81 mmole) 1,3-propane sultone dissolved in 50 ml THF were added.

The reaction mixture was refluxed for 48 h under a nitrogen atmosphere. After cooling, the reaction mixture was added with 5 ml methanol and then evaporated to dryness under reduced pressure. The residue was shaken well with 50 ml ethanol/water (85/15 v/v) mixed solvent, and filtered. This procedure was repeated three more times, and the resulting crude product was then recrystallized from ethanol/water (85/15) three times, and the light brown color in the product was removed by refluxing the solution with carbon black and subsequent filtration. 2,5-Di(sodium 3-oxypropanesulfonate)-2,5-dioctyl hexane was obtained in 19% yield). ^1H NMR (CDCl_3) results are listed in table IV-4.

Synthesis of 2,5-di(sodium 3-oxypropanesulfonate)-2,5-didecyl hexane: By a similar procedure, 2,5-di(sodium 3-oxypropanesulfonate)-2,5-didecyl hexane was obtained in 20% yield. ^1H NMR (CDCl_3) results are listed in table IV-4. Element analysis: bihydrate: theory : C: 53.20, H:9.48 ; Found: C:53.26 , H: 9.24.

Synthesis of 2,5-di(sodium 3-oxypropanesulfonate)-2,5-didodecyl hexane: By a similar procedure, 2,5-di(sodium 3-oxypropanesulfonate)-2,5-didodecyl hexane was obtained in 19 % yield ^1H NMR (CDCl_3) results are listed in table IV-4.

Synthesis of 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dihexyl hexane: By a similar procedure, 2,5-di(sodium 3-oxypropanesulfonate)-2,5-dihexyl hexane was obtained in 9 % yield.

The ^1H NMR spectrum of one of the final products 2,5-di(sodium 3-oxypropanesulfonate)-2,5-didecyl hexane is shown in Figure IV -2.

The results are summarized in Table IV-4.

Table IV-4. Summary of synthesis of 2,5-di(sodium 3-oxypropane-sulfonate)-2,5-dialkyl hexanes

Compound	Final yield(%)	^1H NMR(D_2O)
$(\text{C}_8\text{SO}_3\text{Na})_2(\text{CH}_2)_2$	19	4.8~4.5(D_2O), 3.7~3.3 (4H, w), 3.1~2.7 (4H, w), 2.2~1.7 (4H, w), 1.7~1.0 (32H, s), and 1.0~0.7 (12H, m).
$(\text{C}_{10}\text{SO}_3\text{Na})_2(\text{CH}_2)_2$	20	4.8~4.5 (D_2O), 3.7~3.3 (4H, w), 3.1~2.7 (4H, w), 2.2~1.7 (4H, w), 1.7~1.0 (40H, s), and 1.0~0.7 (12H, m). The relative peak area (mm) is 3:3:3:31:9 (H is in the order listed above). Total area = 60 mm
$(\text{C}_{12}\text{SO}_3\text{Na})_2(\text{CH}_2)_2$	19	4.8~4.5(D_2O), 3.7~3.3 (4H, w), 3.1~2.7 (4H, w), 2.2~1.7 (4H, w), 1.7~1.0 (48H, s), and 1.0~0.7 (12H, m).

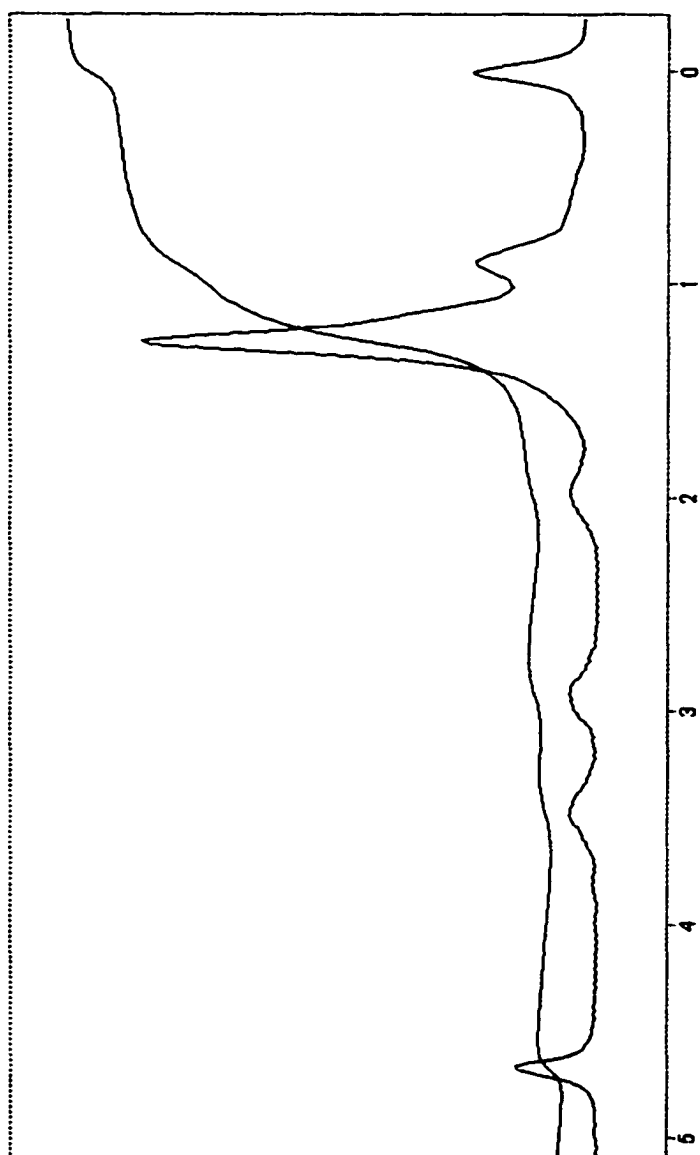


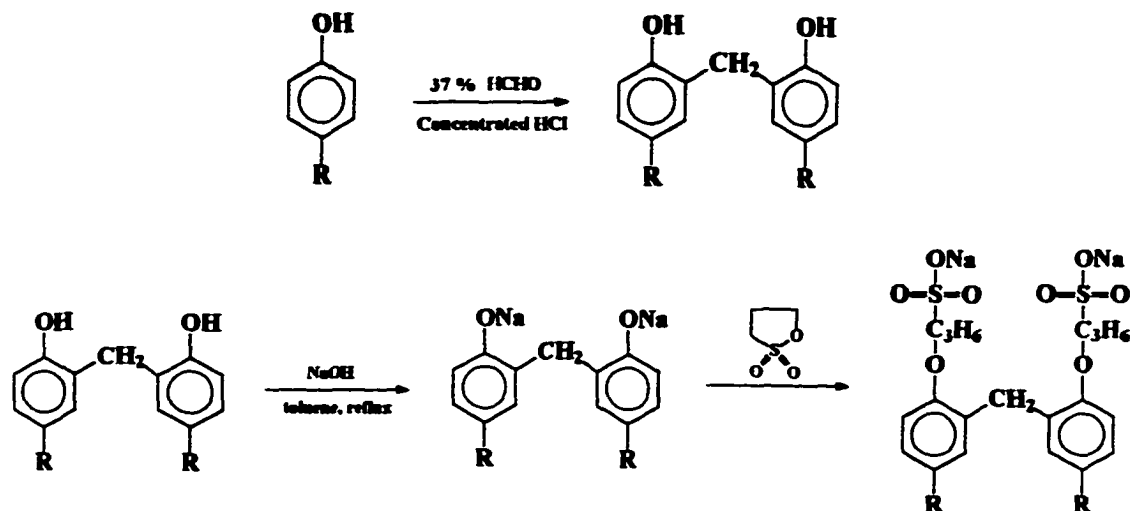
Figure IV-2: ^1H NMR spectrum of 2,5-di(sodium 3-oxypropanesulfonate)-2,5-didecyl hexane in D_2O .

IV-2b. Synthesis of 2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dialkyldiphenyl methane.

Symbol $(C_nArSO_3Na)_2CH_2$, where $n = 9$ and 12 (branched chain)

The synthesis of [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dialkyldiphenyl] methane was carried out in two steps (Scheme 5-5): In the first synthetic step, the gemini surfactant precursor, (2,2'-dihydroxy-5,5'-dialkyldiphenyl) methane, was synthesized by reacting para-alkyl phenol (branched chain, may also contain ortho-position) with 37 % formaldehyde solution in water in the presence of concentrated hydrogen chloride. The excess amount of para-n-alkyl phenol was distilled off and (2,2'-dihydroxy-5,5'-dialkyldiphenyl) methane was obtained as a residue. In the following synthetic step, the obtained (2,2'-dihydroxy-5,5'-dialkyldiphenyl) methane was reacted with sodium hydroxide to form corresponding sodium salt by azeotropic distillation with toluene followed by an addition of 1,3-propanesultone in toluene.

Scheme IV-3. Synthesis of [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dialkyldiphenyl] methane



$R = C_9H_{19}$, is a trimer of propylene ($CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-$)

$R = C_{12}H_{25}$, is a tetramer of propylene ($CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-$)

Synthesis of (2,2'-dihydroxy-5,5'-dinonyldiphenyl) methane:

22.0 g (0.1 mole) para-nonyl phenyl (Acros Organics Co. Meriden, CT. 99% purity)., 100 ml xylenes, 3.0 ml (0.04 mole) 37 % formaldehyde solution in water and 0.4 ml concentrated hydrochloric acid (molar ratios of para-nonyl phenol/formaldehyde/conc. HCl = 1:0.4:0.05) were charged into a three-necked round-bottom flask which was equipped with a gas

inlet tube and a Dean-Stark trap. The top of the Dean-Stark trap was connected with a condenser. The reaction mixture was stirred at room temperature for 1 hour and then warmed to 50~60 °C for another two hours under a nitrogen atmosphere. Finally, the reaction mixture was heated to reflux at solution temperature about 105~110 °C for 4 hours. Water was collected in the Dean-Stark trap during the course of reaction. After cooling, the reaction mixture was transferred into a flask, and the solvent was removed with a rotary evaporator under reduced pressure. The obtained materials were finally subject to vacuum distillation to remove unreacted para-nonyl phenyl (collected at 106~108 °C/0.02 mmHg). 31.6 g (70 % yield based on para-nonyl phenol) light brown viscous (2,2'-dihydroxy-5,5'-dinonyldiphenyl) methane was obtained as residue.

¹HNMR (CDCl₃): δ 0.30 ~ 2.00 (38H, s, para -C₉H₁₉), δ 3.70 ~ 4.10 (2H, m, -CH₂- bridge), δ 6.6 ~ 7.4 (6H, m, phenyl) and δ 7.6 ~ 8.1 (2H, m, -OH).). The relative peak area is 19:1:3:1 (H is in the order listed above). Elemental analysis: calc. :C 82.24, H: 10.68 and O: 7.07; Found: C:82.21, H: 10.32 and O: 6.66.

Synthesis of (2,2'-dihydroxy-5,5'-didodecyldiphenyl) methane:

By a similar procedure, 36.5 g (68 % yield based on para-

dodecyl phenol) light brown viscous (2,2'-dihydroxy-5,5'-didodecyldiphenyl) was obtained as residue. ^1H NMR (CDCl_3): δ 0.30 ~ 2.00 (50H, s, $-\text{C}_{12}\text{H}_{25}$), δ 3.70 ~ 4.10 (2H, m, $-\text{CH}_2-$ bridge), δ 5.6 ~ 6.6 (2H, b, $-\text{OH}$), δ 6.6 ~ 7.5 (6H, m, phenyl). The relative peak area is 25:1:1:3 (H is in the order listed above).

Synthesis of [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dinonyldiphenyl] methane: 22.6 g (0.05 mole) (2,2'-dihydroxy-5,5'-dinonyldiphenyl) methane, 150 ml toluene and 4.0 g (0.1 mole) sodium hydroxide was added to a three-necked round-bottom flask which was equipped with a gas inlet tube, a pressure-equalized addition funnel and a Dean-Stark trap with a condenser. The reaction mixture was heated at 120 $^{\circ}\text{C}$ to reflux under a nitrogen atmosphere. About 1.8 ml water was collected in a Dean-Stark trap through azeotropic distillation with toluene in about 1 hour. The reaction mixture was then cooled to about 50 $^{\circ}\text{C}$ and 20.0 g (0.16 mole) 1,3-propane sultone dissolved in 50 ml toluene was added dropwise in about 15 minutes. The reaction mixture was re-heated to about 120 $^{\circ}\text{C}$ and refluxed for overnight. 38.3 g (yield 98 %) crude product was obtained after removing solvent under reduced pressure and followed by drying in a vacuum oven at 80 $^{\circ}\text{C}$ for 24

hours. 30.1g [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dinonyldiphenyl] methane was obtained after Soxhlet extraction the crude product with acetone for 24 hours. . ¹HNMR (CDCl₃) results are listed in table IV-5. Here, the peaks for -CH₂ and -CH₃, overlapped a great deal and could not be separated. This is the evidence that the chain is not straight chain and that the nonylphenol is a mixture of isomers. Elemental analysis: bihydrate: theory :C: 57.20, H: 8.04; Found: C:57.29, H: 7.62.

Synthesis of [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-didodecyldiphenyl] methane:

By a similar procedure, 19.7 g (yield 92 %) crude product was obtained after removing solvent under reduced pressure and followed by drying in a vacuum oven at 80 °C for 24 hours. 14.3g [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-didodecyldiphenyl] methane was obtained after Soxhlet extraction the crude product with acetone for 24 hours. . ¹HNMR (CDCl₃) results are listed in table IV-5. Here again, the peak of H in straight chain, for -CH₂ and -CH₃, overlapped in a great deal and hardly to be separated. This is the evidence that the chain is not straight chain. mp: 223~225 °C. Elemental analysis: bihydrate: theory :C: 59.97, H: 8.43; Found: C:60.04, H: 8.12.

The ^1H NMR spectrum of the one of the gemini surfactants, [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dinonyldiphenyl] methane, is shown in Figure IV-3.

The results are summarized in Table IV-5.

Table IV-5. Summary of synthesis of 2,2'-di(sodium 3-oxypropane-sulfonate)-5,5'-dialkyldiphenyl methane

Compound	Final yield(%)	^1H NMR(D_2O)
$(\text{C}_9\text{ArSO}_3\text{Na})_2\text{CH}_2$	77	7.9~6.4 (6H, m), 4.8~4.6 (m, D_2O), 4.3~3.9 (2H, m), 3.9~3.4 (4H, m), 3.4~2.7 (4H, m), 2.5~1.9 (4H, m), and 1.9~0.2 (38H, s). The relative peak area (mm) is 5.5:2.0:3.5:3.5:3.5:37 (H is in the order listed above). Total area=55mm
$(\text{C}_{12}\text{ArSO}_3\text{Na})_2\text{CH}_2$	67	7.9~6.4 (6H, m), 4.8~4.6 (m, D_2O), 4.3~3.9 (2H, m), 3.9~3.4 (4H, m), 3.4~2.7 (4H, m), 2.5~1.9 (4H, m), and 1.9~0.2 (50H, s).

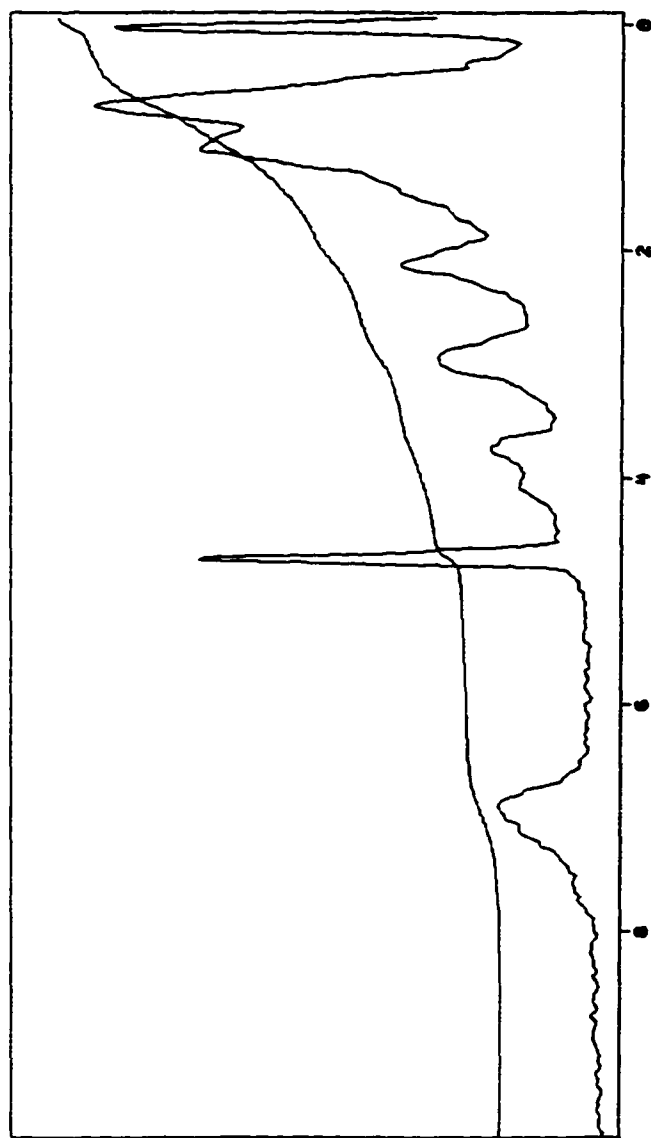


Figure IV-3. ^1H NMR spectrum of [2,2'-di(sodium 3-oxypropanesulfonate)-5,5'-dinonyldiphenyl] methane in D_2O .

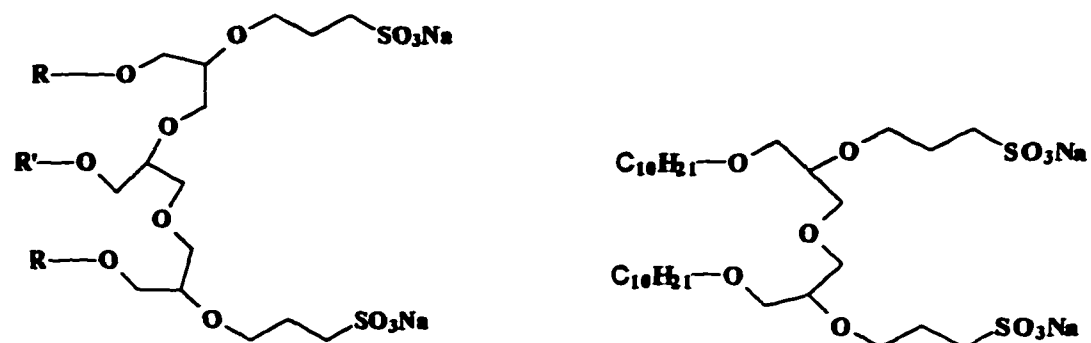
IV-3. Other Surfactants Used in the Studies

1. Sodium decanesulfonate ($C_{10}H_{21}SO_3Na$, symbol: $C_{10}SO_3Na$) and dodecanesulfonate ($C_{12}H_{25}SO_3Na$, symbol: $C_{12}SO_3Na$) with purity > 98% were purchased from Research Plus, Inc., Bayonne, NJ. The surfactants were further purified by passing their aqueous solutions through octadecylsilanized columns several times prior to use for surface tension measurements.
2. Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$, symbol: $C_{12}SO_4Na$) with purity > 99%, was also purchased from Research Plus, Inc., Bayonne, NJ.
3. $C_{12}H_{25}(OC_2H_4)_xSO_4Na$ (symbol: $C_{12}E_xSNa$ $x=1$ and 2) and $C_{14}H_{29}(OC_2H_4)_xSO_4Na$ (symbol: $C_{14}E_xSNa$ $x=2$ and 4) with purity > 99% were obtained as a courtesy of Dr. Stephen W. Morrall of the Procter and Gamble Co.
4. Disodium 1,3-bis decyl-3,5-disulfonatediphenyl ether (DADS) with purity > 99.2% was the courtesy of a research sample of Dr. Charles E. Coburn of the Dow Chemical Co. (Midland, MI).
5. $C_{12}H_{25}(OC_2H_4)_xOH$ (symbol: $C_{12}EO_x$) ($x=2, 3, 4, 7$ and 8) were purchased from Nikko Chemical Co., Tokyo, Japan. Gas

chromatography measurements indicated the compounds had purity > 98%.¹⁰²

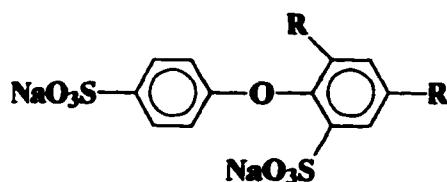
6. N,N-Dimethyl-tetradecanamine oxide $C_{14}H_{29}N(CH_3)_2O$ with purity > 95% was obtained from Ethyl Corporation, Baton Rouge, LA, courtesy of Dr. Kerry Hughes.
7. N-Dodecyl-2-pyrrolidone (symbol: $C_{12}P$), N-Decyl-2-pyrrolidone (symbol: $C_{10}P$), N-Octyl-2-pyrrolidone (symbol: C_8P) were the courtesy of GAF corporation.
8. N-dodecylpyridinium chloride (symbol: $C_{12}NCl$) was synthesized in this Lab. with a purity of 100.08%, as determined by the two phase dye transfer titration.^{101,102} The sample was further purified by passing through C_{18} SEP-PAK.
9. Gemini surfactants with symbol $C_8C_1C_8$, $C_{10}C_1C_{10}$, $C_8C_8C_8$ and $C_{10}OC_{10}$ (Scheme IV-4) were research samples courtesy of Professor Okahara, Osaka University, Japan.

Scheme IV-4. Chemical structures of some gemini surfactants



$C_8C_1C_8$: $R=C_8H_{17}$, $R'=CH_3$
 $C_{10}C_1C_{10}$: $R=C_{10}H_{21}$, $R'=CH_3$

$C_{10}C_{10}(SO_3)_2Na_2$



$C_{10}DADS$: $R=C_{10}H_{21}$

IV-4. Preparation of Aqueous Surfactant Solutions

The water used for the preparing of surfactant solutions was deionized first and then distilled twice, the last distillation from

alkaline permanganate solution through a 3-ft Vigreux column with quartz condenser.

For the surfactant solutions purified by passing through the SEP-PAK¹⁰³ (see below), the concentration of the surfactant solutions were determined by two-phase titration in the presence of an acidic mixed indicator.¹⁰⁴⁻¹⁰⁷ The standard cationic surfactant solution used in titrating the anionic surfactant solution was prepared from disobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride (Hyamine 1622). The purity of Hyamine 1622 was pre-determined by titrating against standard sodium dodecyl sulfate (BDH Chemical, Ltd., Poole, England).

The procedure used in determining the concentration of cationic gemini surfactant was similar to that used for the $C_{12}SO_3Na$ surfactant in which an anionic surfactant ($C_{12}SO_3Na$) with known concentration was used.

IV-5. Surface Tension Measurements

All surface tension measurements were carried out with the use of Wilhelmy vertical plate technique,¹⁰⁸ using a sand-blasted platinum plate of approximately 5 cm perimeter. The plate was calibrated

against quartz distilled water (specific conductivity, 1.11 mho, at 25°C) prior to the measurement of surfactant solutions.

A 200 ml double-jacked flask with circulated water was used in surface tension measurement. The circulated water was pumped from an isothermal bath which maintained the desired temperature ± 0.02 °C

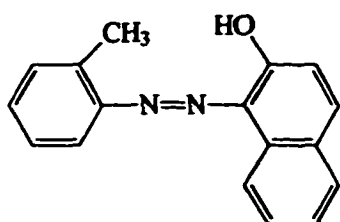
Sodium chloride, sodium bromide and potassium chloride used in adjusting ionic strength of surfactant solutions were baked in a porcelain casserole at red heat over six hours to remove trace amounts of organic compounds. The surface tensions of the aqueous solutions of these baked salts were measured to ensure the absence of traces of surface-active impurities. The surface tensions of 0.1 M NaCl , 0.1 M NaBr and 0.1 M KCl aqueous solution are 72.3, 72.2 and 72.3 mN/m at 25°C.

IV-6. Solubilization study

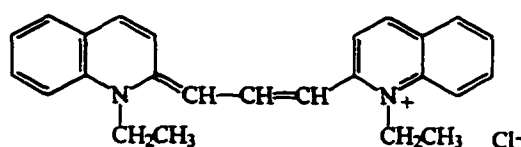
Orange OT and pinacyanol chloride(scheme IV-5) were used as the solutes for a solubilization study.

For orange OT, a saturated solution of the dye in methanol was prepared. To each of a series of 15 ml stoppered test tubes, 2 ml of the

Scheme IV-5. Chemical structure of Orange OT and Pinacyanol Chloride
Chloride dyes



Orange OT



Pinacyanol Chloride

dye solution were added and the solvent removed on a hot water bath. Ten ml of the surfactant solutions of various concentrations were added to each of the above test tubes which then were put on a mechanical shaker for at least 12 hours. The clear supernatant surfactant solution was used to take the visible spectrum in the wavelength range of 473 nm, using a Perkin-Elmer Lambda 3B UV/r/s spectrophotometer.

For pinacyanol chloride, the dye (purchased from Aldrich Chemical Co.) was prepared in methanol at a concentration of 6×10^{-4} M. To 3 ml samples of gemini surfactant solution with different gemini

surfactant concentrations, 5 μ l of the dye solution were added. The solutions were allowed to equilibrate for 20 min before absorbance measurement. The absorbances at 610 nm were taken using a Perkin-Elmer Lambda 3B UV/r/s spectrophotometer.

IV-7. Wetting Test

The Draves wetting test¹⁰⁹ (Draves, 1939) was used as a wetting test for surfactant solutions. A 5 g skein of gray, naturally waxed cotton yarn (54-in. loops containing 120 threads) is attached to a 3 g hook and totally immersed in a tall cylinder of surfactant solution by means of a weight tied to the hook by a thread. The surfactant solution displaces the air in the skein by a spreading wetting process and when sufficient air has been displaced, the skein suddenly sinks in the cylinder. The time for skein suddenly skin is recorded. The better the wetting agent, the shorter the time for sinking to occur.

IV-8. Foaming Test

The Ross-Miles method¹¹⁰ was used as a foaming test. Two hundred ml of a solution of surfactant contained in a pipette of

specified dimensions with a 2.9-mm-i.d. orifice is allowed to fall 90 cm onto 50 mL of the same solution contained in a cylindrical vessel maintained at a given temperature by means of a water jacket. The height of the foam produced in the cylindrical vessel is read immediately after all the solution has run out of the pipette (initial foam height) and then again after a given amount of time (in general, 5 min.).

IV-9. Other Methods

¹HNMR spectra were recorded on a Varian EM-360 90 MHz NMR spectrometer. CDCl₃ and D₂O were used as solvents.

Elemental Analysis for carbon, hydrogen and nitrogen were reported by Quantitative Technologies Inc., Whitehouse, NJ and Desert Analyticals, Tucson, Arizona.

CHAPTER V. RESULTS AND DISCUSSION

V-1. 2,3-Butanediol- α - ω -Di(dimethylalkylammonium Bromide) Cationic Gemini Surfactant Series [symbol: $(C_nN)_2(OH)_2$]

V-1-1. Synthesis and Characterization of 2,3-Butanediol- α - ω - di(dimethyl-alkylammonium bromide)

Generally, diquatarnary ammonium gemini surfactants have relatively low solubilities in water. By introducing two hydroxyl groups on the flexible spacer, the solubility these diquatarnary geminis has been considerably improved compared with cationic gemini surfactants with a rigid hydrophobic spacer.³² The solubilities of the C_8 , C_{10} , C_{12} , and C_{14} homologs are 20g/L, 2g/L, 1.5g/L, and 0.3g/L, respectively. As a result of improved solubility, the surface tension measurements could easily be conducted at room temperature.

V-1-2. Interfacial Properties

The surface tension vs. log molar concentration (log C) curves for $(C_{10}N)_2(OH)_2$, $(C_{12}N)_2(OH)_2$, $(C_{14}N)_2(OH)_2$ and $(C_{16}N)_2(OH)_2$ (the $(C_{18}N)_2(OH)_2$ curve can not be obtained due to the low solubility) in H_2O

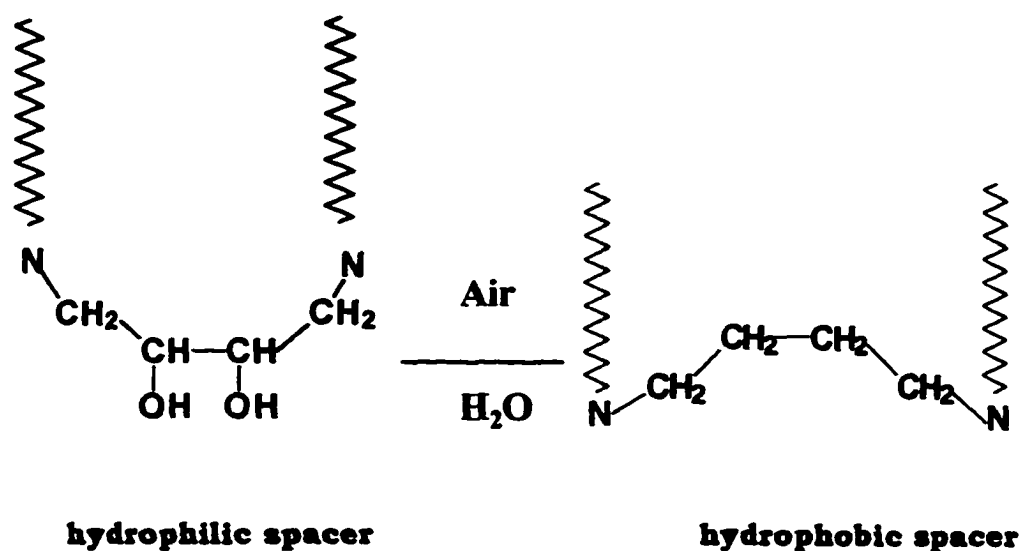
at 25°C are shown in Figure 1 and the data listed in Table 1. The C₈, C₁₀, C₁₂, and C₁₄ members of this series in 0.1 M NaBr at 25°C are shown in Figure 2 and data listed in Table 1, C₁₀, C₁₂ and C₁₄ members in 0.1 M NaCl at 25°C are shown in Figure 3 and data listed in Table 1. From the curves in swamping amount of electrolyte, pC₂₀, cmc, γ_{cmc} , Γ_{max} , and A_{min} values can be determined ⁴⁸ by using a value of 1 for the coefficient in the Gibbs adsorption equation (equation II-13). Values are listed in Table 2 along with data on the (C_nN)₂Ar series and on reference compounds containing one alkyl chain and one quaternary ammonium group.

V-1-3. pC₂₀ Values

pC₂₀ values (which measure the efficiency of adsorption of the surfactant at the interface) of members of the (C_nN)₂(OH)₂ series are listed in Table 2. From Table 2, it can be seen that the pC₂₀ values are much larger than the comparable conventional surfactants indicating the much higher efficiency of adsorption of gemini surfactants compared to conventional surfactants. It is also higher than the other comparable cationic gemini surfactants with a hydrophobic spacer. This is possibly because the two -OH groups form H-bonds with H₂O molecules in, and thus facilitate bending of the spacer towards the

aqueous phase to form the convex micelle surface. For the $(\text{RN}(\text{CH}_3)_2\text{CH}_2\text{CH}_2)_2^{2+}2\text{Br}^-$ 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. The orientation of geminis having flexible spacers, one with hydrophilic character, the other with hydrophobic character, are shown below. Because the H-bonding formed between the -OH of $(\text{C}_n\text{N})_2(\text{OH})_2$ and an aqueous solution compensates for the energy required for the two positively charged N to approach each other, the molecules with a hydrophilic spacer become more closely packed at the interface than the ones with a hydrophobic spacer (scheme V-1). This is also indicated by the areas per surfactant molecule, calculated from the slopes of the surface tension-log C plots.

Scheme V-1. The arrangement of gemini surfactants with hydrophilic and hydrophobic flexible spacers at water-air interface



It also can be seen that the pC_{20} values increase with an increase in the number of carbon atoms in the hydrophobic chain (n). The longer the chain length 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. Notice that the higher homologs deviate from the linear plots (see below).

As expected for these doubly-charged compounds, the C_{20} decreases sharply with increase in the ionic strength of the solution and with increased binding of the counter-ion to the quaternary N. Thus, the C_{20} decreases with solvent in the following order: $H_2O > 0.1\text{ N NaCl} > 0.1\text{ N NaBr}$. The much lower C_{20} values in 0.1 M NaBr than in 0.1 M NaCl are observed because Cl^- is a less tightly bound counterion than Br^- (due to the greater hydration of Cl^- , compared to Br^-).

V-1-4. Critical Micelle Concentrations

CMC values for $(C_nN)_2(OH)_2$ series are listed in Table 2, along with conventional surfactants and comparable cationic gemini surfactants. It is clear that the cmc values of this series are much smaller than the comparable conventional surfactants indicating the much greater tendency to aggregate to micelles for gemini surfactants than comparable conventional surfactants. The cmc values of this series decreases as the length of the alkyl chain increases from 8-14 carbon atoms in salt solution, or from 10-14 carbon atoms in H_2O . Plots of $\log \text{cmc}$ vs n , for members of the $(C_nN)_2(OH)_2$ series in H_2O and 0.1 N NaBr are shown in Fig. 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). Menger and Littau.²⁶ observed the higher cmc values for the longer carbon chains than the lower homologs, and provided the evidence for submicellar formation for those longer geminis by spectral data. Devinsky and his colleagues¹¹¹ observed the deviation of the log cmc vs. n in the series they studied and explained the deviation as due to the different kind of aggregates formed in these two stages.

From the log cmc vs. n values for this series (not considering the deviation of the higher homolog), we calculate the A, B, values in the equation [V-1]:

$$\log \text{cmc} = A + Bn \quad [V-1]$$

in 0.1 M NaBr, the A = 4.47, B = 0.7, the actual value (≈ 0.35) for each -CH₂- group is half of the B in the above equation. This B value is equivalent to the B value for a conventional surfactant (generally B ≈ 0.32), this means that each -CH₂- group in the gemini surfactant makes as much contribution to the micellization as in a conventional surfactant, and agrees with Zana's recent work.¹¹²

The cmc values of the members (n=10-14) of the (C_nN)₂(OH)₂ series in H₂O are all about 1.5 orders of magnitude smaller than the comparable conventional surfactants (with one hydrophobic group of the same carbon length 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 spacer 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 also believed due to the more favorable steric factors in the $(C_nN)_2(OH)_2$ series than in the ones having a hydrophobic spacer between the two hydrophilic groups.

For the $(C_nN)_2Ar$ compounds, with a rigid hydrophobic spacer, micellization would be even more difficult, since it would 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 counter-ion to the quaternary N. Thus, the cmc decreases with solvent in the following order: $H_2O > 0.1$ N NaCl > 0.1 N NaBr. The much lower cmc values in 0.1 M NaBr than in 0.1 M NaCl is again because Cl^- is a less tightly bound counterion than Br^- (due to the greater hydration of Cl^- , compared to Br^-).

V-1-5. Maximum Surface(excess) Concentration ($\Gamma_{\max}$), Minimum Area Per Molecule at the Aqueous Solution/Air Interface ($A_{\min}$) and γ_{cmc}

$\Gamma_{\max}$ and $A_{\min}$ values were calculated only in solutions that contained swamping amounts of counter-ion in order to avoid any ambiguity in the value of the coefficient in the Gibbs adsorption equation ⁴⁸ (equation II-13) used to calculate these values. This is particularly important for these double-charged compounds where m can vary 1 to 3. $\Gamma_{\max}$ and $A_{\min}$ values for $(C_nN)_2(OH)_2$ series are listed in Table 2. The $\Gamma_{\max}$ 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 $\Gamma_{\max}$ values also increase (and the $A_{\min}$ values decrease), as expected, with increase in the alkyl chain length. This indicates that the molecules are more tightly packed in the water-air interface for the longer alkyl chain surfactants. With increase in the value of $\Gamma_{\max}$, the value of γ_{cmc} decreases. Thus, the γ_{cmc} of these compounds are all lower in 0.1 N NaBr than in 0.1 N NaCl solution (the effectiveness of a surfactant in reducing the surface tension of a solvent is proportional to the effectiveness of adsorption of the surfactant $\Gamma_{\max}$.⁴⁸ The results are 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.

V-1-6. Premicellar Aggregation

Despite the greatly increased surface activity of gemini surfactants, a most unusual phenomenon is observed when the carbon atoms in the alkyl chains of gemini is increased beyond a certain number. The surface properties of the molecule increase less than expected, and eventually start to decrease with increase in the number of carbons in the alkyl chains (Figures 1,2,3). As mentioned above, surface activity normally increases with increase in the length of the alkyl chain in surfactants (i.e., both the critical micelle concentration (cmc) and the C_{20} value - the bulk phase concentration required to decrease the surface tension by 20 dynes/cm) decrease. However, in these geminis, when the carbon atoms in the alkyl chains exceed a certain number, whose value depends upon the molecular environment (e.g., ionic strength and temperature of the solution), the cmc and C_{20} values first decrease less than expected, and then start to increase with further increase in the length of the alkyl chain (Fig. 1,2,3). An increase in the cmc with increase in alkyl chain length of some geminis with hydrophobic spacers between the two hydrophilic groups was

observed by Menger in 1991²⁵, who attributed it to premicellar self-association promoted by the rigid, hydrophobic spacers. We have found ³²⁻³⁴ that premicellar self-association is a phenomenon shown generally by gemini surfactants, even those with flexible, hydrophilic spacers, when their alkyl chains are sufficiently long and that the molecules associate to form a soluble, non-surface active complex.

V-1-7. Calculation of Premicellar Self-Association Equilibrium Constant

The equilibrium constant for this premicellar self-association can be calculated in the following manner. It is well known that the log of the cmc and the log of the C_{20} value are linear functions of the number of carbon atoms in the straight alkyl chain of the surfactant ^{113,48}. This is true also for geminis whose alkyl chains are below a certain critical length (Figures 1, 2). Assuming that, in the absence of self-association, this would be true also for geminis with alkyl chains above this critical length, we can calculate the expected cmc and C_{20} values for the higher homologs by extrapolating from those of the lower ones, and from the expected surface tension (γ) - log molar surfactant concentration (C) plots for the higher homologs (Figures 1, 2). From these plots (expected in the absence of premicellar association), and

from the actual, observed γ - log C plots for the same compounds, we can calculate equilibrium constants (K_{eq}) for the self association reaction (equations [V-2], [V-3]):



$$K_{eq} = \frac{[S_x]}{[S]^x} \quad [V-3]$$

Since this association results in a marked reduction in the surface activity of the system, we can assume that the complex formed has little or no surface activity. The observed surface tension of the solution can be assumed to be due only to the monomeric surfactant present. In order to determine its concentration, we construct 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 since the plot is linear between these two points, we can draw the plot between these two points, called expected γ -log C plot. Thus, for any experimental value of γ , we can determine the value of [S] at that value of γ from the expected γ -log C plot, since only the non-aggregated S causes the

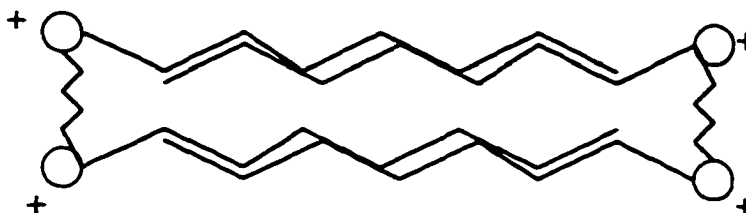
observed value of γ . The value of $[S_x]$ is then the difference between the actual surfactant concentration of the solution minus $[S]$, divided by x . In this fashion, values of K_{eq} for different values of x can be calculated.

We now assume small integral values for x ($=2,3,4$), substitute $[S]$ and $[S_x]$ values into equation [V-3] 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 3 for values of $x=2,3$ and 4. Since K_{eq} when $x=2$ is in the units of $(\text{mol/l})^{-1}$, when $x=3$, in $(\text{mol/l})^{-2}$; and when $x=3$, in $(\text{mol/l})^{-3}$, in order to compare them in the same units, the values of K_{eq} when $x=3$ were converted to their square roots, and when $x=4$, to their cube roots. These values are listed in Table 3. It is apparent that the K_{eq} values are not very different for $x=2,3$, and 4, indicating that a series of oligomers are being formed. The slightly larger values for $x=2$ indicate that this oligomer is slightly more probable than the higher ones.

It is to be expected that, in these premicellar aggregates, the molecules of geminis will be arranged with their (similarly charged) hydrophilic groups at opposite ends of the structure and with their hydrophobic groups oriented toward each other in a manner somewhat similar to that in a very small bilayer or lamellar micelle (scheme V-2). Since aggregation of any type involves the approach of two similarly

charged monomeric molecules to each other, it is to be expected that aggregation will be facilitated by the same factors that facilitate micellization, e.g., an increase in the ionic strength of the solution, an increase in the length of the alkyl hydrophobic groups, and a decrease in the charge on the hydrophilic group. All these factors should increase the value of K_{eq} . Inspection of K_{eq} values in Table 3 show that the K_{eq} is larger for C_{14} in 0.1 M NaBr than C_{16} in H_2O . This indicates that the ionic strength of the solution plays a major role in the association.

Scheme V-2 The possible arrangement of self-association of $(C_{16}N)_2(OH)_2$ (premicelle formation)



V-1-8. Solubilization study of $(C_{16}N)_2(OH)_2$

A solubilization study was conducted on $(C_{16}N)_2(OH)_2$ surfactant solutions at different concentrations in order to see if there is any solubilization in the premicellar region, since only micelles can

solubilize material. Solutions which solubilize the dye Orange OT show orange color and have a maximum absorbance at 473 nm. Figure 41 shows the maximum absorbance(A) - log surfactant molar concentration (C) plot.

As we know from previous (V-1-3) section, $(C_{16}N)_2(OH)_2$ has an experimental cmc value of 5×10^{-5} and an expected cmc value of 1×10^{-5} . From Figure 41, not only can the surfactant with a concentration above the experimental cmc solubilize the dye but also the solution with a concentration between the experimental and expected cmc values. This is additional evidence of premicelle formation.

V-1-9. Interaction of $(C_nN)_2(OH)_2$ With Other Anionic Surfactants

Figure 6 shows the surface tension (γ) - log surfactant molar concentration (C) plots for a typical $(C_nN)_2(OH)_2$ - $C_{12}SNa$ system, showing synergy in surface tension reduction efficiency and effectiveness and synergy in mixed micelle formation as a result of strong interaction between the two component surfactants, from which β parameters were calculated. Data for various systems are listed in Table 4.

β° values: The C_8 and C_{10} homologs of this series, when mixed with either of the anionic surfactants, $C_{12}SNa$ or $C_{10}SNa$, all show very strong interactions, as indicated by their very negative β° values, since the electrostatic nature of the hydrophilic groups of the two different surfactants formation dominates their interaction strength. $(C_8N)_2(OH)_2$ has somewhat weaker interaction than $(C_{10}N)_2(OH)_2$ with the same anionic surfactants, as expected from its shorter alkyl chains and the resulting weaker Van der Waals interaction. Interaction is also weaker when the chain length of the anionic surfactant is decreased. The addition of the tetraoxyethylene group (E_4) between the alkyl chain and the hydrophilic head in $C_{12}E_4SNa$ decreases the interaction with the cationic C_8 and C_{10} geminis slightly, possibly because of the steric factor introduced by the bulky E_4 group or the lower charge density on the bulk hydrophilic head group. However, when the C_{12} gemini is mixed with the same anionic surfactants, a very large change is observed. This will be discussed below (section V-1-11).

The electrostatic nature of the interaction between the two surfactants is evident from the larger negative β° value in 0.1 M NaCl than in 0.1 M NaBr for the $(C_{10}N)_2(OH)_2$ - $C_{12}SNa$ system. The less hydrated (and consequently, smaller) Br^- binds more strongly to the positive quaternary N than does the more highly hydrated (and

consequently, larger) Cl^- . The Br^- therefore decreases the positive charge of the N more effectively than does the Cl^- , with the result that the cationic-anionic interaction is stronger in 0.1 M NaCl than 0.1 M NaBr (Table 14).

β^m values: Interaction of $(\text{C}_8\text{N})_2(\text{OH})_2$ and $(\text{C}_{10}\text{N})_2(\text{OH})_2$ with C_{12}SNa and C_{10}SNa are also strong in the mixed micelles, although less so than in the mixed monolayer at the aqueous solution/air interface, as evidenced by the fact that they are much less negative than the β^s values. The interaction in the micelle with anionic surfactants also increases in the order: 0.1 M NaBr < 0.1 M NaCl, indicating the dominant electrostatic effects.

The large difference between β^m and β^s values has been observed previously in our laboratory^{50,51} for anionic geminis. It is believed to be due to the steric factor in micelle formation. Steric considerations are much more important at the curved interface involved in micelle formation than in monolayer formation at a planar interface. Increased bulkiness in the hydrophobic group has been shown to inhibit micellization relative to adsorption at the aqueous/air interface.^{50,107} Here, the two hydrophobic groups in the gemini molecule inhibit mixed micelle formation. β^m values (like β^s values) are more negative in 0.1 M

NaCl than in 0.1 M NaBr for the same system, again indicating the electrostatic nature of the interaction.

As can be seen from the data in Table 4, the molar ratio of the two surfactants in the surfactant mixtures is about 1:1 at both the aqueous solution/air interface and in the micelle phase in almost every case. This means that the mixed interface and mixed micelle are both charged (since they contain a doubly charged dicationic and singly-charged anionic in an approximately 1:1 ratio). The neutral 1:2 molar product would probably tend to precipitate from solution.

The negative β value of $C_{10}N(OH)_2 - C_{12}EO_7$ in 0.1 M NaBr is very small (table 4, figure 21) indicating the smaller synergistic interaction of the two. This has been attributed⁵⁰ to the weaker electrostatic interaction of partially protonated ether oxygen atoms of the polyoxyethylenated non-ionic surfactant with doubly charged cationic gemini surfactant.

V-1-10. Synergism

The existence of synergism in mixtures containing two surfactants has been shown to depend not only on the strength of the interaction between them (measured by the value of the β parameter), but also on the relevant properties of the individual surfactant components of the mixture (section II-4)^{48,114}. From the data in Table 5, it is apparent that all the

mixtures investigated containing C_8 or C_{10} diquats, whether they are in 0.1 M NaCl or 0.1 M NaBr, show synergism in surface tension reduction efficiency.

The degree of synergism in surface tension reduction efficiency measured by the quantity, $(C_1^o - C_{12,min})/C_1^o$ or $1 - (C_{12,min}/C_1^o)$, (equation II-10) is close to 1 for the C_8 and C_{10} diquats with anionic surfactants, indicating a great degree of synergism.

The degree of synergism in mixed micelle formation is measured by the value of $1 - (C_{12,min}^m/C_1^m)$ (maximum=1) (equation II-11). Values are given in Table 5. Here, also, the values for $(C_8N)_2$ and $(C_{10}N)_2$ diquats are close to 1 indicating a high degree of synergism, although not as high as for surface tension reduction efficiency.

Synergism in surface tension reduction effectiveness exists when $\beta^o - \beta^M$ is negative and $|\beta^o - \beta^M| > \left| \ln \frac{C_1^o C_2^M}{C_2^o C_1^M} \right|$. All the systems investigated for $(C_8N)_2$ and $(C_{10}N)_2$ have the potential for showing synergism in surface tension reduction effectiveness (Table 5).

Thus, according the theory we described in chapter II, all the systems we investigated containing the C_8 and C_{10} diquats as components show very strong synergetic interaction, both in the mixed monolayer at the aqueous solution-air interface and in mixed micelle formation in the

aqueous phase. For example, the system $(C_8N)_2-C_{12}SNa$ ($\alpha=0.667$, $\beta^a = -31$ and $\beta^m = -14$), showed strong synergism in surface tension reduction efficiency, in surface tension reduction effectiveness, and in mixed micelle formation. The mixture of them had a pC_{20} ⁴⁸ value (the negative log of the surfactant molar concentration in the aqueous phase required to reduce the surface tension by 20 mN/m-a measure of surface tension reduction efficiency) of 5.7, and a γ_{cmc} value of 27 mN/m at its cmc of 1.3×10^{-4} M, while the cationic by C_8 itself had a pC_{20} of 5.2, and a γ_{cmc} value of 38.2 mN/m at its cmc of 1.1×10^{-2} M and the anionic had a pC_{20} value of 3.4, and a γ_{cmc} value of 36.8 mN/m at its cmc of 2.5×10^{-3} .

For the systems which show very strong interaction (very negative β values), very sharp slopes of surface tension - log C plot were obtained for the mixture. For example, from the slope of the γ - log C plot for the $(C_8N)_2(OH)_2 - C_{12}SNa$ system ($\alpha=0.322$) shown in Figure 8, the average area per molecule at the aqueous solution/air interface⁹⁷ for the mixture ($43\text{\AA}^2$) is lower than that the area per molecule of either the cationic ($75\text{\AA}^2$) or anionic ($44\text{\AA}^2$) surfactant by themselves, in spite of the 1:1 molar ratio of the two surfactants there. This is reasonable, since strong interaction at the solution-air interface ($\beta^a=-31$) should result in closer packing of the molecules there.

Table 4 lists some of the β^s , β^M values calculated for the above systems which show synergism.

V-1-11. Nonmicellar Mixed Surfactant Association

On the other hand, when the C_{12} homolog, $(C_{12}N)_2(OH)_2$, was mixed with $C_{12}SNa$ under the same conditions (0.1 M NaCl or 0.1 M NaBr, 25°C), an unexpected result was obtained. Not only did the mixture show no synergism in any of the respects mentioned above, but also the surface tension of the mixture increased with increasing concentration of the anionic surfactant in the mixture. No β parameter values could be calculated. Consequently, these two surfactants cannot be showing a repulsive interaction (such an interaction would have a positive β value). Our current hypothesis is that the cationic gemini and anionic surfactants interact so strongly, because of the increased interaction expected from both the increase and matching of the lengths of the hydrophobic groups¹¹⁵, that they form a small, symmetrical complex. Since the surface tension of the solution increases when interaction between the two surfactants occurs, it can be assumed that these aggregates have little or no surface activity. Interaction to form these aggregates reduces the monomer concentrations of the individual surfactants that contribute to the

reduction of the surface tension, thus producing the increase in surface tension observed. Any factor that inhibits the interaction should reduce the formation of these kinds of aggregates. Thus, when $(C_{12}N)_2(OH)_2$ was mixed with the anionic surfactant $C_{12}E_4SNa$ (Figure 22), which has a bulky hydrophilic head group, the system showed sharply reduced interaction but β parameters could still be calculated ($\beta^s = -6$, $\beta^m = -5$) and some synergism was observed (shown above in the systems which show synergism), in contrast to the situation described above, where all the hydrophilic head groups were smaller, and therefore more readily packed together.

V-1-12. Calculation of Equilibrium Constant for Nonmicellar Mixed Surfactant Association

In order to better understand this novel association phenomenon, we assume that the equilibrium for forming small aggregates in the bulk solution from the diquat (D) and the anionic surfactant(A) can be expressed as follows ([V-4]):



and an equilibrium constant, K_{eq} , can be calculated ([V-5]):

$$K_{eq} = \frac{[DA_x]_{eq}}{[D]_{eq}[A]_{eq}^x} \quad [V-5]$$

When the surface activity of D is » A, as is usually the case with mixtures of ionic geminis and conventional surfactants having approximately similar alkyl chain lengths, and since the DA_x complex appears to have little or no surface activity, the surface tension of the mixture must be due essentially to [D]. The value of $[D]_{\text{equ}}$ in the mixture at any value of γ can consequently be obtained from the γ -log C of D alone. The values of $[DA_x]_{\text{equ}}$ and $[A]_{\text{equ}}^x$, can be obtained from $[D]_{\text{equ}}$ and the initial concentrations, $[D]_{\text{in}}$ and $[A]_{\text{in}}$ in the mixture for various values of x . Assuming values of x ($\approx 1/2, 1, 2$), we can then calculate K_a , from equations ([V-6]-[V-8]),

$$\text{Thus, for } x=1, \quad K_a = \frac{[D]_{\text{in}} - [D]_{\text{equ}}}{[D]_{\text{equ}}([A]_{\text{in}} - [D]_{\text{in}} + [D]_{\text{eq}})} \quad [\text{V-6}]$$

$$\text{for } x=2, \quad K_a = \frac{[D]_{\text{in}} - [D]_{\text{equ}}}{[D]_{\text{equ}}([A]_{\text{in}} - 2[D]_{\text{in}} + 2[D]_{\text{equ}})^2} \quad [\text{V-7}]$$

$$\text{and for } x=1/2 \quad K_a = \frac{[D]_{\text{in}} - [D]_{\text{equ}}}{[D]_{\text{equ}}([A]_{\text{in}} - 1/2([D]_{\text{in}} - [D]_{\text{equ}}))^{1/2}} \quad [\text{V-8}]$$

The following mixtures were investigated (all show no synergism) at 25°C:

1. $(C_{12}N)_2(OH)_2$ - $C_{10}SO_3Na$ in 0.1 M NaBr at $\alpha \approx 0.14$
2. $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha \approx 0.33, 0.50, 0.67$

3. $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ in 0.1 M NaCl at $\alpha=0.17, 0.27$
4. $(C_{12}N)_2(OH)_2$ - $C_{12}E_2SO_4Na$ in 0.1 M NaBr at $\alpha=0.167(pH=8.3)$
5. $(C_{12}N)_2(OH)_2$ - $C_{12}SO_4Na$ in 0.1 M NaCl at $\alpha=0.433, 0.489$

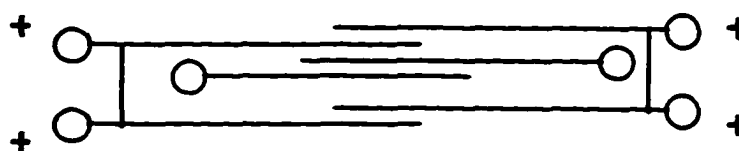
Figures 24 - 28 are the surface tension $-\log C$ plots of all above systems. The calculated equilibrium constants are listed in Table 6-11. Table 12 listed the equilibrium constants for $(C_{14}N)_2(OH)_2$ - $C_{12}SO_3Na$ system in 0.1 M NaCl at 25°C.

From Table 7,10,11, we can see that only when $X=1$ is K_{as} relatively constant for a $[DA_x]$ change of two orders of magnitude. This indicates that the two surfactants in the complex are likely to be in a 1:1 molar ratio. The possible arrangement of this association is shown in scheme V-3. From Tables 6, 8 and 9, it is still possible of $X=1/2$ for tables 6 and 8 and $X=2$ for table 9. Table 12 lists K_{as} values when $x=1$ for the mixtures investigated which show this phenomenon.

Comparing the K_{as} for all the abnormal association of $(C_{12}N)_2(OH)_2$ with anionic conventional surfactants in 0.1 M NaBr solution, $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ has the largest K_{as} $((1.27-2.04) \times 10^5)$ while $(C_{12}N)_2(OH)_2$ - $C_{12}E_2SO_4Na$ has the smallest $((0.80-1.08) \times 10^4)$. This is because of the chain lengths match for the $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ system, making them easy to associate. The large head

group of $C_{12}E_2SO_4Na$ has steric hindrance for the association therefore the K_{as} is the smallest. In 0.1 M NaCl, the K_{as} is bigger for $(C_{12}N)_2(OH)_2 - C_{12}SO_4Na$ than for $(C_{12}N)_2(OH)_2 - C_{12}SO_3Na$. It is possible that the SO_4^{2-} , which has a symmetrical tetrahedral geometry in contrast to SO_3^{2-} , is more suitable to associate with the two hydrophilic groups of the gemini molecules. Comparing the K_{as} of $(C_{12}N)_2(OH)_2 - C_{12}SO_3Na$ in 0.1 M NaBr and in 0.1 M NaCl, the K_{as} is smaller in 0.1 M NaCl than 0.1 M NaBr. Although the looser bonding of N^+ with Cl^- than N^+ with Br^- makes the higher positive charge of the N^+ more suitable for association with the anionic surfactant, the positively charged head of the 1:1 cationic-anionic interaction product first formed may repel a similar unit more strongly in NaCl than in NaBr medium in forming a dimer (or other oligomer) (see Scheme V-2). It is possible that this repulsion is a factor determining the extent of this association.

cheme V-3 The possible arrangement of association of $(C_{12}N)_2(OH)_2$ with anionic conventional surfactant



1:1 dimer

Examination of the γ -log C plots of the $(C_{12}N)_2(OH)_2$ - $C_{12}SNa$ mixtures and of $(C_{12}N)_2(OH)_2$ and $C_{12}SNa$ by themselves, shown in Fig. 25, indicates that the slopes of the mixtures have almost the same values as that of $(C_{12}N)_2(OH)_2$ by itself. This is additional evidence that only the monomeric $(C_{12}N)_2(OH)_2$ left in the solution causes the observed reduction of the surface tension.

$(C_{12}N)_2(OH)_2$, can show synergistic interaction with anionic conventional surfactants or show abnormal interaction with anionic conventional surfactants which depend on the structure of the anionic surfactant and whether the two mixture of surfactants are suitable to form non-micelle association.

The K_a values for the abnormal interactions of $(C_{12}N)_2(OH)_2$ with anionic conventional surfactants are all smaller than the self

association K_{eq} of $(C_{14}N)_2(OH)_2$ in 0.1 M NaBr or $(C_{16}N)_2(OH)_2$ in H_2O . This is because the orientation of self-association is different with the abnormal mixed surfactant interaction association. It is believed that there is a much stronger tail-tail interaction in the self-association (scheme V-2) process than in the abnormal interaction of $(C_{12}N)_2(OH)_2$ with an anionic conventional surfactant. Here again, the second step of the abnormal interaction (Scheme V-3) of $(C_{12}N)_2(OH)_2$ with the anionic conventional surfactant determines the extent of the association.

V-1-13. Foaming Test

Foaming tests for $(C_nN)_2(OH)_2$ were performed by the Ross-Miles method. The results are shown in Table 13. The $(C_{12}N)_2(OH)_2$ shows best foaming ability of all the $(C_nN)_2(OH)_2$.

Cationic surfactants always show poor foaming in this test and in similar tests due , not to some inherent lack of foaming ability, but to the dewetting of the walls of the glass foaming apparatus as a result of adsorption of the cationic surfactant onto it with its hydrophobic group oriented towards the aqueous phase, causing foam rupture. The $(C_nN)_2(OH)_2$ series has a hydrophilic anionic flexible spacer in between the two hydrophilic groups giving these cationic gemini relatively higher foaming ability and increased stability of the foaming.

V-2. Anionic Gemini Surfactant of Series I $[(C_nSO_3Na)_2(CH_2)_2]$

V-2-1. Characterization of Anionic $(C_nSO_3Na)_2(CH_2)_2$

V-2-1a. Solubility

$(C_8SO_3Na)_2(CH_2)_2$ is easily dissolved at 10g/L, while the $(C_{10}SO_3Na)_2(CH_2)_2$, and $(C_{12}SO_3Na)_2(CH_2)_2$, homologs have solubility at about 2g/L, and 1.5g/L, respectively. Surface tensions of these gemini surfactants in pure water and in 0.1 M NaCl can easily be measured at 25°C. By contrast, the solubility of $C_{12}SO_3Na$ is about 0.5g/L. The surface tension measurement is difficult for $C_{12}SO_3Na$ in 0.1 M NaCl above cmc.

V-2-1b. Interfacial Properties (pC_{20} values)

The surface tension vs. log molar concentration (log C) curves for $(C_8SO_3Na)_2(CH_2)_2$ and $(C_{10}SO_3Na)_2(CH_2)_2$ in H_2O at 25°C are shown in Fig. 29, and the data for surface tension measurements are listed in Table 14. The C_6 , C_8 , C_{10} , C_{12} , members of this series in 0.1 M NaCl at 25°C are shown in Fig.30 and the data are listed in Table 14 also. From the curves in swamping amount of electrolyte, pC_{20} , cmc, γ_{cmc} ,

and $A_{\min}$ values can be determined by taking the coefficient constant = 1 (see chapter II). Values obtained are listed in Table 15.

It is obvious that the pC_{20} values are much larger than the comparable conventional surfactants, indicating the much higher efficiency in adsorption of gemini surfactants compared to conventional surfactants. This is attributed to the unique gemini molecular structure (having two hydrophobic chains) which enhances the hydrophobic characteristics of gemini and therefore results in a stronger tendency to adsorb at the surface. The data of the area per molecule at the air/water interface in Table 15 indicates that the $(C_6SO_3Na)_2(CH_2)_2$, $(C_8SO_3Na)_2(CH_2)_2$ and $(C_{10}SO_3Na)_2(CH_2)_2$ have more closely packed structures than conventional single chain surfactants. The $(C_8SO_3Na)_2(CH_2)_2$ has a value of $52 \text{ \AA}^2/\text{molecule}$ and the $(C_{10}SO_3Na)_2(CH_2)_2$ has a value of $42 \text{ \AA}^2/\text{molecule}$ at the air/water interface, that correspond to $26 \text{ \AA}^2/\text{chain}$ and $21 \text{ \AA}^2/\text{chain}$, respectively, much smaller than $44 \text{ \AA}^2/\text{molecule}$ for closely related conventional $C_{12}SO_3Na$ analogs.

The results also indicate that the pC_{20} values, as expected, increase with increased number of carbon atoms in the hydrophobic chain (n). Figure 31 shows the linear relation between pC_{20} ($-\log C_{20}$)

and n for these geminis in 0.1 M NaCl. Here again the C_{12} gemini has a higher pC_{20} value than the C_{10} , but it is smaller than expected.

V-2-1c. Critical Micelle Concentrations

The cmc values for $(C_6SO_3Na)_2(CH_2)_2$, $(C_8SO_3Na)_2(CH_2)_2$, $(C_{10}SO_3Na)_2(CH_2)_2$ and $(C_{12}SO_3Na)_2(CH_2)_2$ are listed in Table 15. From the surface tension-log C plots of this series (fig. 30) in 0.1 M NaCl. It is clear that the C_{12} homolog of the series does not follow the pattern of the smaller homologs, which is attributed to premicelle formation in the $(C_{12}SO_3Na)_2(CH_2)_2$ solutions. Premicelle formation starts in 0.1 M NaCl when the chain length is 12 carbon atoms, which is a different alkyl chain length for premicelle formation when compared with the $(C_nN)_2(OH)_2$ series of cationic geminis (which is 16). This can be explained by considering the actual number of carbon atoms in the $(C_nN)_2(OH)_2$ gemini hydrophobic groups.(see below).

Examining the structure of the $(C_8SO_3Na)_2(CH_2)_2$, there are 4 more carbon atoms besides the alkyl chain. So, the equivalent carbon atoms of each hydrophobic chain for $(C_8SO_3Na)_2(CH_2)_2$ is 10. With the same method, the equivalent carbon atoms of each hydrophobic chain for $(C_{10}SO_3Na)_2(CH_2)_2$ is 12, for $(C_{12}SO_3Na)_2(CH_2)_2$ is 14.

The cmc value of $(C_8SO_3Na)_2(CH_2)_2$ (6.3×10^{-4} M) is much smaller than the value of $C_{12}SO_3Na$ (2.5×10^{-3} M) in 0.1 M NaCl at 25°C, indicating the much stronger tendency for gemini surfactants to aggregate to form micelles than comparable conventional surfactants. The cmc values of this gemini series decrease as the length of the alkyl chain increases from 8 to 10 carbon atoms in salt solution.

Plots of $\log$ cmc vs. n , for members of the $(C_nSO_3Na)_2(CH_2)_2$ series, in 0.1 N NaCl are shown in Fig. 31. From the plot, it is easy to see the deviation of $(C_{12}SO_3Na)_2(CH_2)_2$ which is believed due to the aggregation of the monomeric gemini to small aggregates with little or no surface activity (see below).

As expected for these doubly-charged compounds, the cmc decreases sharply with increase in the ionic strength of the solution.

V-2-1d. Maximum Surface (excess) Concentration (Γ_{max}), Minimum Area Per Molecule at the Aqueous Solution/Air Interface (A_{min}) and γ_{cmc}

A_{min} values were calculated in solutions containing swamping amounts of counter-ion in order to avoid any ambiguity in the value of the coefficient in the Gibbs adsorption equation (chapter II) used to calculate these values. This is particularly important for these double-charged compounds. A_{min} values are listed in Table 15. The A_{min} values

decrease with increase in the alkyl chain length from 8 to 10. However, $A_{\min}$ values for $(C_{12}SO_3Na)_2(CH_2)_2$ is much larger than that of $(C_8SO_3Na)_2(CH_2)_2$ and $(C_{10}SO_3Na)_2(CH_2)_2$. This results indicate that the $(C_{12}SO_3Na)_2(CH_2)_2$ gemini molecules are much more loosely packed in the water-air interface compared to $(C_6SO_3Na)_2(CH_2)_2$, $(C_8SO_3Na)_2(CH_2)_2$ and $(C_{10}SO_3Na)_2(CH_2)_2$. This may be attributed to the removal of the surfactants from the interface in forming premicellar aggregates in solution.

V-2-1e. Premicellar Aggregation

Here again we observed that the surface properties of the molecules increase less than expected, and eventually start to decrease with increase in the number of carbons in the alkyl chains. As mentioned above, surface activity normally increases with increase in the length of the alkyl chain in surfactants i.e., both the critical micelle concentration (cmc) and the C_{20} value decrease. These geminis start to show deviation at carbon chain length of 12. This is supportive to our conclusion, drawn from the previous studies of cationic gemini surfactants, that the premicellar self-association is a common phenomenon for geminis regardless of charge type as well as differentiation in the flexibility or hydrophilicity of the spacers. In

summary, the soluble, non-surface active complexes caused by the formation of premicelle association will be formed when the alkyl chains reach a critical length.

V-2-1f. Calculation of Premicellar Self-Association Equilibrium Constant

According to the theory for calculating premicellar self-association equilibrium constants that we established above (section v-1-8), we can draw the expected surface tension-log C plot for homologs showing self association by extrapolating the pC_{20} vs. n and log cmc vs. n plots to those homologs from the plots for the lower homologs. From the expected and experimental curve of $(C_{12}SO_3Na)_2(CH_2)_2$, we can calculate the K_{eq} for C_{12} . The results are shown in Table 16. The results indicate that K_{eq} for $(C_{12}SO_3Na)_2(CH_2)_2$ are essentially constants for $x=2, 3$ and 4 at different γ values indicating that a series of oligomers are being formed. K_{eq} for $(C_{12}SO_3Na)_2(CH_2)_2$ at $x=2$ is bigger than for $x=3$ or 4 indicating that the driving force for forming the dimer aggregate is greater. The system is therefore more likely to form dimers as the premicellar aggregates.

V-2-1g. Solubilization study of the $(C_{12}SO_3Na)_2(CH_2)_2$

In 1946, Corrin et al established the use of a dye, pinacyanol chloride, to investigate micellization of anionic surfactants. The method was based on the fact that the dye's absorbance at 610 nm increases dramatically as a micelle forms and binds the dye.

Since $(C_{12}SO_3Na)_2(CH_2)_2$, has a very high cmc value compared to the lower homolog, we conducted the solubilization studies on this compound by using the method above: The dye (purchased from Aldrich Chemical Co.) was prepared in methanol at a concentration of 6×10^{-4} . To each 3 ml of gemini surfactant solution which has a different concentration, add 5 μ l of dye solution prepared above. The solutions allowed to equilibrate for 20 min before absorbance measurement. The absorbances at 604 nm were taken using a Perkin-Elmer Lambda 3B UV/vis Spectrophotometer. The result is shown in Fig. 43. The solutions all gave micelle-type spectra (a "blue color" in visual terms) at concentrations over the experimental cmc and lighter blue color roughly at the concentration between the expected and experimental cmc. This result gave additional evidence of premicelle formation.

V-2-2. Interaction of $(C_8SO_3Na)_2(CH_2)_2$ With Other Cationic Surfactants

The surface tension (γ) - log surfactant molar concentration (C) plots for the $(C_8SO_3Na)_2(CH_2)_2$ - $C_{12}NCl$ and $(C_{10}SO_3Na)_2(CH_2)_2$ - $C_{12}NCl$ systems are shown in Figures 32 and 33, respectively. As a result of strong interactions between the two component surfactants, synergy in surface tension reduction was observed. The quantitative measure of interaction parameters (β) were calculated. The results for the two systems are listed in Table 17.

As expected, the synergistic interactions of $(C_8SO_3Na)_2(CH_2)_2$ or $(C_{10}SO_3Na)_2(CH_2)_2$ with the cationic conventional surfactant C_{12} pyridinium chloride ($C_{12}NCl$) are very strong. The C_{20} , cmc, γ_{cmc} values of the mixtures are much smaller than those of the individual surfactants. Strong synergism in surface tension reduction efficiency, surface tension reduction effectiveness, and in mixed micelle formation is therefore observed. The strong synergistic interactions of these surfactants in solution illustrate that the electrostatic interaction is a dominant driving force for synergistic interactions.

The large difference between β^m and β^s values, observed in mixtures containing the cationic geminis, is also observed in the

mixtures of the $(C_8SO_3Na)_2(CH_2)_2$ -, or $(C_{10}SO_3Na)_2(CH_2)_2$ - $C_{12}NCl$ systems. Here, again, the two hydrophobic groups in the gemini molecule evidently inhibit mixed micelle formation.

Comparing the β^m and β^s values for anionic gemini-conventional cationic surfactant mixtures with those for cationic gemini-conventional anionic surfactant, the interactions for cationic gemini - conventional anionic surfactants, for example, $(C_{10}N)_2(OH)_2$ - $C_{12}SNa$ (β^s value = -37, β^m = -15) are much stronger than anionic gemini-conventional cationic surfactant, for example, $(C_{10}SO_3Na)_2(CH_2)_2$ - $C_{12}NCl$ (β^s value = -20, β^m = -17). The less favored synergistic interactions of anionic gemini-conventional cationic surfactants in this case may be due to the greater distance between the hydrophilic groups.

The mixture of $(C_{12}SO_3Na)_2(CH_2)_2$ - $C_{12}NCl$ shows no synergistic interaction at all, probably due to the premicelle formation in the $(C_{12}SO_3Na)_2(CH_2)_2$. The interaction is so complicated that the surface tension points for the mixture at any mole fraction are at random locations in between the two individual curves and we can't draw a curve for it (see Figure 42).

V-2-3. Foaming Test

Foaming tests for $(C_nSO_3Na)_2(CH_2)_2$ series were performed by the Ross-Miles method. The results are shown in Table 18. The $(C_8SO_3Na)_2(CH_2)_2$ showed the best foaming ability of all the $(C_nSO_3Na)_2(CH_2)_2$ compounds. The worst foaming performance of $(C_{12}SO_3Na)_2(CH_2)_2$ is probably due to premicelle formation, making it much less effective in reducing the surface tension.⁴⁸

V-2-4. Wetting Test

Table 19 lists the Draves wetting test¹⁰⁹ results for the $(C_nSO_3Na)_2(CH_2)_2$ series. Wetting time is longer for the longer chain $(C_nSO_3Na)_2(CH_2)_2$ than the shorter ones which is the same trend as observed for conventional surfactants.⁴⁸ Generally, the gemini surfactant has a relatively longer wetting time than the comparable conventional surfactant which is believed due to the relatively larger size of the gemini surfactant, making it diffuse more slowly in the solution.

V-3. Anionic Gemini Surfactant Series II [(C_nArSO₃Na)₂CH₂]

V-3-1. Characterization of Anionic (C_nArSO₃Na)₂CH₂ series (II)

V-3-1a. Solubility

(C₉ArSO₃Na)₂CH₂, which is a mixture of isomers, is easily dissolved at 8 g/L, while the C₁₂, homolog has a solubility of about 0.8 g/L in H₂O. In 0.1 M NaCl, the solubilities are 3g/L and 0.4 g/L for C₉ and C₁₂, respectively. As a result, surface tensions can easily be measured at 25°C, whereas measurement for the C₁₂SO₃Na in 0.1 M NaCl (it has a solubility of 0.5 g/L) is difficult above the CMC.

V-3-2b. Interfacial Properties

The surface tension vs. log molar concentration (log C) curves (C₉ArSO₃Na)₂CH₂ and (C₁₂ArSO₃Na)₂CH₂ in H₂O at 25°C are shown in Fig.34 and the data are listed in Table 20. The C₉, C₁₂, members of this series in 0.1 M NaCl at 25°C are shown in Fig.35 and data are listed in Table 20 also. Values of pC₂₀, cmc, γ_{cmc} and A_{min} are listed in Table 21 along with data for C₁₂SO₃Na.

V-3-1c. pC₂₀ Values

pC₂₀ values of the (C₉ArSO₃Na)₂CH₂ and (C₁₂ArSO₃Na)₂CH₂ are listed in Table 21. From Table 21, it can be seen that the pC₂₀ value of (C₉ArSO₃Na)₂CH₂ is much larger than the comparable conventional

surfactants, as seen for the other gemini series. The area per molecule data at the air/water interface listed in Table 21 show more closely packed gemini surfactants than conventional single chain length of surfactants. $(C_{12}ArSO_3Na)_2CH_2$ has a pC_{20} value greater than $(C_9ArSO_3Na)_2CH_2$ indicating the decrease in surface property of $(C_{12}ArSO_3Na)_2CH_2$ due to premicelle formation.

V-3-1d. Critical Micelle Concentrations

Again, as in the other gemini series, the cmc value of $(C_9ArSO_3Na)_2CH_2$ is much smaller than the comparable conventional surfactants. The cmc value of $(C_9ArSO_3Na)_2CH_2$ in H_2O is 1.1×10^{-3} M and 2.5×10^{-5} M in 0.1 M NaCl which are equivalent to that of $(C_{12}N)_2(OH)_2$ (7.0×10^{-4} M in H_2O and 2.1×10^{-5} M in 0.1 M NaCl). This is agree to that the equivalent C number of $(C_9ArSO_3Na)_2CH_2$ is $12\frac{1}{2}$ ($7\frac{1}{2}$ for alkyl chain, $3\frac{1}{2}$ for phenol group and $1\frac{1}{2}$ for $(CH_2)_3$). The $(C_{12}ArSO_3Na)_2CH_2$ compound has a higher cmc value than $(C_9ArSO_3Na)_2CH_2$. This result is again consistant with premicelle formation. The equivalent carbon atoms in each hydrophobic chain in $(C_{12}ArSO_3Na)_2CH_2$ is 15 (10 carbon atoms for alkyl chain, $3\frac{1}{2}$ for phenol group and $1\frac{1}{2}$ for $(CH_2)_3$).

Again, the cmc value for $(C_9ArSO_3Na)_2CH_2$ (2.5×10^{-5}) in 0.1 M NaCl is about 2 orders of magnitude smaller than the comparable

conventional surfactants $C_{12}SO_3Na$. The cmc value of $(C_9ArSO_3Na)_2CH_2$ (with the equivalent of $11\frac{1}{2}$ carbon atoms for each hydrophobic chain) is roughly comparable to the cmc of $(C_8SO_3Na)_2(CH_2)_2$ ($cmc=6.3\times 10^{-5}$) (10 equivalent carbon atoms). Note that $(C_9ArSO_3Na)_2CH_2$ has more carbon atoms than $(C_8SO_3Na)_2(CH_2)_2$ molecule and should have had much lower cmc value. This is another indication branched chain in $(C_9ArSO_3Na)_2CH_2$ rather than a straight chain molecule.

As expected, here again, the cmc decreases sharply with increase in the ionic strength of the solution.

V-3-1e. Maximum Surface (excess) Concentration (Γ_{max}), Minimum Area Per Molecule at the Aqueous Solution/Air Interface (A_{min}) and γ_{cmc}

Γ_{max} and A_{min} values (in 0.1 M NaCl) were calculated in solutions containing swamping amounts of counter-ion in order to avoid any ambiguity in the value of the coefficient in the Gibbs adsorption equation (Chapter II) used to calculate these values. The A_{min} value of $(C_9ArSO_3Na)_2CH_2$ is 86 (table 21) which means each hydrophobic chain has a area of 43, where comparable conventional $C_{12}H_{25}C_6H_4SO_3Na$ has a area of 46 ⁴⁸. This indicates that the molecules are not much more tightly packed in the water-air interface for $(C_9ArSO_3Na)_2CH_2$ than for the conventional surfactants.

V-3-1f. Premicellar Aggregation

Here again we observed that the surface properties of the molecule increase less than expected for the C_{12} homolog.

We couldn't quantitatively calculate the self-association equilibrium constant for this series according to the theory we established since we only have 2 compounds in the series. But qualitatively, self-association definitely exists in the system when the alkyl chain length of the compound is 12 (the total number of equivalent carbon atoms is $13\frac{1}{2}$ for each hydrophobic chain) or higher in the series which has the same chain length for $(C_nSO_3Na)_2(CH_2)_2$ at which premicelle starts to form.

V-3-2. Foaming Test

Foaming tests for $(C_nArSO_3Na)_2CH_2$ series were performed by Ross-Miles method. The results are shown in Table 18. The $(C_9ArSO_3Na)_2CH_2$ shows much better foaming ability than the $(C_{12}ArSO_3Na)_2CH_2$, since the C_{12} has little surface activity.

V-4. CONCLUSIONS

Three series of cationic and anionic gemini surfactants of high purity were synthesized. The studies of their surface properties showed:

1. The gemini surfactants have much higher surface and micellization properties than comparable conventional surfactants, reflected by very low C_{20} and cmc values.
2. For optimized performance of cationic diquatery ammonium gemini surfactants, the spacer of gemini surfactant should be more flexible and contain hydrophilic functional groups.
3. lower surface activities of the gemini surfactant were observed when the alkyl chain length exceeds a critical chain length. For diquatery ammonium cationic geminis, the critical chain length is likely to be 14 in 0.1 M salt solution. For the two series of disulfonate anionic geminis the critical alkyl chain length is likely to be 12 in 0.1 M salt solution; the equivalent length of the entire hydrophobic group is 14. The formation of premicellar aggregates at the concentration below the cmc values for all kinds of gemini surfactants was used to explain the lower surface activities observed for the geminis having alkyl chain length exceeding the

critical chain length. Pioneering work on the quantitative calculation of the equilibrium constant for the premicelle formation was developed. From these equilibrium constant calculations, the premicelle could be a series of oligomers, but more likely to be a dimer. This is probably because of the very strong Van der Waals interaction of the two hydrophobic chains.

The studies of molecular interaction of mixed binary surfactant solutions containing a gemini surfactant and a conventional surfactant with different charge type indicated that much stronger interactions occurred compared to the conventional surfactant solutions:

1. The synergistic interaction is much stronger at the air-water interface than in the micelle due to the steric hindrance of putting two hydrophobic groups in the micelle. This results in a greater probability for exhibiting synergism in both surface tension reduction efficiency and effectiveness than the corresponding conventional surfactants, but a lower probability of showing synergism in mixed micelle formation when they mix with different charge type conventional surfactants.
2. The non-synergistic interactions of gemini surfactants with conventional surfactants of different charge type, observed for

certain gemini surfactants having the alkyl chain length exceeding the critical chain length, were attributed to the formation of small, soluble, non-micellar aggregates (having no surface activity) of two surfactants. The critical chain length to abolish synergistic interactions depends on the structure of the both gemini and conventional surfactants. For the cationic gemini series $(C_nN)_2(OH)_2$ with conventional anionic surfactants, the critical chain length of the gemini surfactant is 12, the chain length of conventional surfactant can be 12 or more. However, a stronger non-synergistic interaction appears to occur when the two chains have the same length. This is due to the strong hydrophobic interaction between the two chains. In addition, if the size of the hydrophilic group of the conventional surfactant is too large, it appears to inhibit this non-synergistic interaction, and the system may show some synergistic interaction $((C_nN)_2(OH)_2 - C_{12}E_4S)$. The systems show stronger non-synergistic interaction in 0.1 M NaBr than in 0.1 M NaCl. It is believed that the positively charged heads of the 1:1 cationic-anionic interaction produced first formed may repel similar units more strongly in the case of in NaCl than in NaBr medium (see Scheme V-2). It is believed that the later step is a factor determining the extent of the

association. A method for the quantitative calculation of the equilibrium constant for this association was established. These calculations indicated that the two surfactants are present in a 1:1 molar ratio in the aggregate in most cases.

V-5. MISCELLANEOUS STUDIES

V-5-1. Interfacial Properties of Some Other Anionic Gemini Surfactants at Different Ionic Strengths

Interfacial properties: The surface tension vs. log molar concentration ($\log C$) curves for $C_{10}DADS$, $C_8C_1C_8$ and $C_{10}C_1C_{10}$ at different ionic strengths are shown in Fig.36-38. From the curves, pC_{20} , cmc , γ_{cmc} , Γ_{max} , and A_{min} values can be determined. Values are listed in Table 22.

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 $C_8C_1C_8$, $C_{10}C_1C_{10}$ and $C_{10}DADS$ in different Na^+ concentration are listed in Table 1. From Table 22, it can be seen that the pC_{20} values increase with increasing ionic strength for all cases, although that for $C_8C_1C_8$ they don't increase as much as for the rest of the compounds. The larger the ionic strength, the larger the pC_{20} value (the smaller the bulk liquid phase concentrations required to attain either saturation adsorption or surface tension reduction of 20 dynes/cm(mN/m)). Figures 39-40 shows the linear relation between $-pC_{20}$ ($\log C_{20}$) and I (ionic strength) for $C_{10}C_1C_{10}$ and $C_{10}DADS$ in NaCl.

Critical micelle concentrations: It is clear that the cmc values of this series decreases as the ionic strength increase. Plots of $\log cmc$ vs I

(ionic strength of the solution) for C₁₀C₁C₁₀ and C₁₀DADS are shown in Figs. 39-40. Here again, the ionic strength has only a little effect on the C₈C₁C₈.

Maximum surface(excess) concentration(Γ_{max}), minimum area per molecule at the aqueous solution/air interface (A_{min}) and γ_{cmc} : Γ_{max} and A_{min} values were calculated only in solutions containing swamping amounts of counter-ion in order to avoid any ambiguity in the value of the coefficient in the Gibbs adsorption equation used to calculate these values. For the gemini surfactants which all have much lower cmc values than the conventional surfactants, the ionic strength of 0.001 M can swamp out the counter-ion effect. Thus, the Gibbs equation can be applied to all the solutions which we studied here to calculate the A_{min} values from the slopes of the γ -log cmc plots.

Surprisingly, the Γ_{max} values are greater (and the A_{min} are smaller) in the order of 0.001 M NaCl < 0.01 M NaCl < 0.1 M NaCl, indicating that the surfactant molecules are more packed in smaller ionic strength (0.001 M NaCl). This is opposite with conventional wisdom: the more stronger the ionic strength, the more packed the surfactants molecule at the solution/air interface for conventional surfactants. As a result of increase in the value of Γ_{max} , the value of γ_{cmc} decreases. Thus, the γ_{cmc} of these compounds are all lower in 0.001

N NaCl than in 0.01 N NaCl and even lower than in 0.1 M NaCl solution.

A full explanation of these unusual surface properties must await future research efforts.

Table 1

Surface Tension-Log C Data of $(C_nN)_2(OH)_2$ at 25°C

Compound	Log C	γ (mN/m)
$(C_{10}N)_2(OH)_2$	-2.0	35.5
in H ₂ O	-2.35	35.5
	-2.4	36
	-2.6	39.7
	-2.7	42.5
	-3.0	46.4
	-3.08	48.6
	-3.3	54.5
	-3.48	57.4
$(C_{12}N)_2(OH)_2$	-3.0	35.4
in H ₂ O	-3.15	35.4
	-3.3	39.2
	-3.46	42.7
	-3.6	45.3
$(C_{14}N)_2(OH)_2$	-3.0	35.9
in H ₂ O	-3.3	35.9
	-4.0	36.0
	-4.3	38.4
	-4.7	42.5

Table 1 continued

	-5.0	46.0
$(C_{16}N)_2(OH)_2$	-3.7	41.4
in H_2O	-4.0	41.4
	-4.3	41.4
	-4.52	43.2
	-4.7	45.0
	-5.0	47.0
$(C_{10}N)_2(OH)_2$	-2.6	37.2
in 0.1 M NaCl	-2.7	37.2
	-3.08	39
	-3.34	41.8
	-3.7	46
	-4.17	50.2
	-4.36	52.1
$(C_{12}N)_2(OH)_2$	-4.3	35.8
in 0.1 M NaCl	-4.4	35.8
	-4.78	37.3
	-5.04	40.4
	-5.44	45.1
	-5.51	46.2
	-5.76	48.04
$(C_{14}N)_2(OH)_2$	-4.0	34.0
in 0.1 M NaCl	-4.29	34.0
	-5.07	35.8

Table 1 continued

	-5.33	39.7
	-5.59	45.6
	-5.87	49.2
$(C_8N)_2(OH)_2$	-1.64	38.3
in 0.1 M NaBr	-1.96	38.13
	-2.1	40.4
	-2.4	44.0
	-2.7	48.1
	-2.9	50.9
	-3	52.5
$(C_{10}N)_2(OH)_2$	-2.7	33.9
in 0.1 M NaBr	-2.9	33.9
	-3.4	34.0
	-3.7	36.5
	-4.1	41.1
	-4.4	42.2
	-4.7	48.3
	-5.1	52.0
$(C_{12}N)_2(OH)_2$	-4.26	31.9
in 0.1 M NaBr	-4.9	32.0
	-5.3	34
	-5.6	38.3
	-5.75	40.6
	-6.19	47.7

Table 1 continued

	-6.3	49.8
$(C_{14}N)_2(OH)_2$	-5.0	29.7
in 0.1 M NaBr	-5.7	29.7
	-6.0	30.5
	-6.23	36.0
	-6.6	44.0

Table 2

Interfacial Properties of $(C_nN)_2(OH)_2$ gemini surfactants and related compounds at 25°C

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

Table 3

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}	$(K_{eq})^{1/2}$	K_{eq}	$(K_{eq})^{1/3}$	
45	1.98×10^{-7}	1.44×10^{-7}	2.49×10^{-21}	1.35×10^{-7}	
40	1.25×10^{-7}	9.14×10^{-8}	6.25×10^{-20}	8.55×10^{-8}	
35	9.77×10^{-8}	4.07×10^{-13}	1.91×10^{-20}	5.76×10^{-8}	
37	9.82×10^{-8}	4.68×10^{-13}	2.51×10^{-20}	6.31×10^{-8}	
43	1.90×10^{-7}	1.84×10^{-14}	2.00×10^{-20}	5.85×10^{-8}	
range	$(0.98-1.25) \times 10^{-7}$	$(0.41-2.1) \times 10^{-14}$	$(0.19-2.5) \times 10^{-21}$	$(0.58-1.35) \times 10^{-7}$	
$(C_{16}N)_2(OH)_2$ in H_2O					
γ	x=2	x=3	x=4		
	K_{eq}	$(K_{eq})^{1/2}$	K_{eq}	$(K_{eq})^{1/3}$	
42	7.00×10^{-8}	1.67×10^{-12}	6.25×10^{-17}	8.55×10^{-5}	
44	8.26×10^{-8}	4.59×10^{-12}	2.87×10^{-18}	1.42×10^{-6}	
47	9.78×10^{-8}	8.25×10^{-12}	7.84×10^{-18}	1.99×10^{-6}	
43	6.69×10^{-8}	2.97×10^{-12}	1.49×10^{-18}	1.14×10^{-6}	
45	9.70×10^{-8}	6.53×10^{-12}	4.95×10^{-18}	1.70×10^{-6}	
range	$(7.00-9.78) \times 10^{-8}$	$(1.67-8.23) \times 10^{-13}$	$(0.63-7.8) \times 10^{-18}$	$(0.86-1.99) \times 10^{-6}$	

Table 4

Interaction Parameters of $(C_8N)_2(OH)_2$, $(C_{10}N)_2(OH)_2$, and $(C_{12}N)_2(OH)_2$ with Anionic Surfactants at 25°C

System	Medium	α	β^σ	β^m	χ^σ	χ^m
$(C_8N)_2(OH)_2$ - $C_{10}SNa$	0.1 M NaBr	0.40	-26	-12	0.49	0.51
$(C_8N)_2(OH)_2$ - $C_{12}SNa$	0.1 M NaBr	0.32-0.86	-30-(-31)	-13-(-15)	0.48	0.50
$(C_8N)_2(OH)_2$ - $C_{12}E_4SO_4Na$	0.1 M NaBr	0.686	-28	-	0.45	-
$(C_{10}N)_2(OH)_2$ - $C_{10}SNa$	0.1 M NaBr	0.017	-34	-14	0.48	0.50
$(C_{10}N)_2(OH)_2$ - $C_{12}SNa$	0.1 M NaBr	0.16-0.67	-31-(-35)	-12-(-20)	0.48	0.50
$(C_{10}N)_2(OH)_2$ - $C_{12}SNa$	0.1 M NaCl	0.22-0.50	-37-(-40)	-15-(-19)	0.44	0.48
$(C_{10}N)_2(OH)_2$ - $C_{12}E_4SO_4Na$	0.1 M NaBr	0.522	-31	-11	0.5	0.5
$(C_{10}N)_2(OH)_2$ - $C_{12}EO_7$	0.1 M NaBr	0.344	-1.2	-1.0	?	?
$(C_{10}N)_2(OH)_2$ - $C_{12}E_4SO_4Na$	0.1 M NaBr	0.522	-31	-11	0.5	0.5
$(C_{12}N)_2(OH)_2$ - $C_{12}E_4SO_4Na$	0.1 M NaBr	0.174	-6	-5	0.68	0.66
$(C_{12}N)_2(OH)_2$ - $C_{14}E_4SO_4Na$	0.1 M NaBr	0.175	-5	-2	0.54	0.46

Table 5

Molecular Interaction and Synergistic Parameters at 25°C

system	β^o	$ \ln(c_1^o/c_2^o) $	$1-C_{12,min}/c_1^o$	β^m	$ \ln(c_1^m/c_2^m) $	$1-C_{12,min}^m/c_1^m$	$\beta^o-\beta^m$	$\ln \frac{(C_1^o/C_2^o)}{(C_1^m/C_2^m)}$
$(C_{10}N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaCl})$	-40.00	0.84	0.99	-19.00	0.61	0.98	21.00	0.23
$(C_{10}N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaCl})$	-41.00	0.84	0.99	-19.00	6.29	0.98	22.00	5.45
$(C_{10}N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaBr})$	-34.00	2.77	0.99	-17.00	1.93	0.95	17.00	0.85
$(C_{10}N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaBr})$	-35.00	2.77	0.99		1.93		35.00	0.85
$(C_{10}N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaBr})$	-35.00	2.77	0.99	-20.00	1.93	0.97	15.00	0.85
$(C_{10}N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaBr})$	-31.00	2.77	0.99	-12.00	1.93	0.87	19.00	0.85
$(C_{10}N)_2(OH)_2-C_{10}SNa/(0.1 \text{ M NaBr})$	-34.00	5.35	0.99	-14.00	4.14	0.81	20.00	1.21
$(C_8N)_2(OH)_2-C_{10}SNa/(0.1 \text{ M NaBr})$	-26.00	0.98	0.99	-12.00	0.69	0.92	14.00	0.28
$(C_8N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaBr})$	-30.00	1.60	0.99	-13.00	1.52	0.97	17.00	0.07
$(C_8N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaBr})$	-31.00	1.60	0.99	-15.00	1.52	0.98	16.00	0.07
$(C_8N)_2(OH)_2-C_{12}SNa/(0.1 \text{ M NaBr})$	-31.00	1.60	0.99	-14.00	1.52	0.98	17.00	0.07
$(C_8N)_2(OH)_2-C_{12}E_4S/(0.1 \text{ M NaBr})$	-28.00	3.54	0.99		3.67		28.00	0.13
$(C_{10}N)_2(OH)_2-C_{12}E_4S/(0.1 \text{ M NaBr})$	-31.00	0.83	0.99	-11.00	0.22	0.93	20.00	0.61
$(C_{12}N)_2(OH)_2-C_{12}E_4S/(0.1 \text{ M NaBr})$	-6.30	4.61	0.11	-4.50	3.69	0.04	1.80	0.92

Table 6
 Equilibrium Constants of $(C_{12}N)_2(OH)_2$ - $C_{10}SO_3Na$ in 0.1 M NaBr

α	$[D]_{in}$	$[A]_{in}$	$[D]_{eq}$	K_{ss}	$K_{ss}(X=2)$ $(K_{ss})^{1/2}$	$K_{ss}(X=1)$	K_{ss}	$K_{ss}(X=1/2)$ $(K_{ss})^2$
0.14	2.93×10^{-6}	1.80×10^{-3}	2.09×10^{-6}	1.51×10^9	3.88×10^4	2.33×10^4	9.55×10^1	9.11×10^3
0.14	1.40×10^{-6}	8.60×10^{-6}	1.00×10^{-6}	6.57×10^9	8.11×10^4	4.88×10^4	1.38×10^2	1.90×10^4
0.14	8.05×10^{-7}	4.95×10^{-6}	6.00×10^{-7}	1.66×10^{10}	1.29×10^5	7.21×10^4	1.55×10^2	2.41×10^4
range					$(3.88-12.9) \times 10^4$	$(2.33-7.21) \times 10^4$		$(9.11-21.1) \times 10^3$

Table 7**Equilibrium Constants of $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ in 0.1 M NaBr**

α	$[D]_{in}$	$[A]_{in}$	$[D]_{eq}$	$K_{eq}(X=2)$		$K_{eq}(X=1)$	$K_{eq}(X=1/2)$	
				K_{eq}	$(K_{eq})^{1/2}$		K_{eq}	$(K_{eq})^2$
0.09	2.88×10^{-5}	2.91×10^{-4}	8.0×10^{-7}	6.34×10^8	2.52×10^4	1.33×10^5	1.77×10^3	3.13×10^6
0.09	2.06×10^{-5}	2.08×10^{-4}	7.0×10^{-7}	1.00×10^9	3.16×10^4	1.51×10^5	2.02×10^3	4.08×10^6
0.137	9.66×10^{-6}	6.08×10^{-5}	1.3×10^{-6}	3.31×10^9	5.75×10^4	1.27×10^5	8.55×10^2	7.31×10^5
0.137	2.18×10^{-5}	1.37×10^{-4}	1.1×10^{-6}	2.08×10^9	4.54×10^4	1.58×10^5	1.67×10^3	2.79×10^6
0.57	7.41×10^{-6}	5.59×10^{-6}	4.7×10^{-6}	2.00×10^{13}	4.47×10^6	2.04×10^5	2.80×10^2	7.84×10^4
0.57	3.29×10^{-6}	2.49×10^{-6}	2.5×10^{-6}	3.82×10^{11}	6.18×10^5	1.88×10^5	2.18×10^2	4.75×10^4
range				$(6.34-2.00 \times 10^5) \times 10^8$	$(2.52-447.0) \times 10^4$	$(1.27-2.04) \times 10^5$	$(2.18-20.2) \times 10^2$	$(4.75-4.08 \times 10^2) \times 10^4$

Table 8

Equilibrium Constant of $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ in 0.1 M NaCl

α	$[D]_n$	$[A]_n$	$[D]_{eq}$	K_{ss}	$K_{ss}(X=2)$ $(K_{ss})^{1/2}$	$K_{ss}(X=1)$	K_{ss}	$K_{ss}(X=1/2)$ $(K_{ss})^2$
0.17	1.31×10^{-5}	6.42×10^{-5}	5.70×10^{-6}	5.38×10^9	2.42×10^4	2.30×10^4	1.68×10^2	2.82×10^4
0.17	1.03×10^{-5}	5.02×10^{-5}	4.20×10^{-6}	1.00×10^9	3.16×10^4	3.28×10^4	2.11×10^2	4.45×10^4
0.217	8.88×10^{-6}	3.20×10^{-5}	4.20×10^{-6}	2.17×10^9	4.65×10^4	4.07×10^4	2.04×10^2	4.17×10^4
0.217	6.27×10^{-6}	2.26×10^{-5}	3.20×10^{-6}	3.53×10^9	5.94×10^4	4.91×10^4	2.09×10^2	4.37×10^4
range					$(2.42-5.94) \times 10^4$	$(2.30-4.91) \times 10^4$		$(2.82-4.45) \times 10^4$

Table 9

Equilibrium Constants of $(C_{12}N)_2(OH)_2$ - $C_{12}E_2SO_4Na$ in 0.1 M NaBr

α	$[D]_0$	$[A]_0$	$[D]_{eq}$	K_{ss}	$K_{ss}(X=2)$ $(K_{ss})^{1/2}$	$K_{ss}(X=1)$	K_{ss}	$K_{ss}(X=1/2)$ $(K_{ss})^2$
0.167	1.05×10^{-4}	5.25×10^{-4}	1.00×10^{-4}	1.97×10^9	4.44×10^4	1.00×10^4	2.28×10^1	5.20×10^2
0.167	2.17×10^{-4}	1.08×10^{-5}	2.00×10^{-6}	7.77×10^9	2.79×10^4	8.02×10^3	2.61×10^1	6.80×10^2
0.167	3.84×10^{-6}	1.92×10^{-5}	3.20×10^{-6}	6.27×10^9	2.50×10^4	1.08×10^4	4.62×10^1	2.13×10^3
range					$(2.50-4.44) \times 10^4$	$(0.80-1.08) \times 10^4$		$(5.20-21.3) \times 10^2$

Table 10

Equilibrium Constants of $(C_{12}N)_2(OH)_2$ - $C_{12}SO_4Na$ in 0.1 M NaCl

α	$[D]_{in}$	$[A]_{in}$	$[D]_{eq}$	$K_{eq}(X=2)$ K_{eq} $(K_{eq})^{1/2}$	$K_{eq}(X=1)$	$K_{eq}(X=1/2)$ K_{eq} $(K_{eq})^2$
0.433	6.26×10^{-6}	8.22×10^{-6}	3.00×10^{-6}	3.94×10^{11} 6.28×10^5	2.21×10^5	4.26×10^2 1.81×10^5
0.433	3.94×10^{-6}	5.17×10^{-6}	1.70×10^{-6}	2.89×10^{12} 1.70×10^6	4.52×10^5	6.57×10^2 4.31×10^5
0.89	8.16×10^{-6}	8.54×10^{-6}	5.80×10^{-6}	2.78×10^{10} 1.67×10^5	1.22×10^5	1.50×10^2 2.24×10^4
0.89	4.76×10^{-6}	4.98×10^{-6}	3.20×10^{-6}	1.42×10^{11} 3.77×10^5	1.43×10^5	2.38×10^2 5.69×10^4
range				$(1.67-17.0) \times 10^5$	$(0.86-4.52) \times 10^5$	$(2.24-4.31) \times 10^5$

Table 11
Equilibrium Constants of (C₁₄N)₂(OH)₂ - C₁₂SO₃Na in 0.1 M NaBr

α	$[D]_{in}$	$[A]_{in}$	$[D]_{eq}$	$K_{eq}(X=2)$		$K_{eq}(X=1)$	$K_{eq}(X=1/2)$	
				K_{eq}	$(K_{eq})^{1/2}$		K_{eq}	$(K_{eq})^2$
0.172	8.33×10^{-6}	4.00×10^{-5}	1.26×10^{-7}	1.17×10^{11}	3.42×10^5	2.05×10^6	1.09×10^4	1.18×10^8
0.178	8.60×10^{-6}	3.97×10^{-5}	1.60×10^{-7}	1.08×10^{11}	3.29×10^5	1.80×10^6	9.45×10^3	6.94×10^7
0.178	1.48×10^{-5}	6.81×10^{-5}	1.50×10^{-7}	6.42×10^{10}	2.53×10^5	1.82×10^6	1.25×10^4	1.56×10^8
0.294	1.11×10^{-5}	2.67×10^{-5}	1.82×10^{-7}	2.58×10^{12}	1.61×10^6	3.81×10^6	1.30×10^4	1.70×10^8
range					$(2.53-16.1) \times 10^5$	$(1.80-3.81) \times 10^6$		$(6.94-17.0) \times 10^7$

Table 12

Systems Containing $(C_{12}N)_2(OH)_2$ Showing no Synergism:

System		$K_{11}(x=1)$
$(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$	0.1 M NaBr	1.66×10^{-5}
$(C_{12}N)_2(OH)_2$ - $C_{10}SO_3Na$	0.1 M NaBr	4.80×10^{-4}
$(C_{12}N)_2(OH)_2$ - $C_{12}E_2SO_4Na$	0.1 M NaBr	9.60×10^{-3}
$(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$	0.1 M NaCl	3.64×10^{-4}
$(C_{12}N)_2(OH)_2$ - $C_{12}SO_4Na$	0.1 M NaCl	2.20×10^{-5}
$(C_{14}N)_2(OH)_2$ - $C_{12}SO_3Na$	0.1 M NaBr	2.80×10^{-6}

Table 13

Foaming Test of $(C_nN)_2(OH)_2$ (concentration: 1g/L)
in H₂O at 25°C (Ross miles method)

Time	$(C_{10}N)_2(OH)_2(mm)$		$(C_{12}N)_2(OH)_2(mm)$		$(C_{14}N)_2(OH)_2(mm)$	
	1 st trial	2 nd trial	1 st trial	2 nd trial	1 st trial	2 nd trial
0 min.	145	145	175	173	128	120
1 min.	135	135	158	158	118	110
2 min.	133	133	157	158	116	110
3 min.	130	130	157	158	116	110
4 min.	130	130	157	158	116	110
5 min.	125	125	156	155	116	110

Table 14

Surface Tension - Log C Data of $(C_nSO_3Na)_2(CH_2)_2$ at 25°C

Compound	Log C	γ(mN/m)
$(C_8SO_3Na)_2(CH_2)_2$	-2.0	40.9
in H ₂ O	-2.38	40.9
	-2.64	40.9
	-3.02	40.9
	-3.26	42.2
	-3.40	47.3
	-3.56	53.8
$(C_{10}SO_3Na)_2(CH_2)_2$	-2.7	40.6
in H ₂ O	-3.0	40.6
	-3.7	40.6
	-4.2	45.0
	-4.4	48.7
	-4.65	55.9
	-4.8	58.5
	-5.04	60.6
$(C_6SO_3Na)_2(CH_2)_2$	-3.0	37.0
in 0.1 M NaCl	-3.1	37.0
	-3.29	40

Table 14 continued

	-3.5	43
	-3.8	48.4
	-4.0	52.2
$(C_8SO_3Na)_2(CH_2)_2$	-3.5	37.1
in 0.1 M NaCl	-3.78	36.8
	-4.3	39.0
	-4.51	42.5
	-4.82	48.8
	-5.1	52.6
$(C_{10}SO_3Na)_2(CH_2)_2$	-4.42	36.7
in 0.1 M NaCl	-4.90	36.7
	-5.19	36.7
	-5.68	41.5
	-5.88	46.0
	-6.3	56.0
	-6.45	60.0
$(C_{12}SO_3Na)_2(CH_2)_2$	-3.34	42.0
in 0.1 M NaCl	-4.1	41.0
	-4.37	42.0
	-4.5	42.0
	-5.18	44.4
	-5.45	46.3
	-6.4	52.8

Table 15Interfacial Properties of $(C_nSO_3Na)_2(CH_2)_2$ gemini surfactants and related compound at 25°C

Compound	medium (25°C)	pC_{20}	CMC (mol/dm ³)	γ_{CMC} (mNm ⁻¹)	A_{min} (nm ² ×10 ²)
$(C_8SO_3Na)_2(CH_2)_2$	H ₂ O	4.4	5.6×10^{-4}	40.9	
$(C_{10}SO_3Na)_2(CH_2)_2$	H ₂ O	4.5	1.2×10^{-4}	40.6	
$(C_8SO_3Na)_2(CH_2)_2$	0.1 M NaCl	4.0	7.9×10^{-4}	37.0	56
$(C_8SO_3Na)_2(CH_2)_2$	0.1 M NaCl	5.0	6.3×10^{-5}	37.0	54
$(C_{10}SO_3Na)_2(CH_2)_2$	0.1 M NaCl	6.1	3.4×10^{-6}	36.7	42
$(C_{12}SO_3Na)_2(CH_2)_2$	0.1 M NaCl	6.3	1.3×10^{-5}	42.2	137
$C_{12}SO_3Na$	0.1 M NaCl	3.3	2.5×10^{-3}	36.2	44

Table 16

K_{eq} of $(C_{12}SO_3Na)_2(CH_2)_2$ premicelle formation in 0.1 M NaCl

γ (mN/m)	$[S]_{eq}$	$[S]_{initial}$	$K_{eq}(2)$	$(K_{eq}(3))^{1/2}$	$(K_{eq}(4))^{1/3}$
52.0	6.30×10^{-08}	6.20×10^{-07}	$7.02 \times 10^{+07}$	$2.72 \times 10^{+07}$	$2.07 \times 10^{+07}$
49.0	7.10×10^{-08}	8.30×10^{-07}	$7.53 \times 10^{+07}$	$2.66 \times 10^{+07}$	$1.95 \times 10^{+07}$
47.0	8.70×10^{-08}	1.20×10^{-06}	$7.35 \times 10^{+07}$	$2.37 \times 10^{+07}$	$1.69 \times 10^{+07}$
44.0	1.00×10^{-07}	1.50×10^{-06}	$7.00 \times 10^{+07}$	$2.16 \times 10^{+07}$	$1.52 \times 10^{+07}$
range			$(7.0-7.5) \times 10^{+07}$	$(2.16-2.72) \times 10^{+07}$	$(1.5-2.1) \times 10^{+07}$

Table 17

Interaction Parameters for interaction of $(C_nSO_3Na)_2(CH_2)_2$ series with $C_{12}NCl$ at 25°C

System	Medium	α	β^σ	β^M	X^σ	X^M
$(C_8SO_3Na)_2(CH_2)_2$	0.1 M	0.113	-18.4	-13.6	0.56	0.56
- $C_{12}NCl$	NaCl					
$(C_{10}SO_3Na)_2(CH_2)_2$	0.1 M	0.136	-20.0	-17.0	0.60	0.57
- $C_{12}NCl$	NaCl					

Table 18

Foaming Test of $(C_nSO_3Na)_2(CH_2)_2$ and $(C_nArSO_3Na)_2CH_2$ series

(concentration: 1g/L) in H₂O at 25°C (Ross miles method in mm)

$(C_8SO_3Na)_2(CH_2)_2$		$(C_{10}SO_3Na)_2(CH_2)_2$		$(C_{12}SO_3Na)_2(CH_2)_2$	$(C_8ArSO_3Na)_2CH_2$		$(C_{12}ArSO_3Na)_2CH_2$
1 st trial	2 nd trial	1 st trial	2 nd trial	1 st trial	1 st	2 nd trial	1 st trial
					trial		
185	180	155	155	32	160	160	22
168	161	135	135	32	154	157	22
165	160	135	135	32	152	157	22
165	157	135	135	32	152	157	22
164	157	135	135	32	151	156	22
161	157	135	135	32	151	155	22

Table 19

Wetting test of $(C_nSO_3Na)_2(CH_2)_2$ and $(C_nArSO_3Na)_2CH_2$ series

(Concentration: 1g/L) in H_2O at $25^\circ C$

	$(C_8SO_3Na)_2(CH_2)_2$	$(C_{10}SO_3Na)_2(CH_2)_2$	$(C_{12}SO_3Na)_2(CH_2)_2$	$(C_8ArSO_3Na)_2CH_2$	$(C_{12}ArSO_3Na)_2CH_2$
1 st	1'32"	5'54"	>10 min	>10 min	>10 min
2 nd	59"	6'36"			
3 rd	58"				

Table 20

Surface Tension - Log C Data of $(C_nArSO_3Na)_2CH_2$ at 25°C

Compound	Log C	γ(mN/m)
$(C_9ArSO_3Na)_2CH_2$	-2.65	38.5
in H ₂ O	-2.83	38.5
	-3.17	41.3
	-3.43	43.8
	-3.69	46.2
	-4.02	50.3
$(C_{12}ArSO_3Na)_2CH_2$	-3.69	54.6
in H ₂ O	-3.96	58.5
	-4.24	62.4
$(C_9ArSO_3Na)_2CH_2$	-3.65	32
in 0.1 M NaCl	-4	32
	-4.43	32
	-4.69	33.18
	-4.87	35.0
	-5.13	37.8
	-5.47	42.76
	-5.74	45.1
	-6.02	47.1

Table 20 continued

$(C_{12}ArSO_3Na)_2CH_2$	-4.04	38.2
in 0.1 M NaCl	-4.30	38.2
	-4.47	41.0
	-4.81	45.5
	-5.20	51.0

Table 21

Interfacial Properties of $(C_nArSO_3Na)_2CH_2$ gemini surfactants and related compound at 25°C

Compound	medium (25°C)	pC_{20}	CMC (mol/dm ³)	γ_{CMC} (mNm ⁻¹)	A_{min} (nm ² ×10 ²)
$(C_9ArSO_3Na)_2CH_2$	H ₂ O	4.1	1.1×10^{-3}	38.5	
$(C_{12}ArSO_3Na)_2CH_2$	H ₂ O				
$(C_9ArSO_3Na)_2CH_2$	0.1 M NaCl	6.3	2.5×10^{-5}	32.0	86
$(C_{12}ArSO_3Na)_2CH_2$	0.1 M NaCl	5.3	4.8×10^{-5}	38.2	69
$C_{12}SO_3Na$	0.1 M NaCl	3.3	2.5×10^{-3}	36.2	44

Table 22

The properties of Geminis in different Na⁺ concentration at 25°C

	C ₈ C ₁ C ₈				C ₁₀ C ₁ C ₁₀				C ₁₀ DADS			
	Na ⁺ conc. (M)	0.100	0.010	0.001	0.100	0.010	0.0010	0.100	0.01	0.001	0.001	0.001
Slope		-16.5	-17.4	-18.4	-13.7	-14.7	-17.7	-8.9	-13.6	-20.8		
A(A ² /I)		57	54	51	69	64	53	106	70	49		
γ _{cmc} (mN/m)		30.0	30.0	29.6	38.1	37.5	33.5	39.0	39.9	36.0		
Γ _{max}		2.9	3.1	3.3	2.4	2.6	3.1	1.6	2.4	3.4		
pC ₂₀		4.8	4.8	4.8	6.2	5.3	4.9	6.3	5.2	4.8		
CMC(M)		1.7×10 ⁻⁴	3.0×10 ⁻⁴	3.4×10 ⁻⁴	8.0×10 ⁻⁶	5.2×10 ⁻⁵	1.4×10 ⁻⁴	1.4×10 ⁻⁵	4.0×10 ⁻⁵	1.0×10 ⁻⁴		

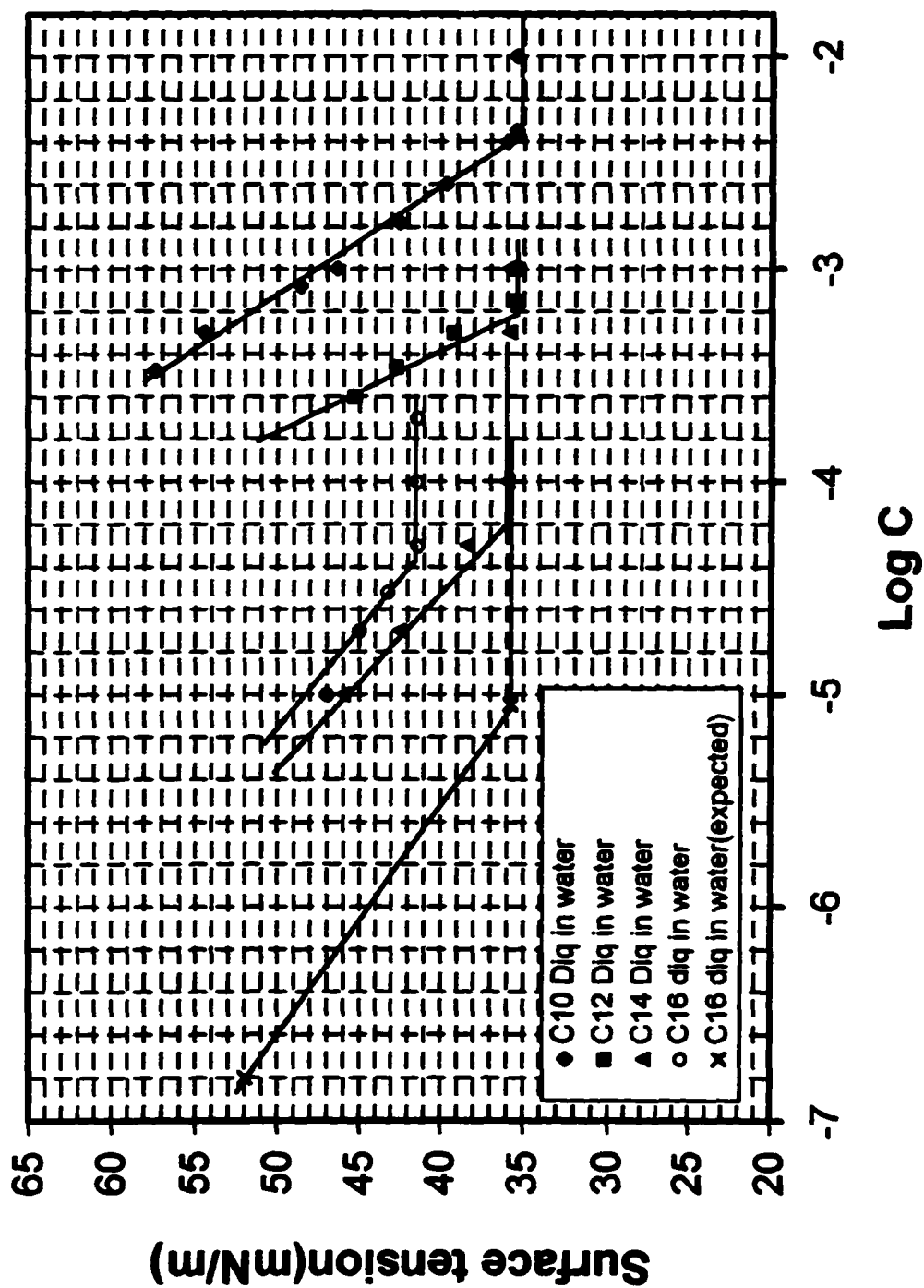


Figure 1: Surface Tension versus log C plots of $(C_nN)_2(OH)_2$ in H_2O at $25^\circ C$

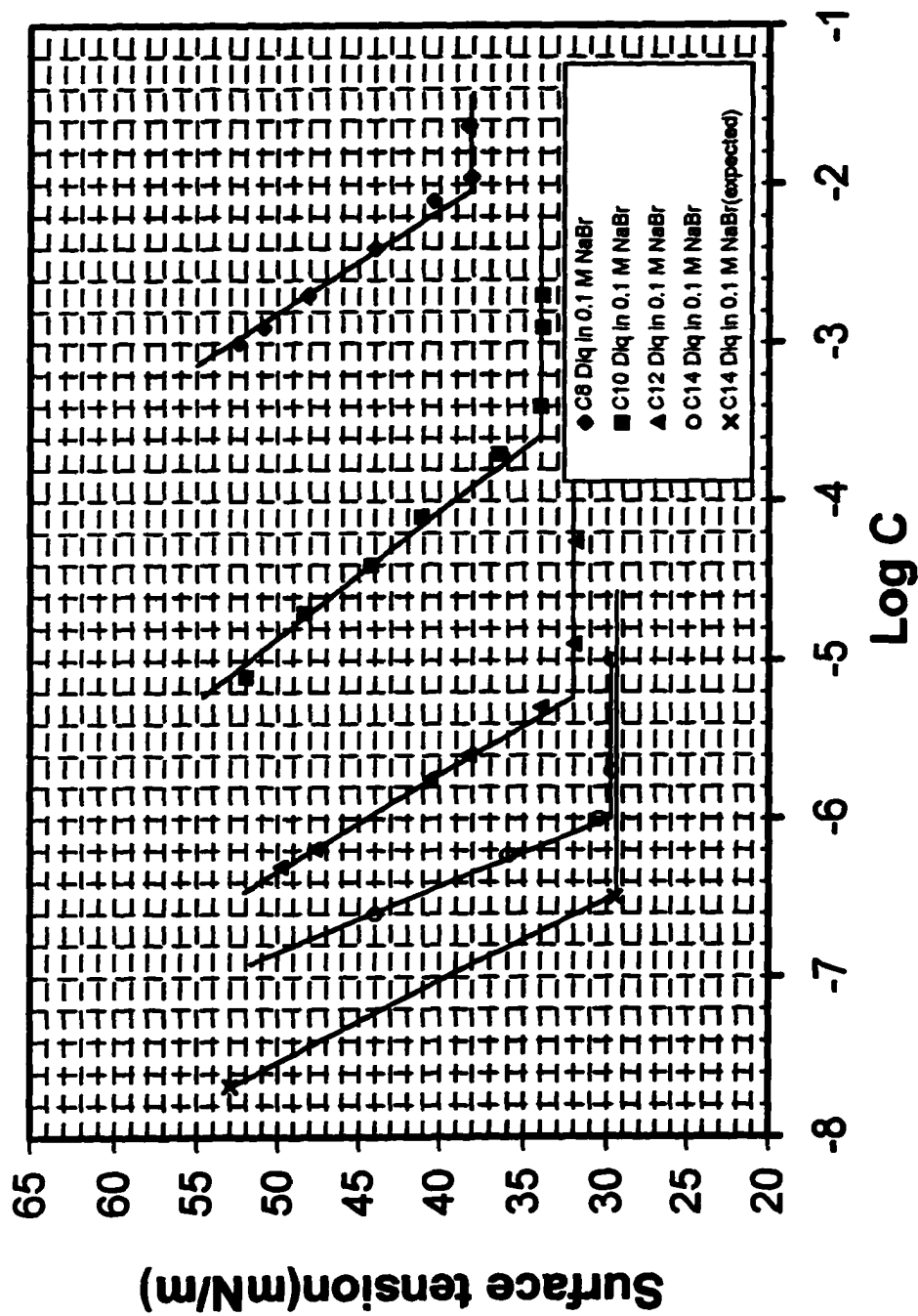


Figure 2: Surface tension vs. log C plot of $(C_nN)_2(OH)_2$ in 0.1 M NaBr at 25°C

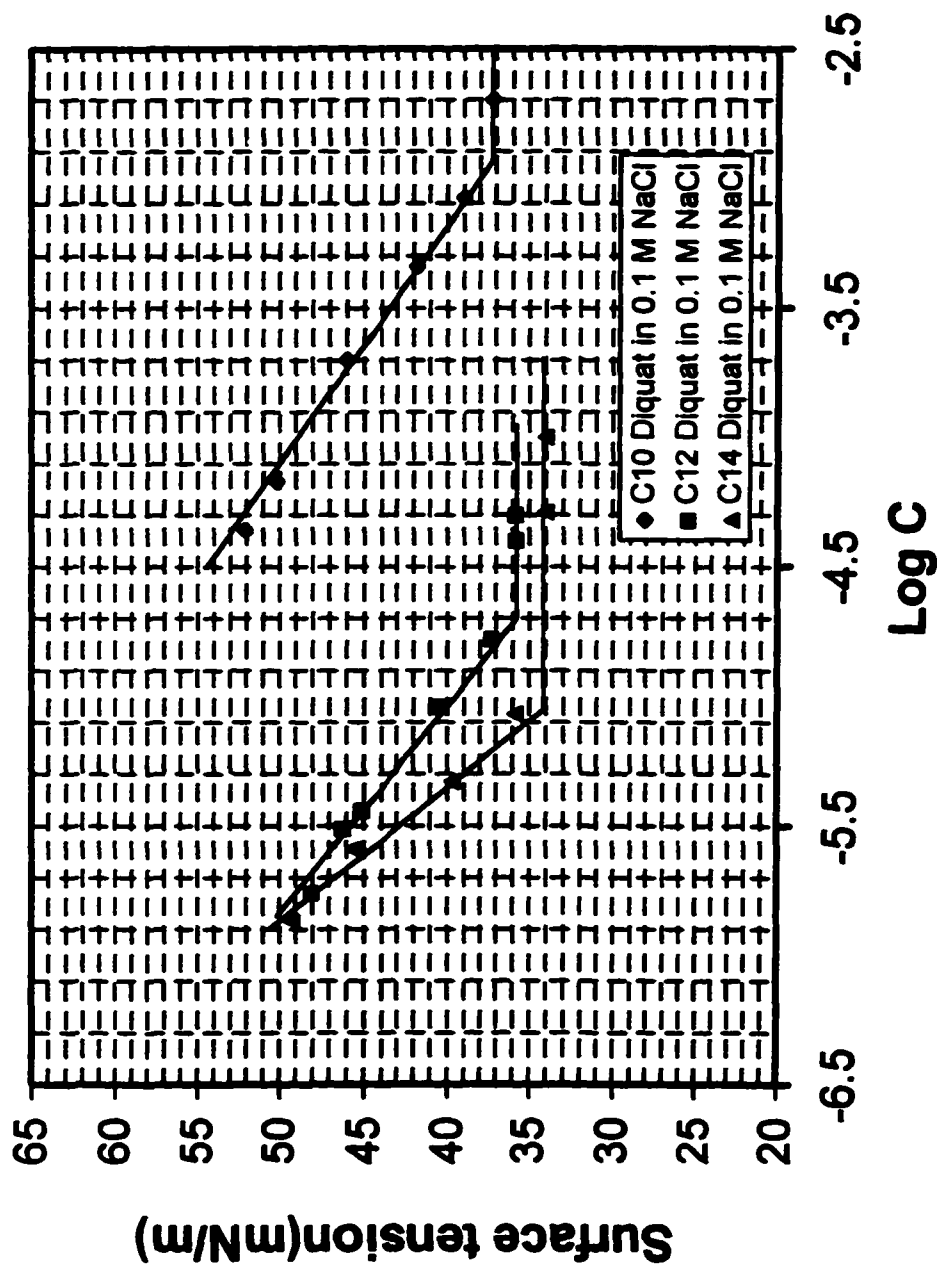


Figure 3: Surface tension versus log C plots of $(C_nN)_2(OH)_2$ in 0.1 M NaCl at 25°C

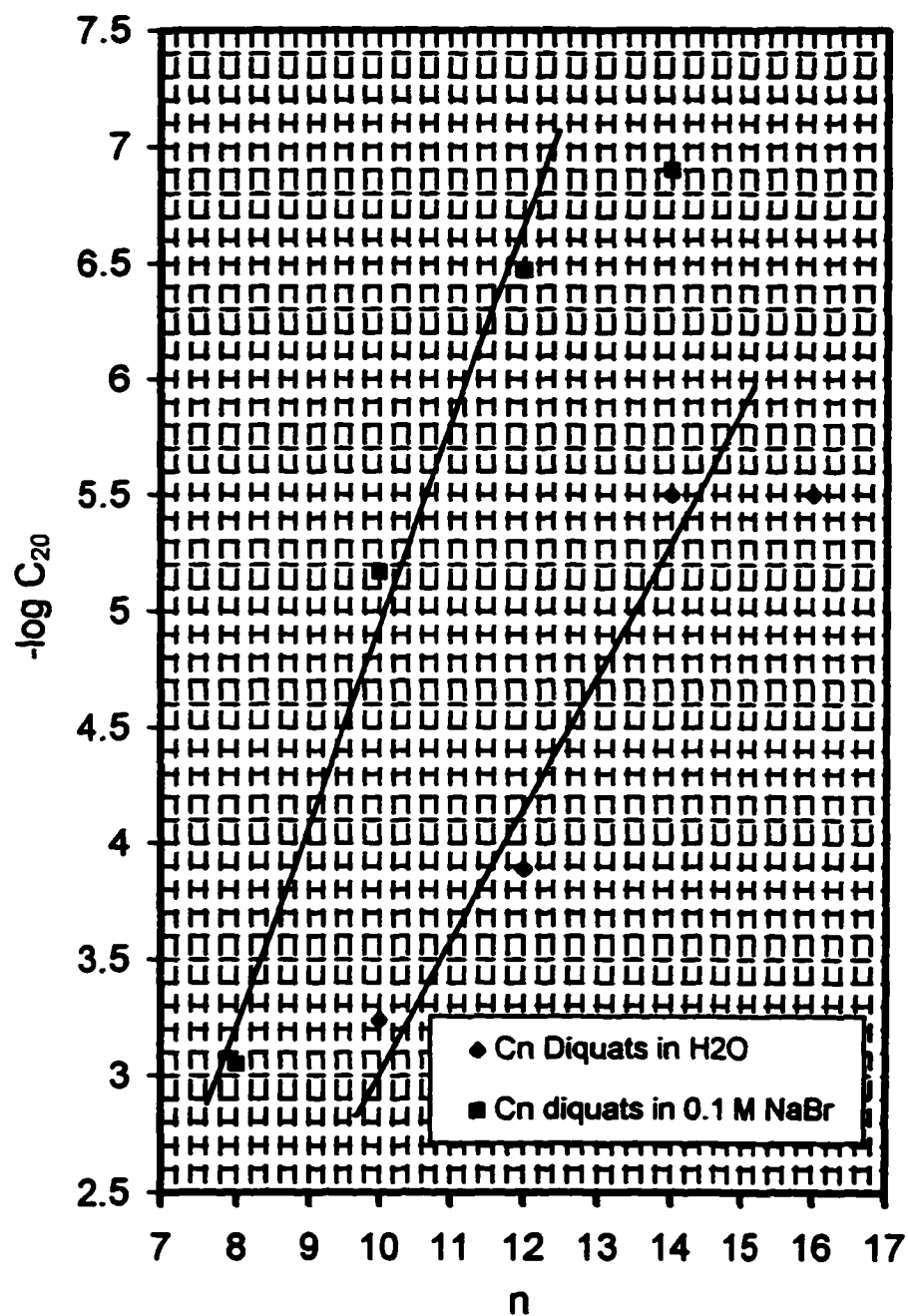


Figure 4: Log C_{20} versus n plots of $(C_nN)_2(OH)_2$ at 25°C

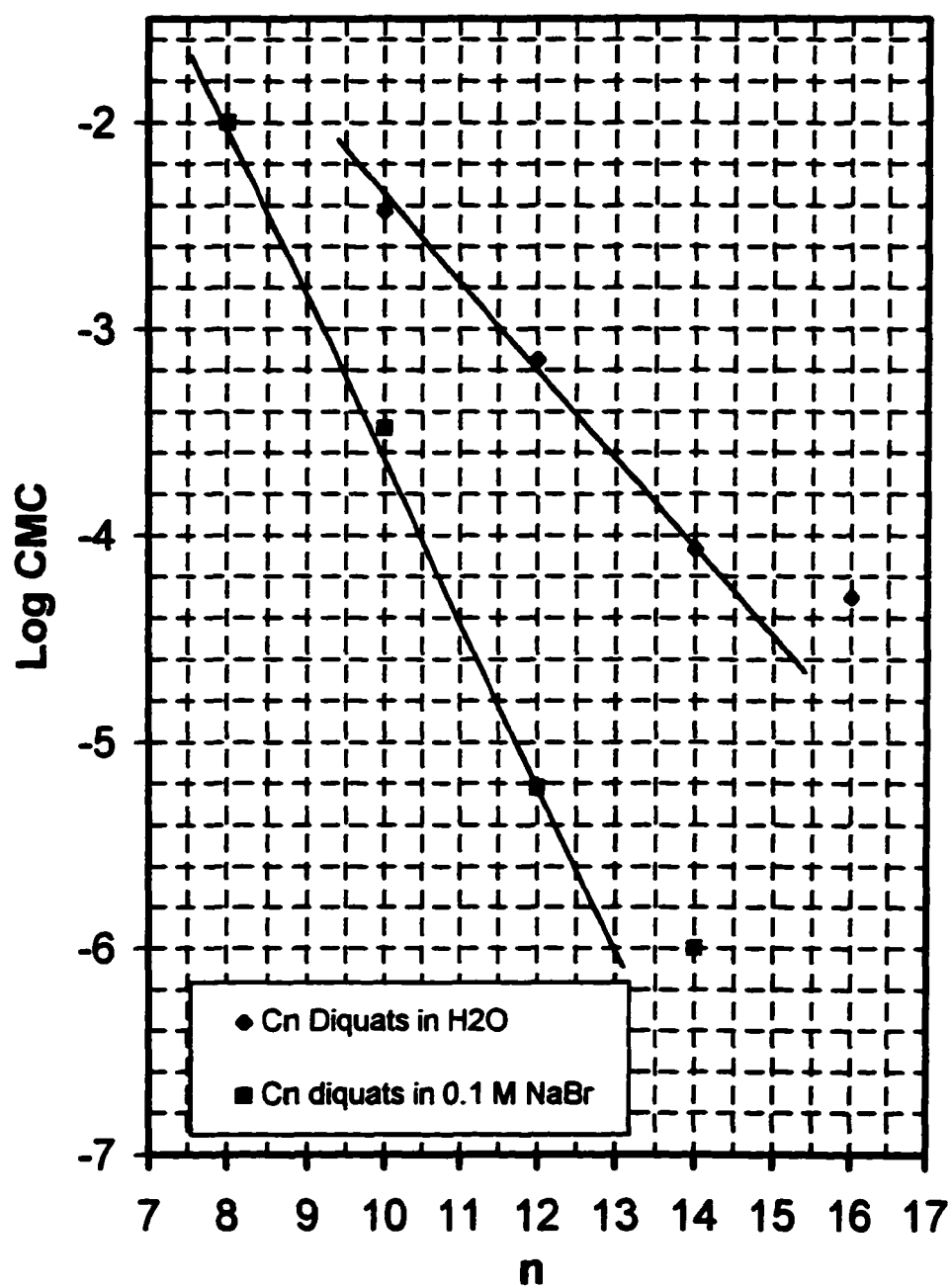


Figure 5: Log cmc versus n plots of $(C_nN)_2(OH)_2$ at 25°C

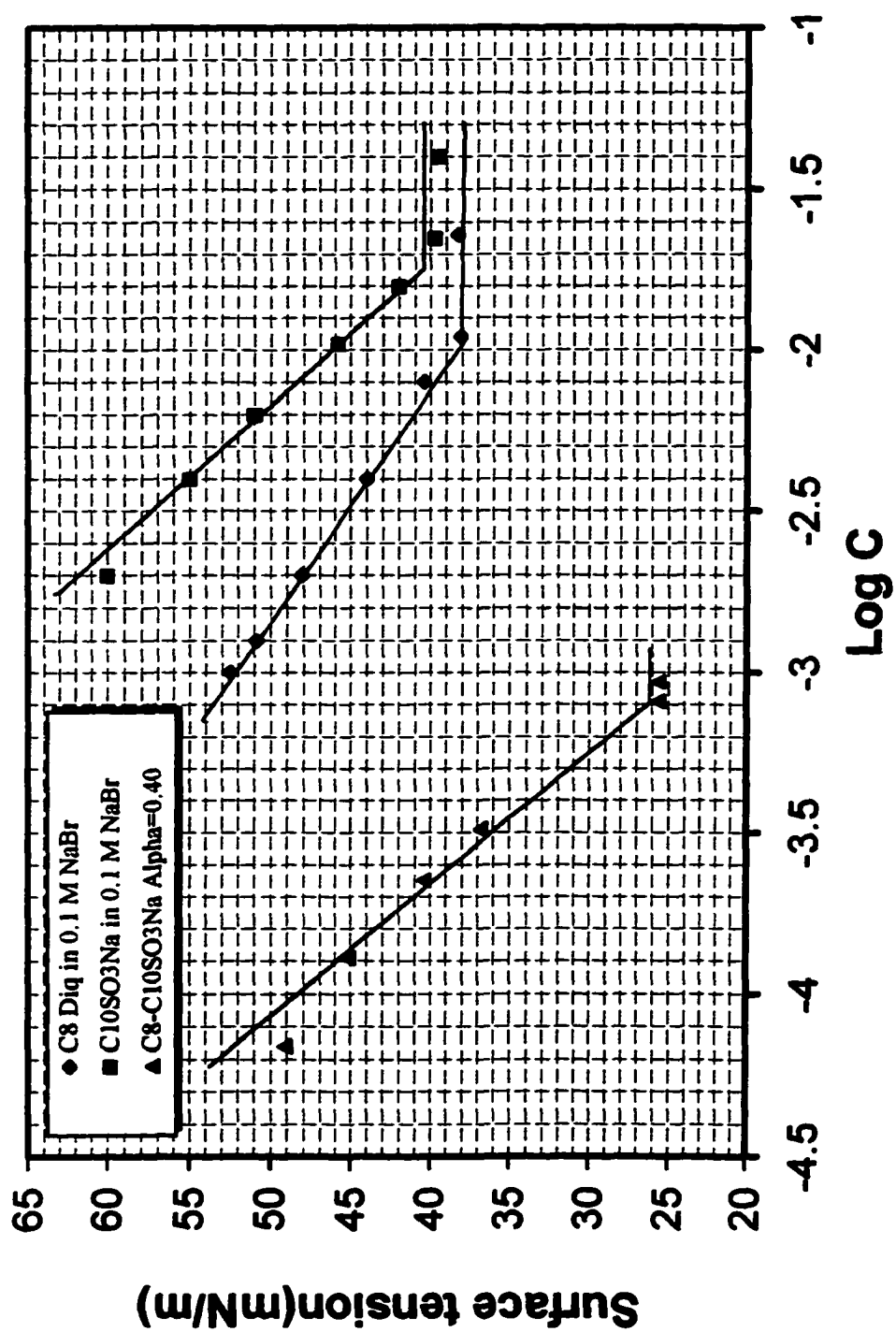


Figure 6: $(C_8)_2(OH)_2$ $C_{10}SO_3Na$ in 0.1 M NaBr at $\alpha=0.40$ at $25^\circ C$

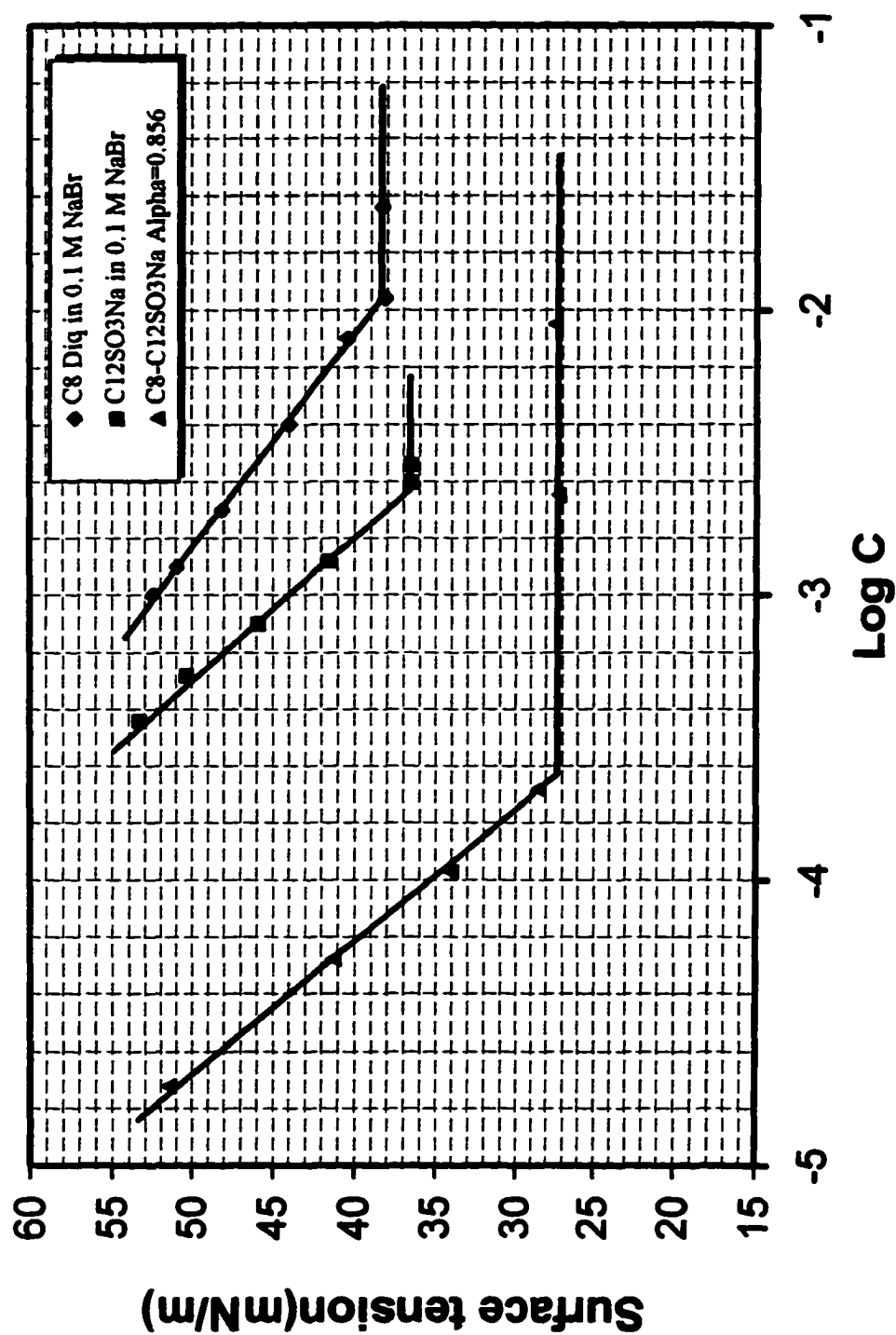


Figure 7: (C₈N)₂(OH)₂-C₁₂SO₃Na in 0.1 M NaBr at $\alpha=0.856(C_8)$ at 25°C

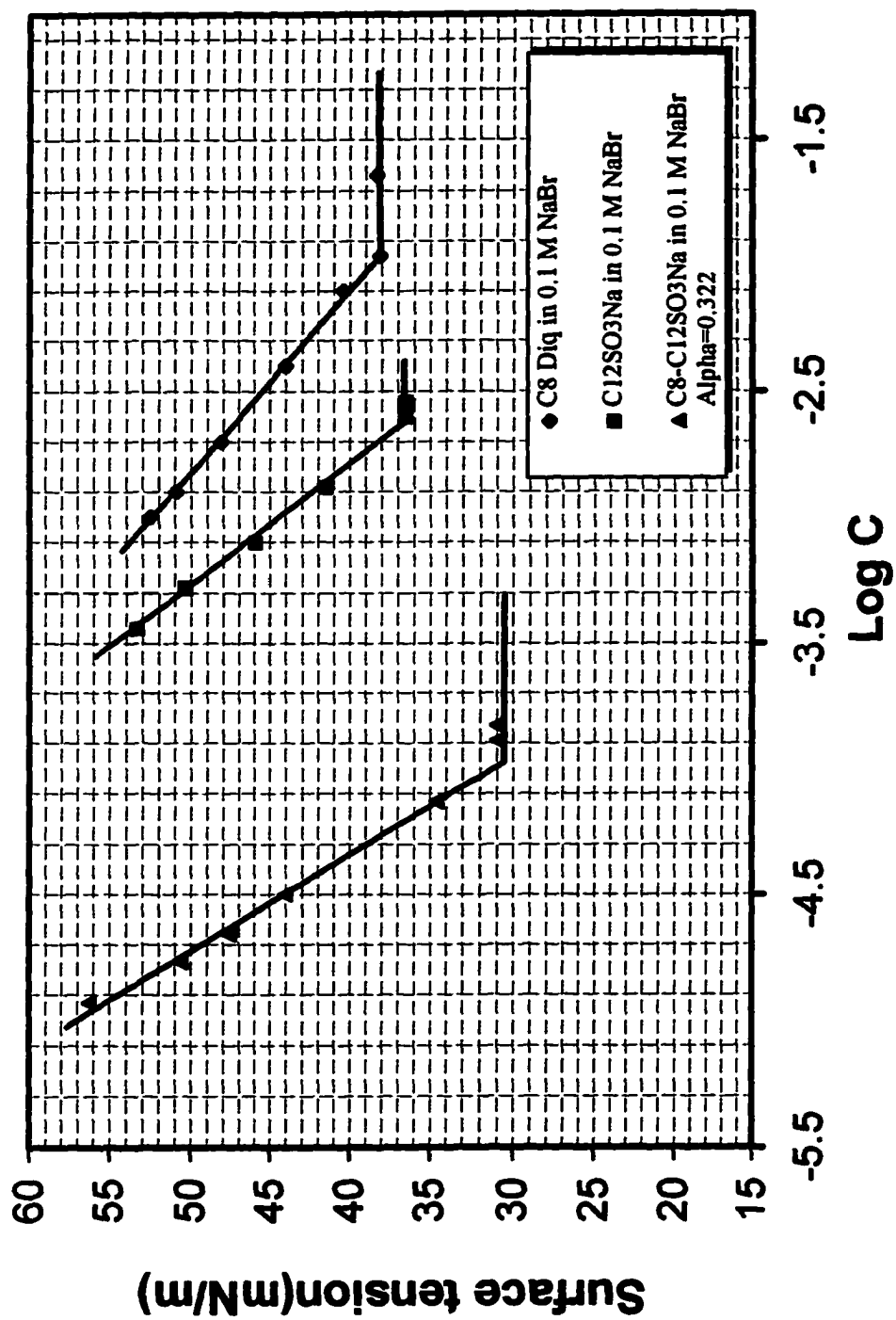


Figure 8: $(C_8N)_2(OH)_2-C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha=0.322(C_8)$ at 25°C

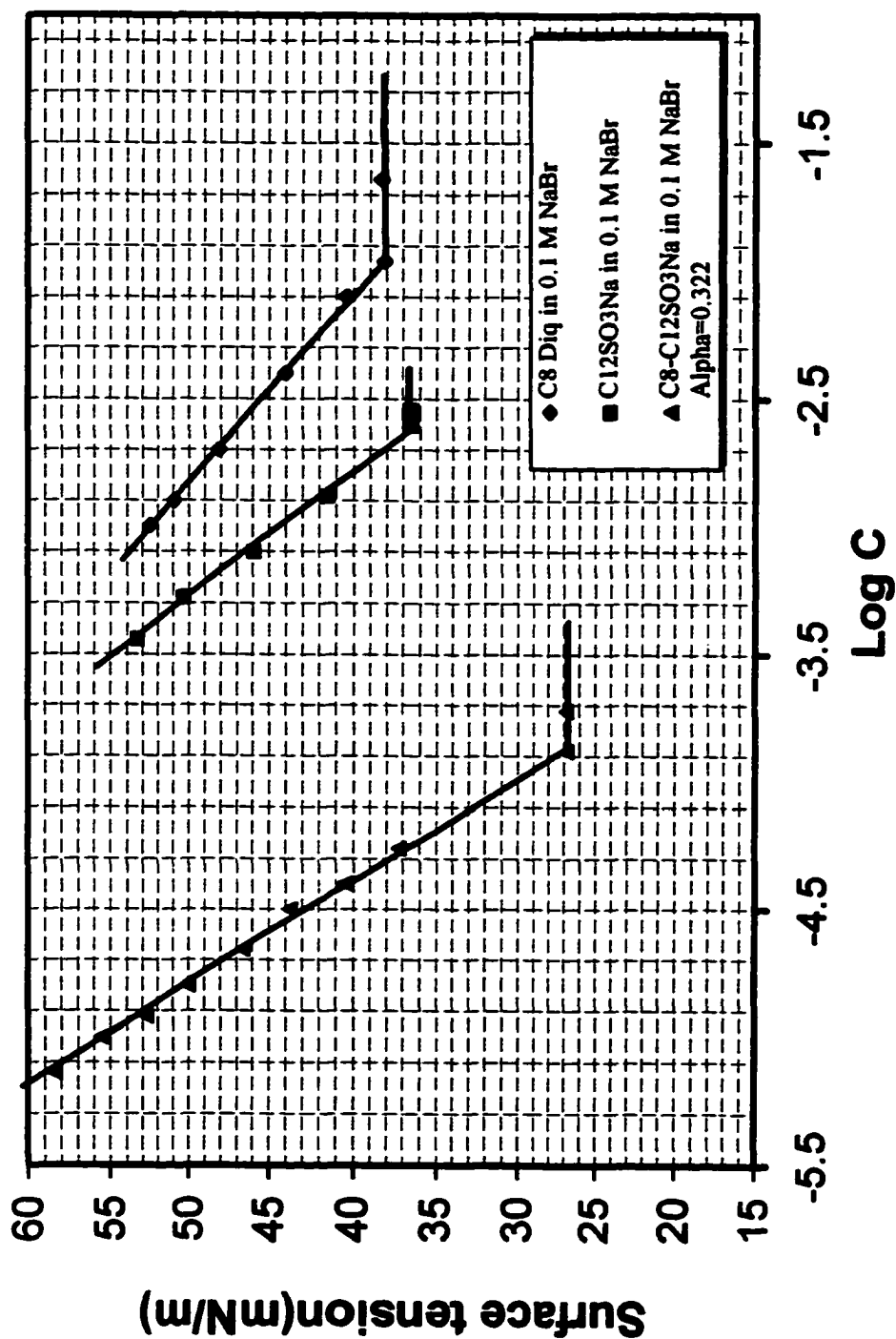


Figure 9: $(C_8N)_2(OH)_2 - C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha=0.50(C_8)$ at 25°C

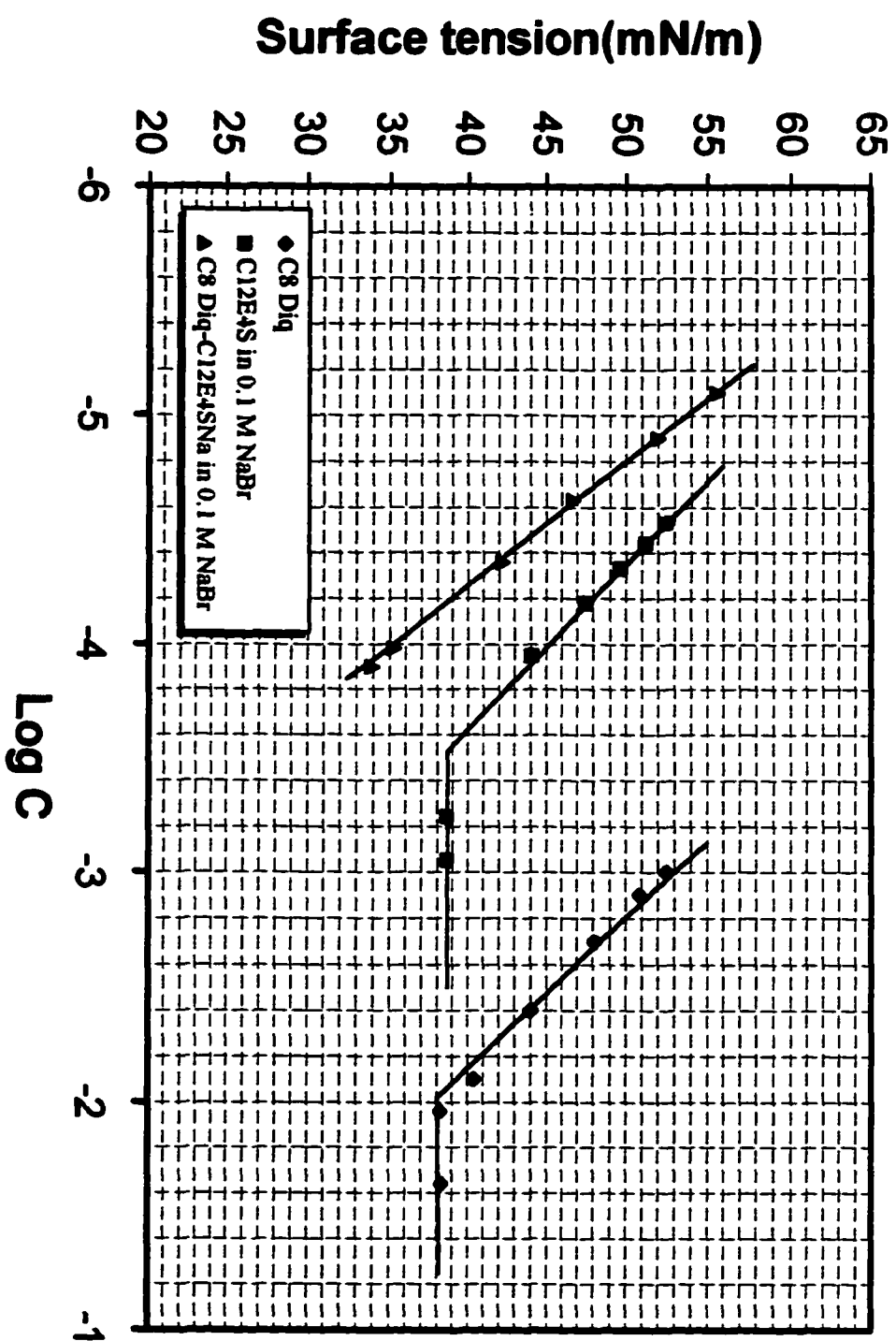


Figure 10: $(C_8N)_2(OH)_2$ $C_{12}E_4SO_3Na$ in 0.1 M NaBr at $\alpha=0.686$ at 25°C

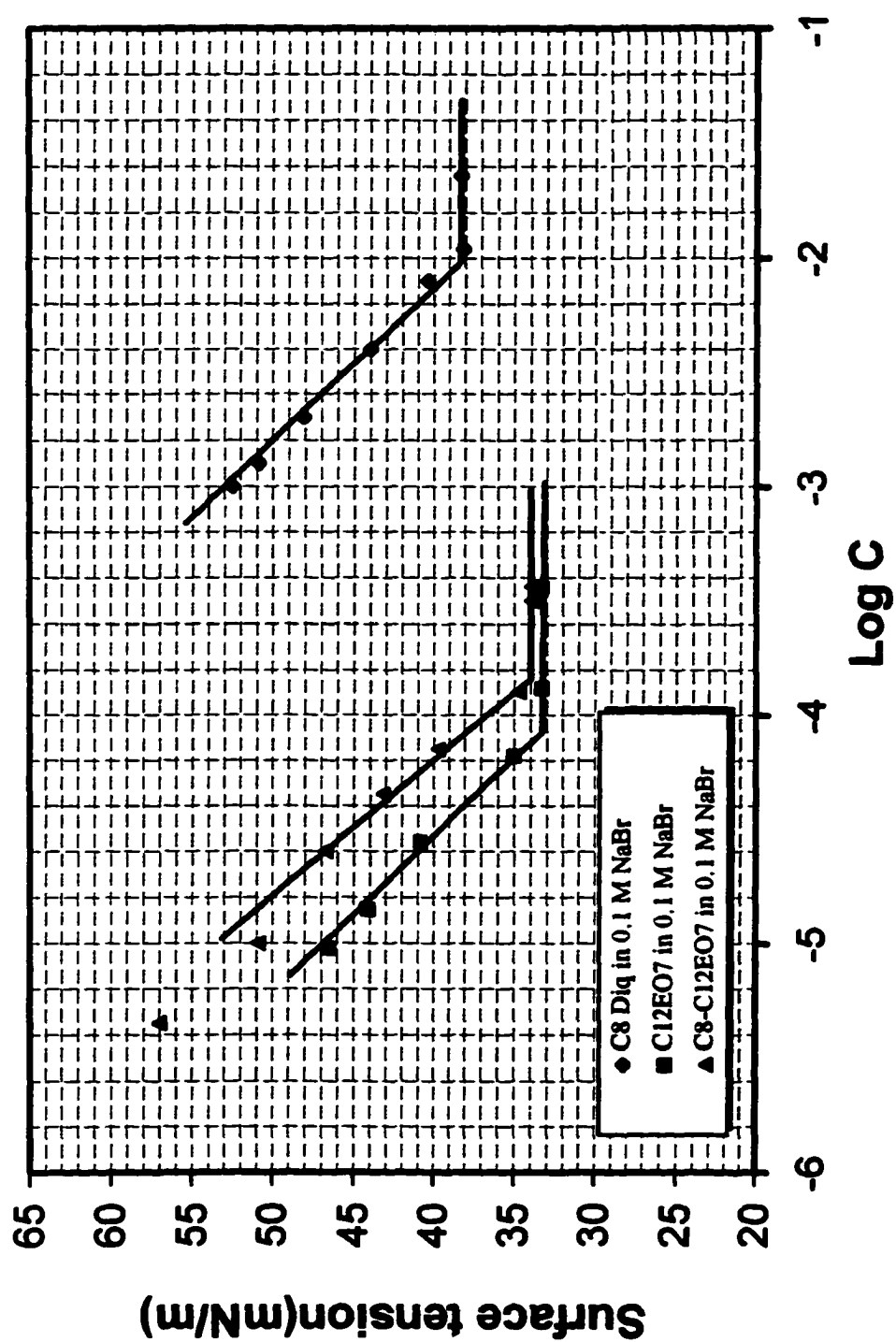


Figure 11: $(C_8N)_2(OH)_2$ $C_{12}EO_7$ in 0.1 M NaBr at $\alpha=0.50$ at 25°C

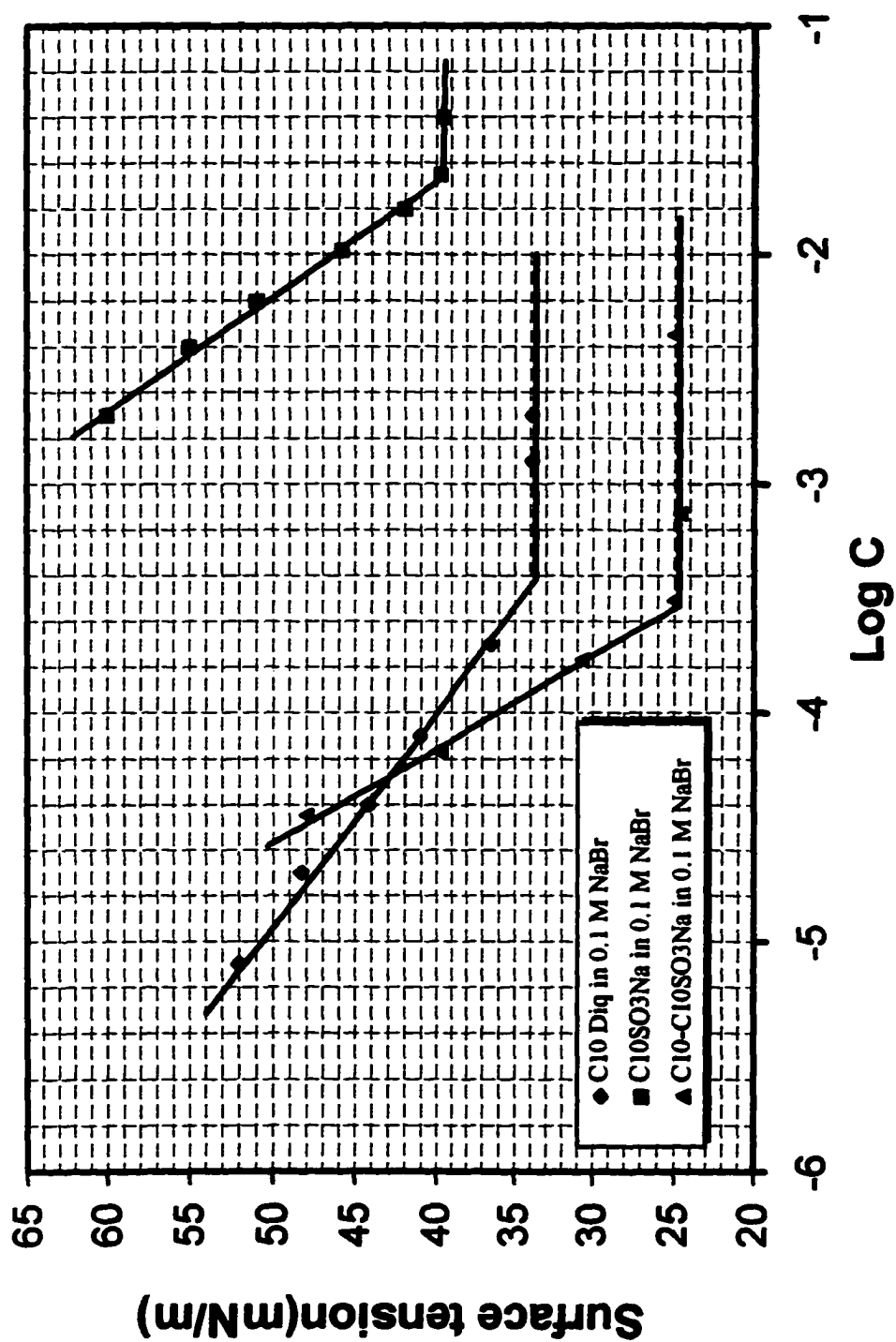


Figure 12: $(C_{10}N)_2(OH)_2 - C_{10}SO_3Na$ in 0.1 M NaBr at $\alpha=0.017$ at 25°C

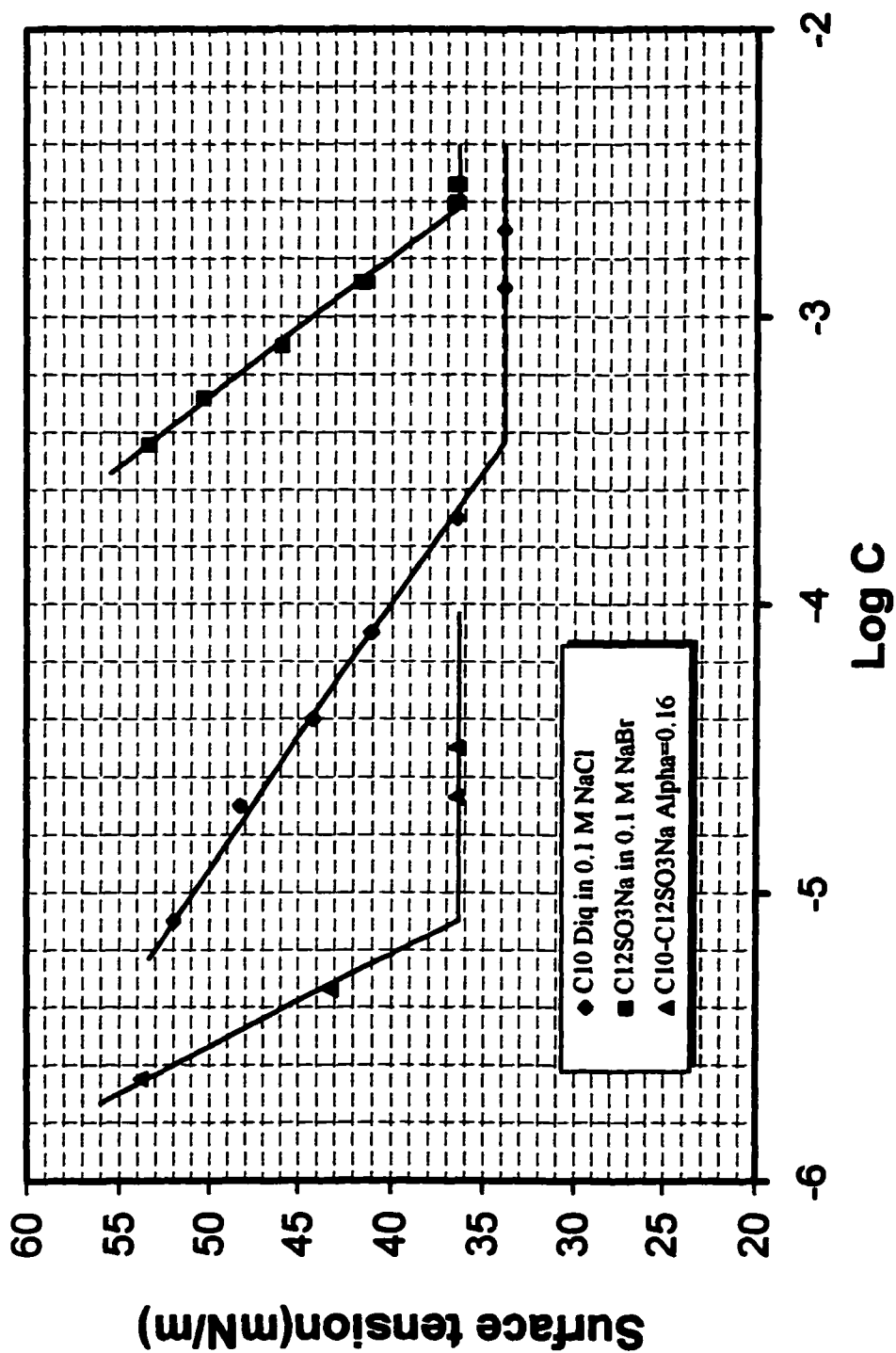


Figure 13: $(C_{10}N)_2(OH)_2-C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha=0.16$ at 25°C

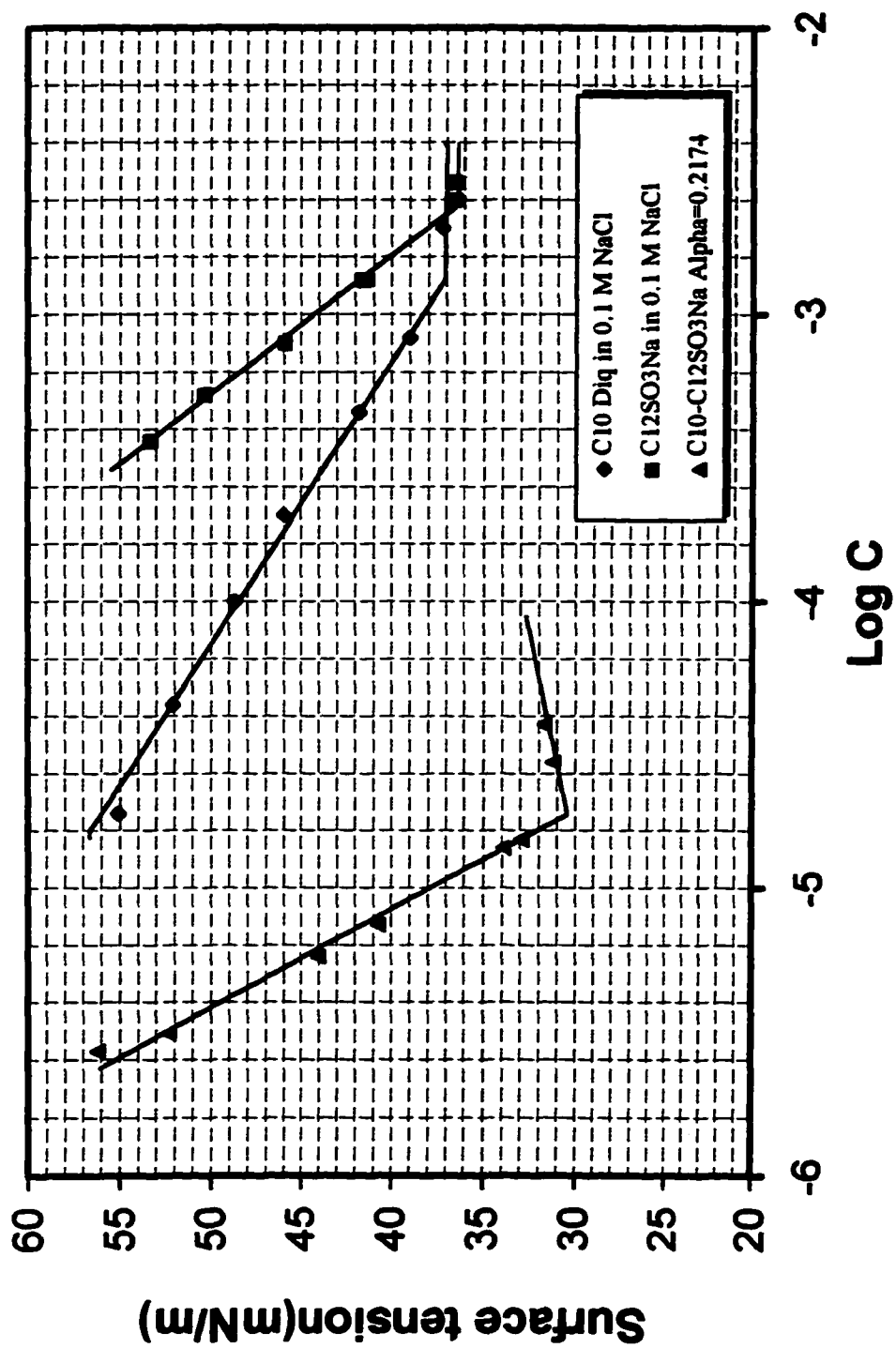


Figure 14: $(C_{10}N)_2(OH)_2 - C_{12}SO_3Na$ in 0.1 M NaCl at $\alpha=0.2174$ at $25^\circ C$

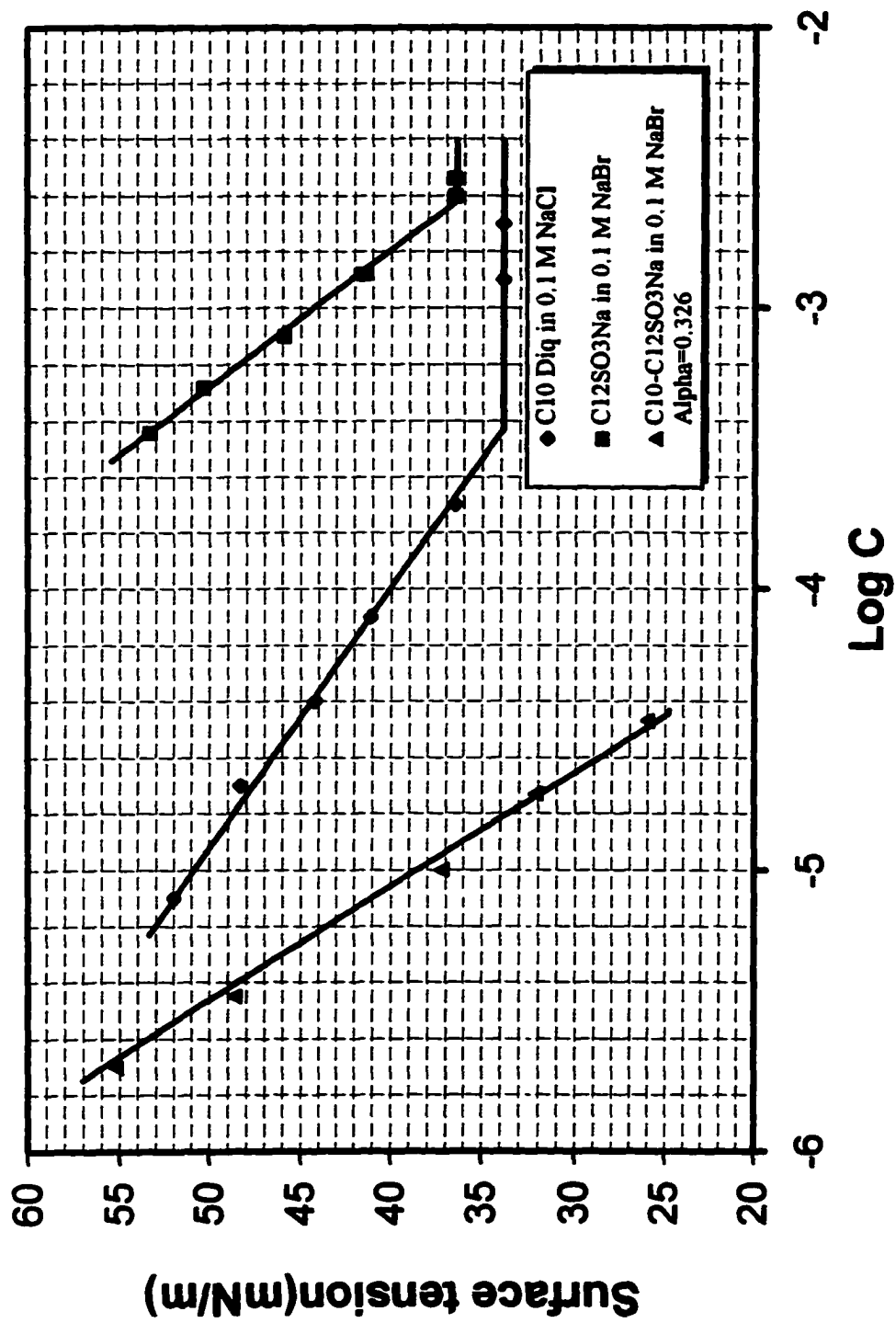


Figure 15: $(C_{10}N)_2 - C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha=0.326$ at $25^\circ C$

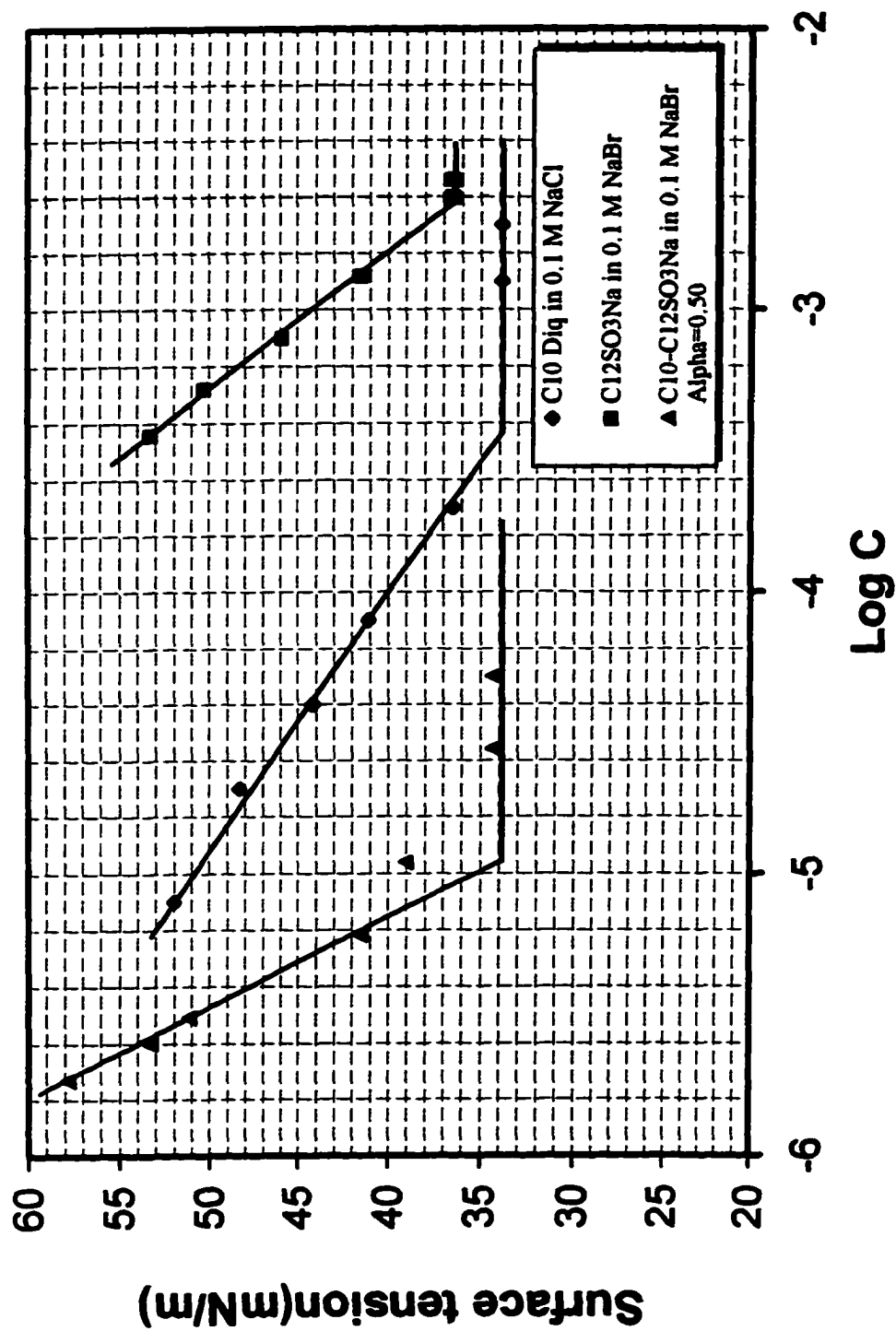


Figure 16: $(C_{10}N)_2(OH)_2 - C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha=0.50$ at $25^\circ C$

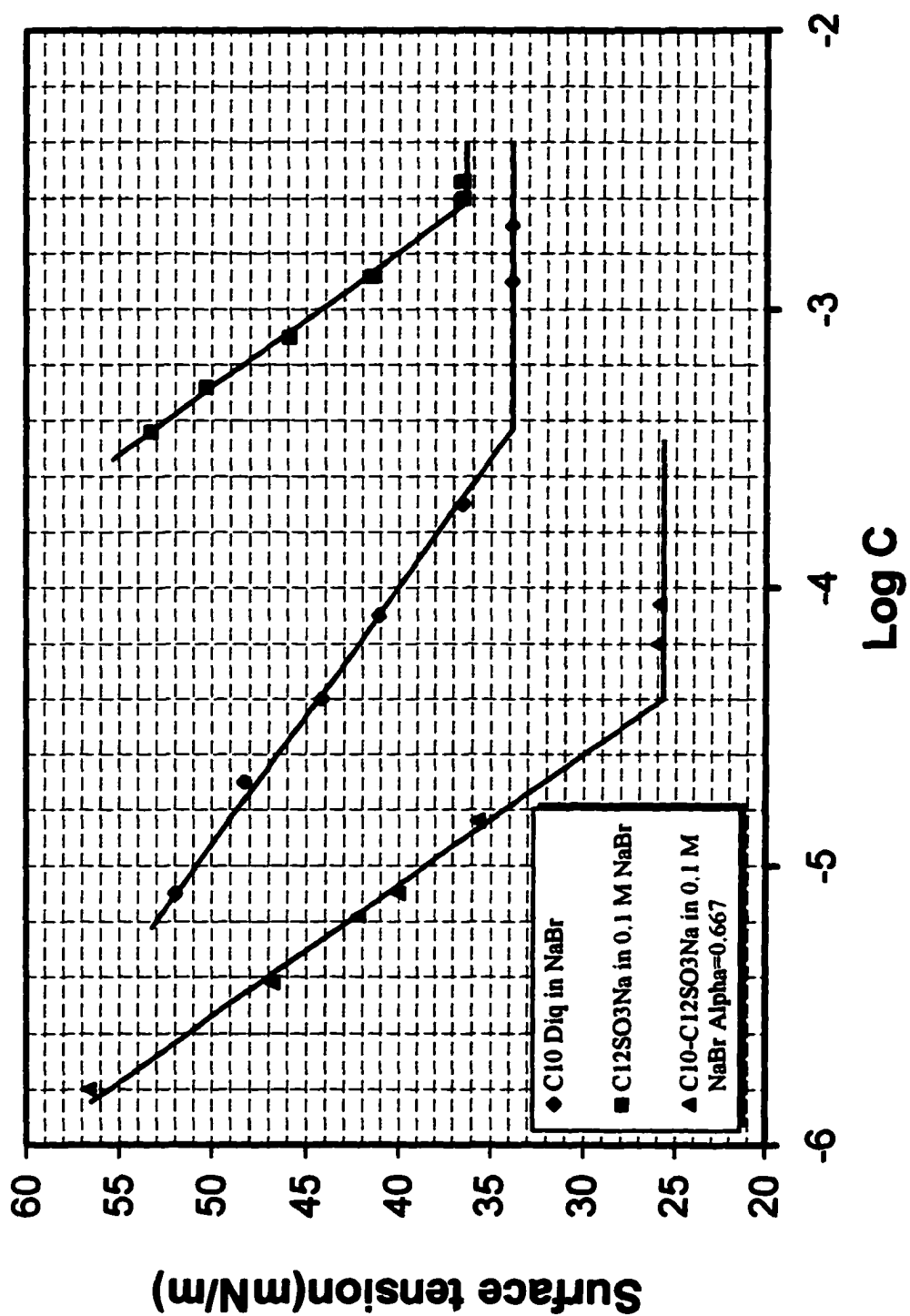


Figure 17: $(C_{10}N)_2(OH)_2 - C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha=0.667$ at $25^\circ C$

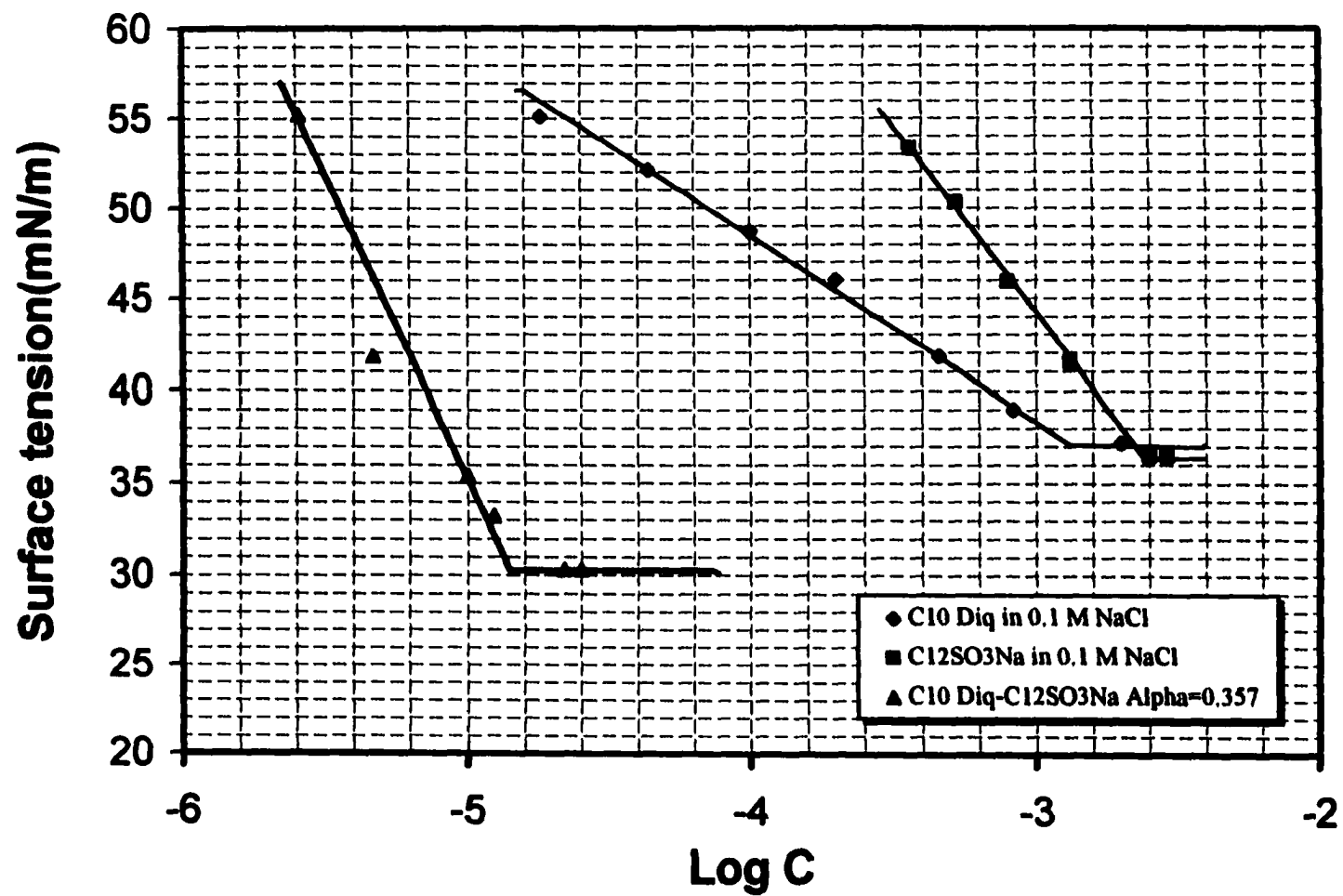


Figure 18: $(C_{10}N)_2(OH)_2$ - $C_{12}SO_3Na$ in 0.1 M NaCl at $\alpha=0.357$ at 25°C

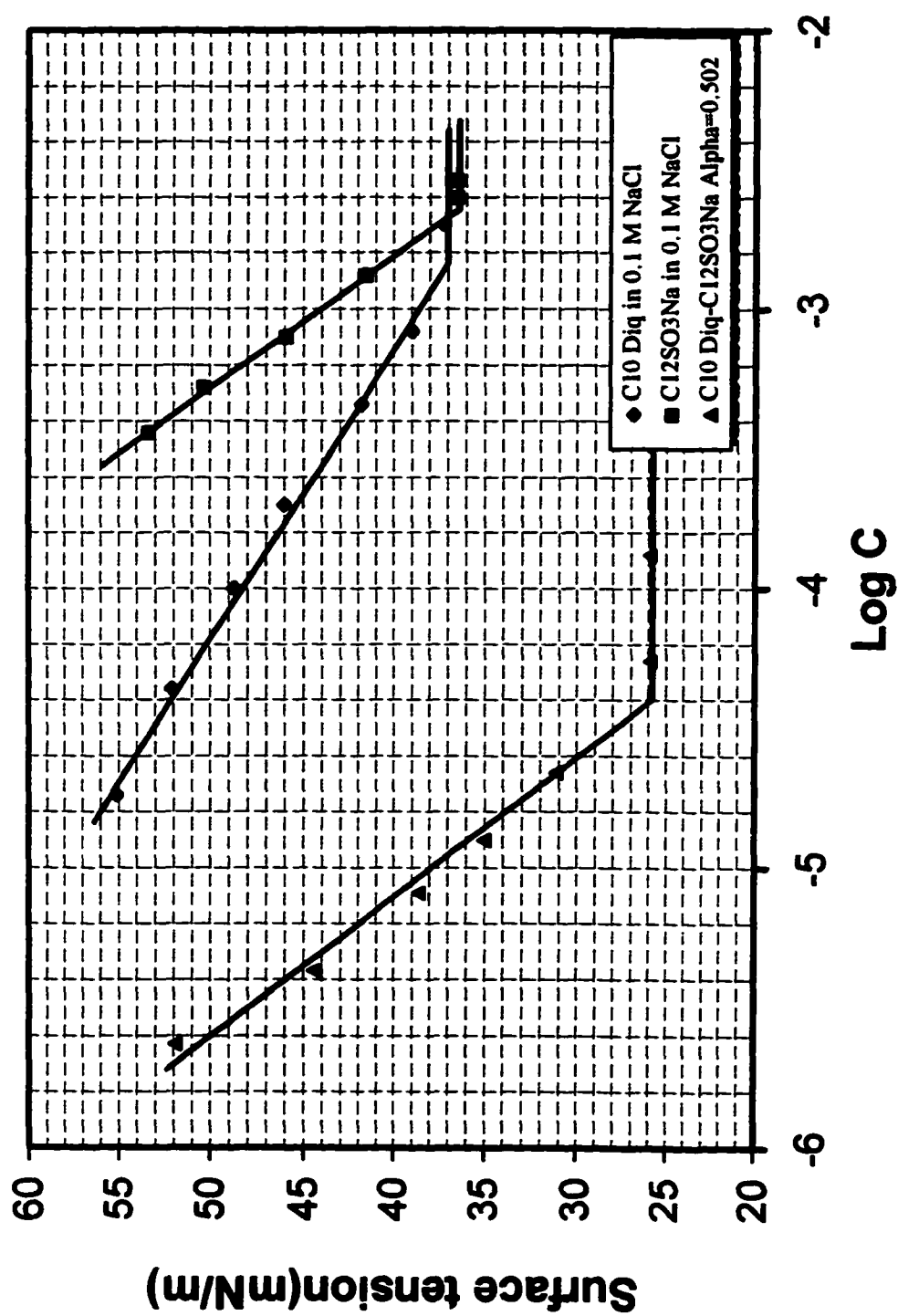


Figure 19: $(C_{10}N)_2(OH)_2 - C_{12}SO_3Na$ in 0.1 M NaCl at $\alpha=0.502$ at 25°C

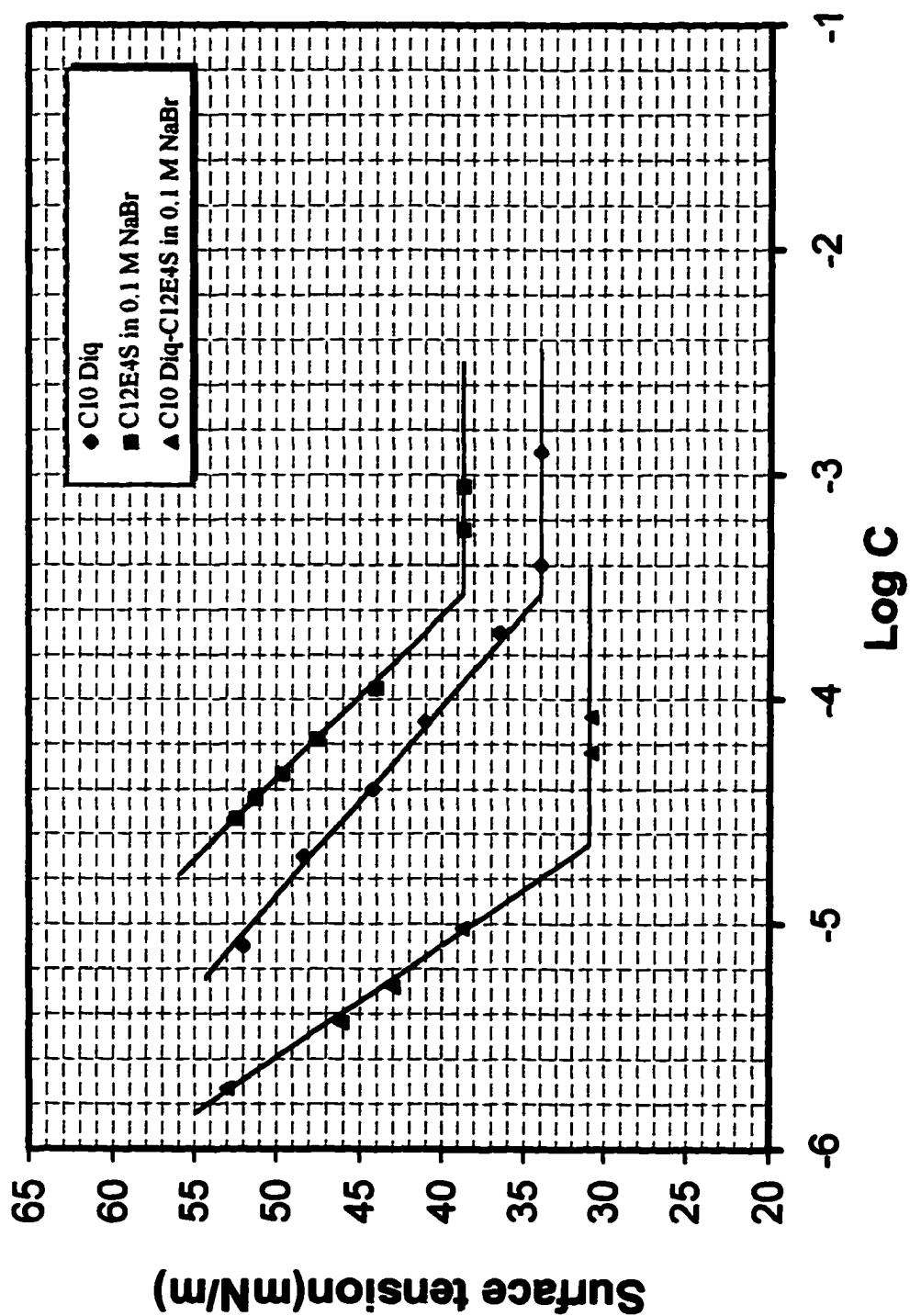


Figure 20: $(C_{10}N)_2(OH)_2-C_{12}E_4SO_4Na$ in 0.1 M NaBr at $\alpha=0.522$ at $25^\circ C$

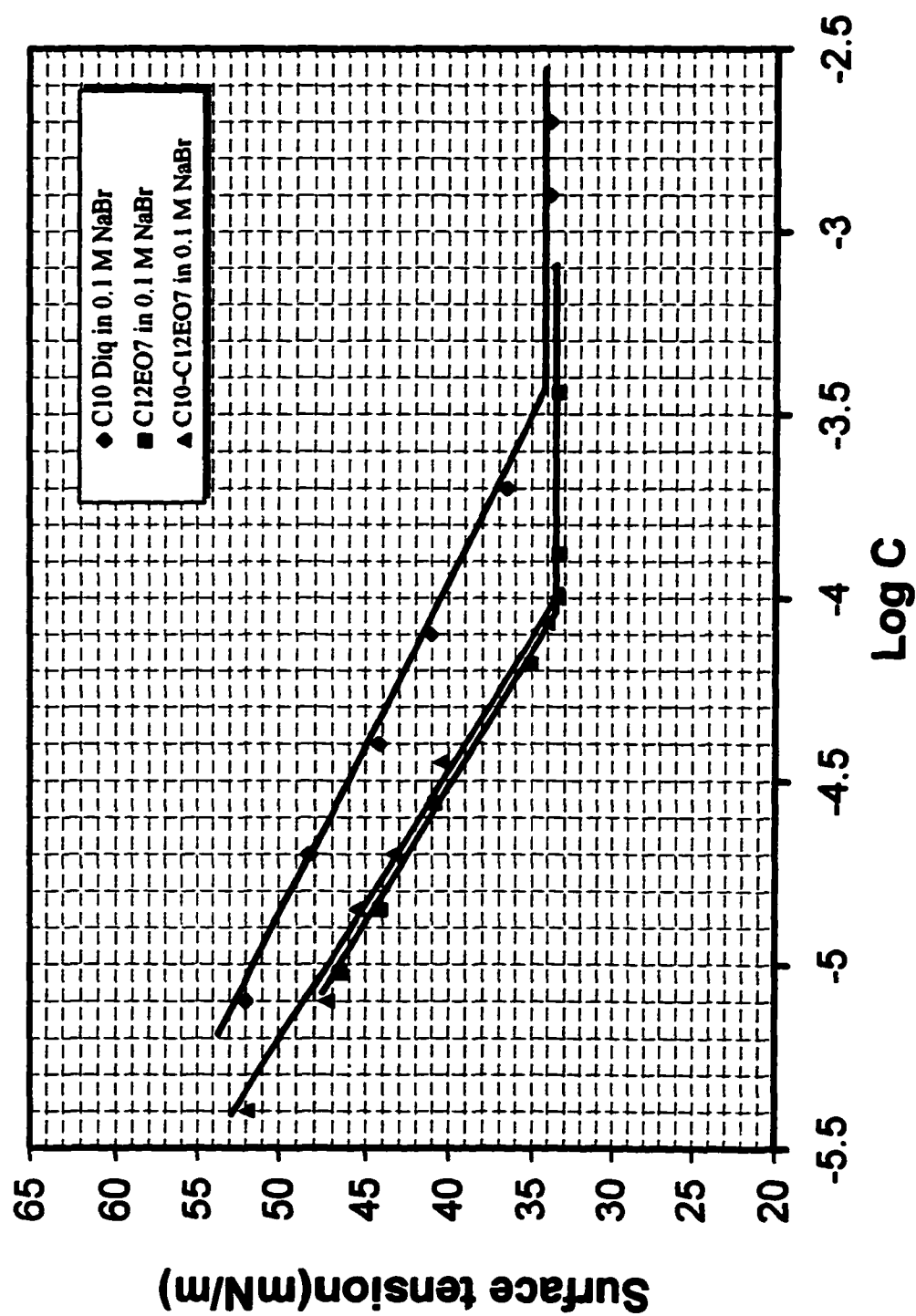


Figure 21: $(C_{10}N)_2(OH)_2-C_{12}EO_7$ in 0.1 M NaBr at $\alpha=0.344$ at 25°C

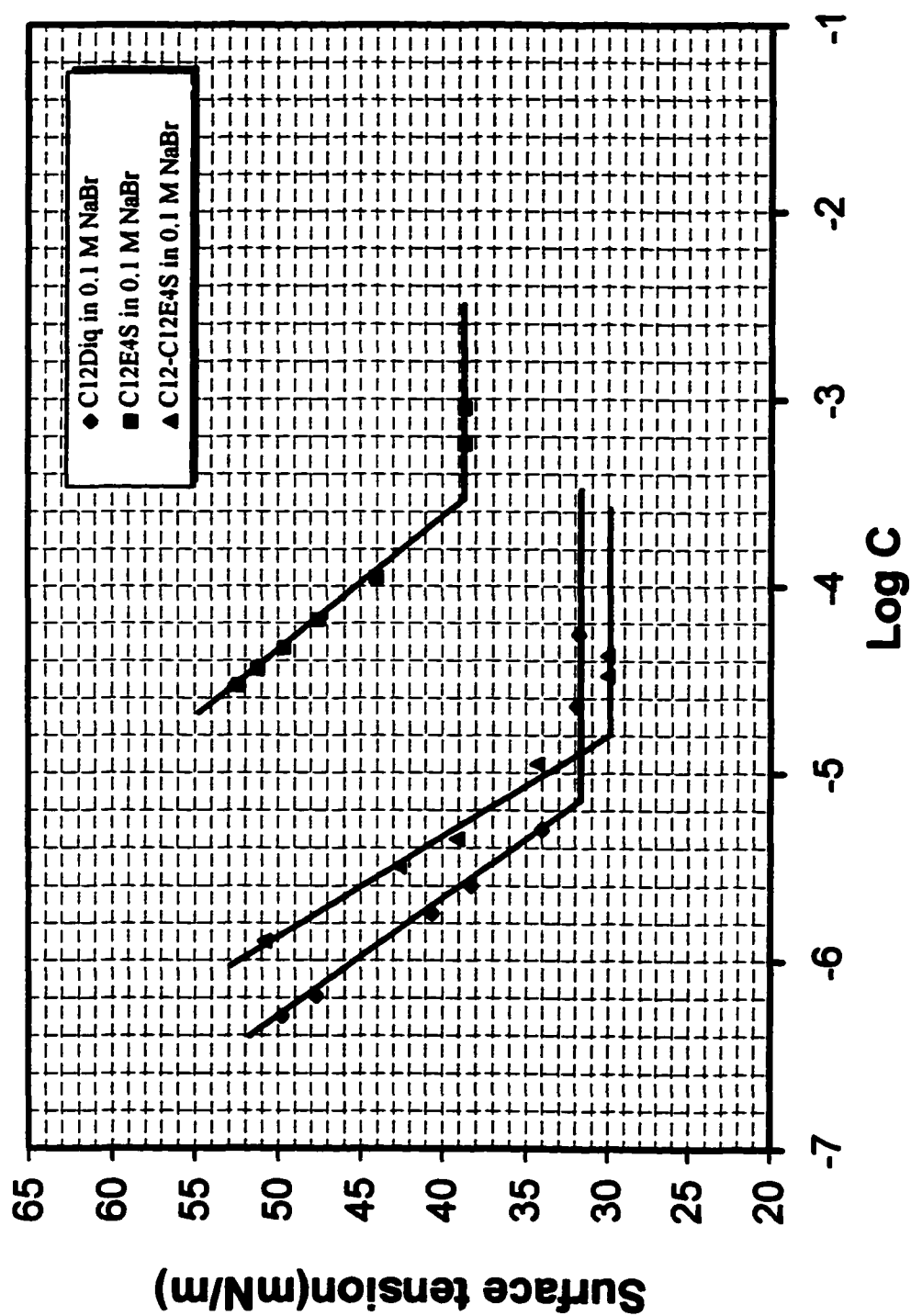


Figure 22: $(C_{12})_2(OH)_2-C_{12}E_4SO_4Na$ in 0.1 M NaBr at $\alpha=0.174$ at $25^\circ C$

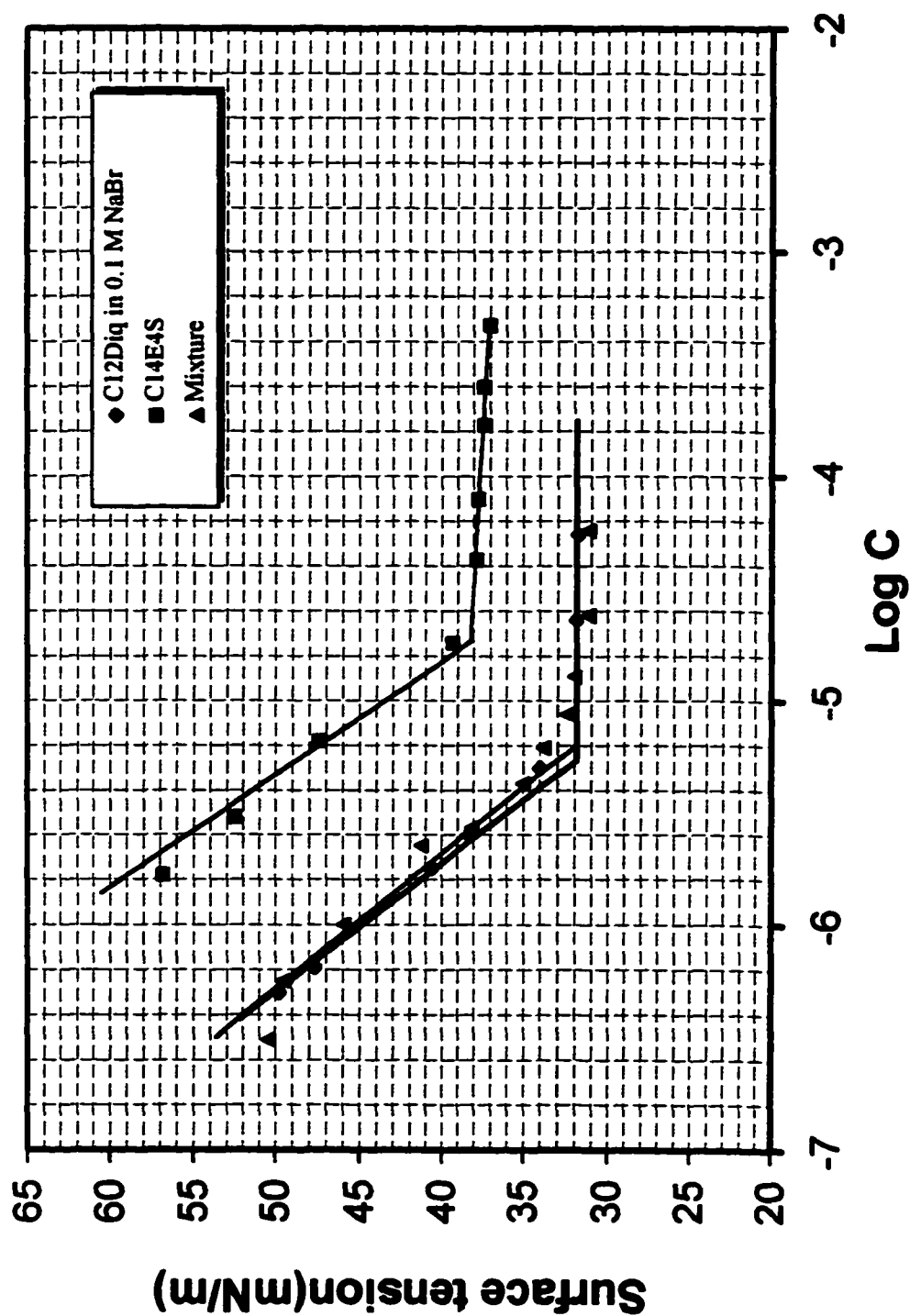


Figure 23: $(C_{12}N)_2(OH)_2-C_{14}E_4SO_4Na$ in 0.1 M NaBr at $\alpha=0.175$ (pH=8.3) at 25°C

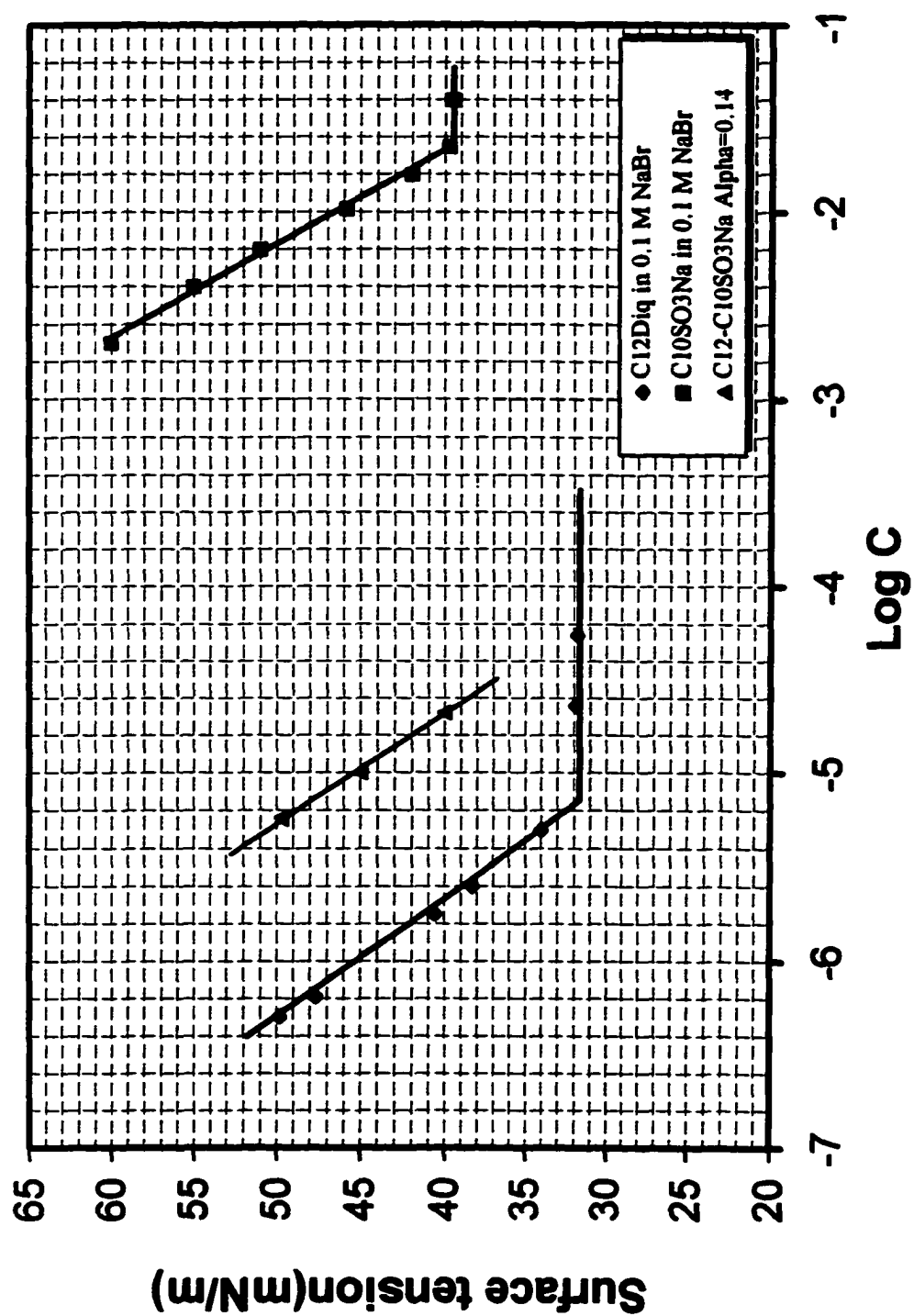


Figure 24: $(C_{12}N)_2(OH)_2-C_{10}SO_3Na$ in 0.1 M NaBr at $\alpha=0.14$ at 25°C

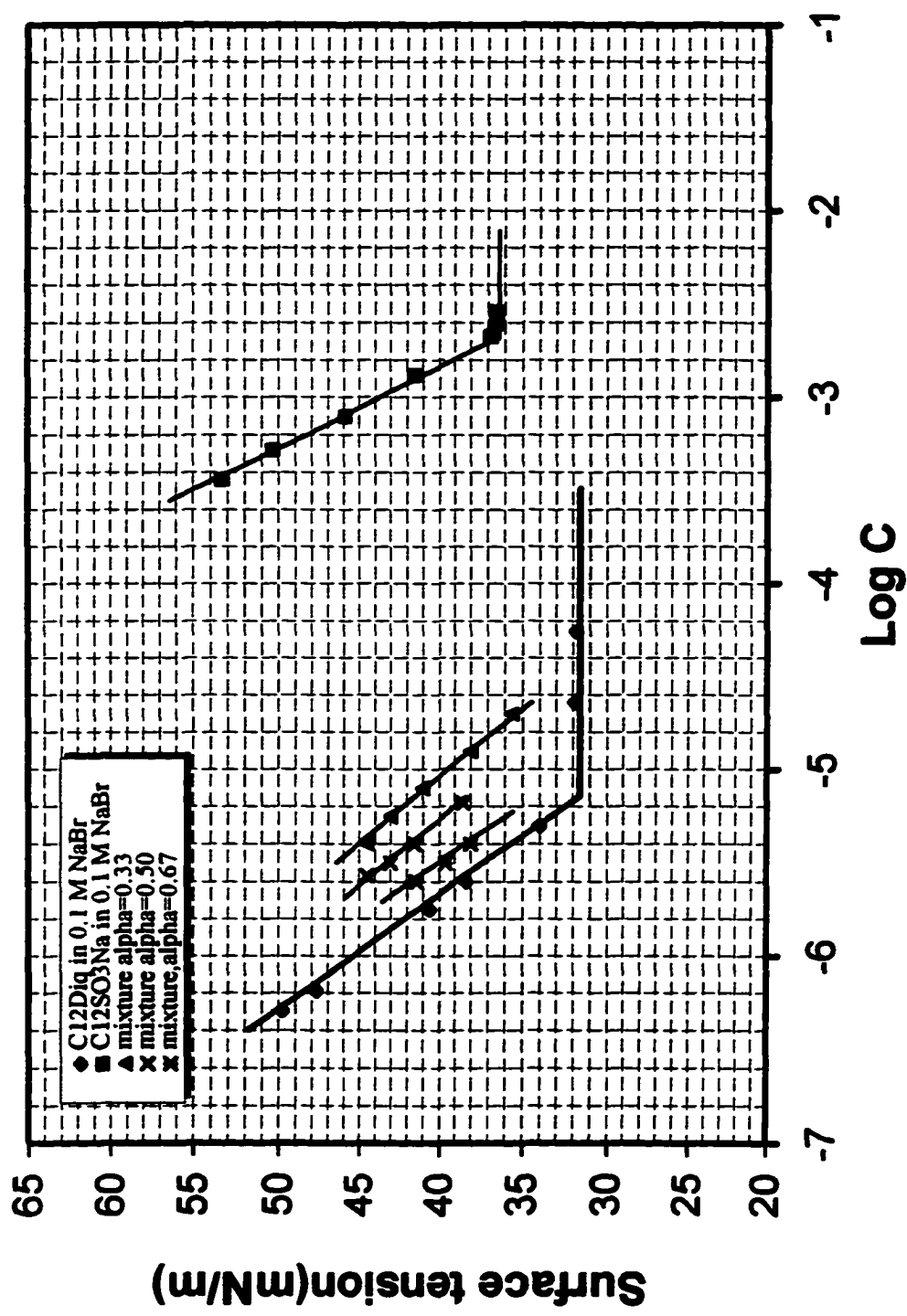


Figure 25: $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ in 0.1 M NaBr at $\alpha=0.33, 0.50, 0.67$ (A=67, 64, 63) at 25°C

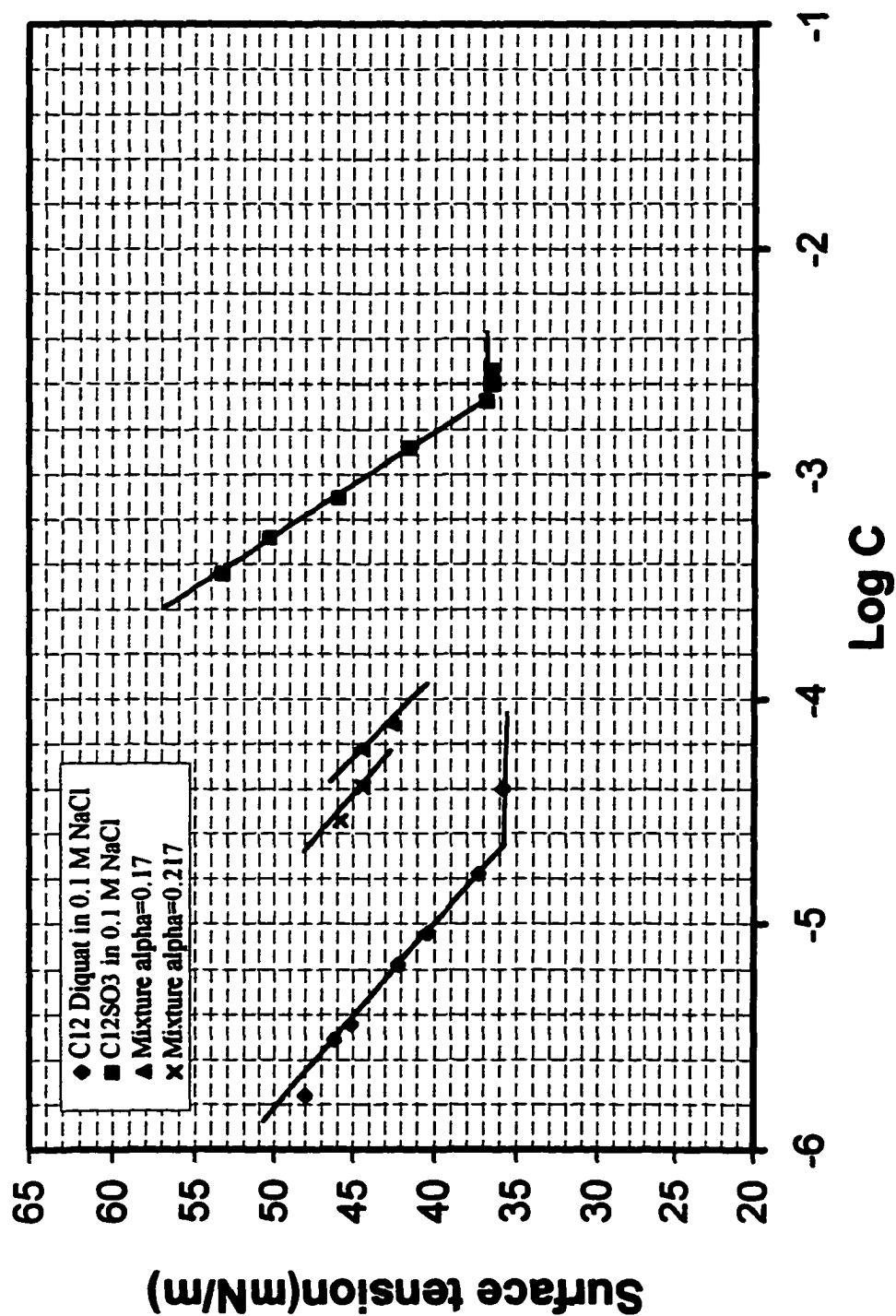


Figure 26: $(C_{12}N)_2(OH)_2$ - $C_{12}SO_3Na$ in 0.1 M NaCl at $\alpha = 0.17, 0.27$ at 25°C

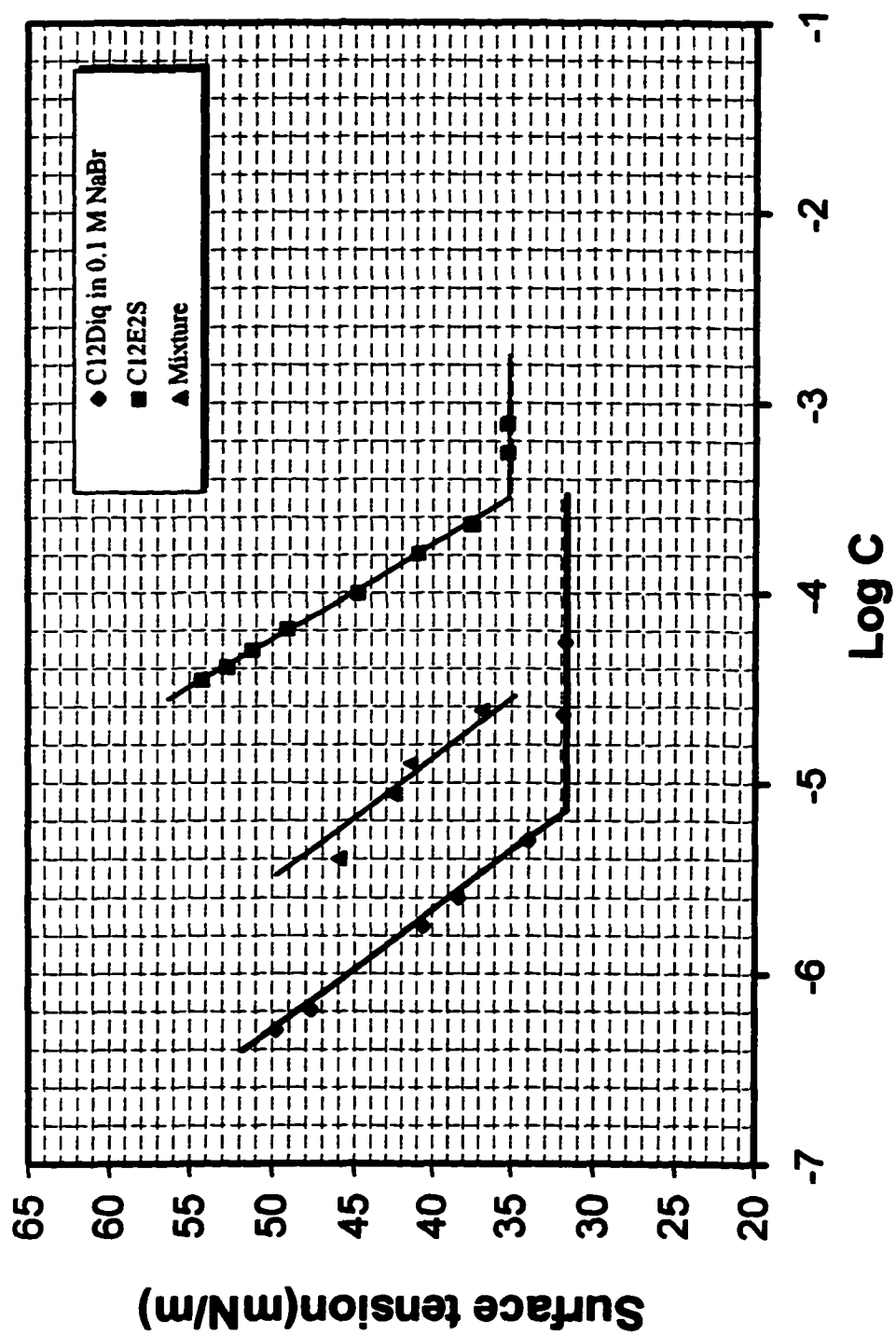
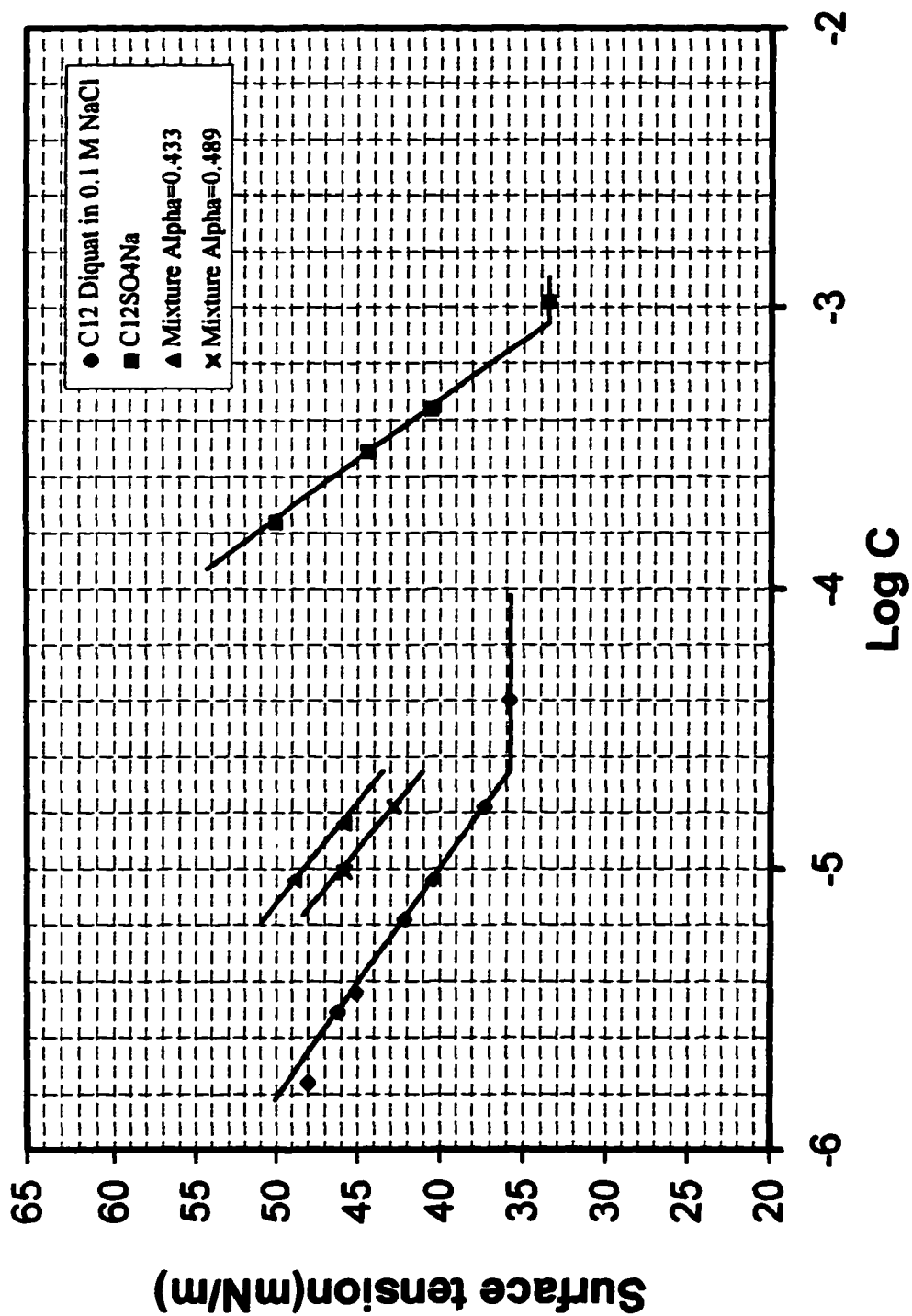


Figure 27: $(C_{12}N)_2(OH)_2$ - $C_{12}E_2SO_4Na$ in 0.1 M NaBr at $\alpha=0.167$ (pH=8.3) at 25°C



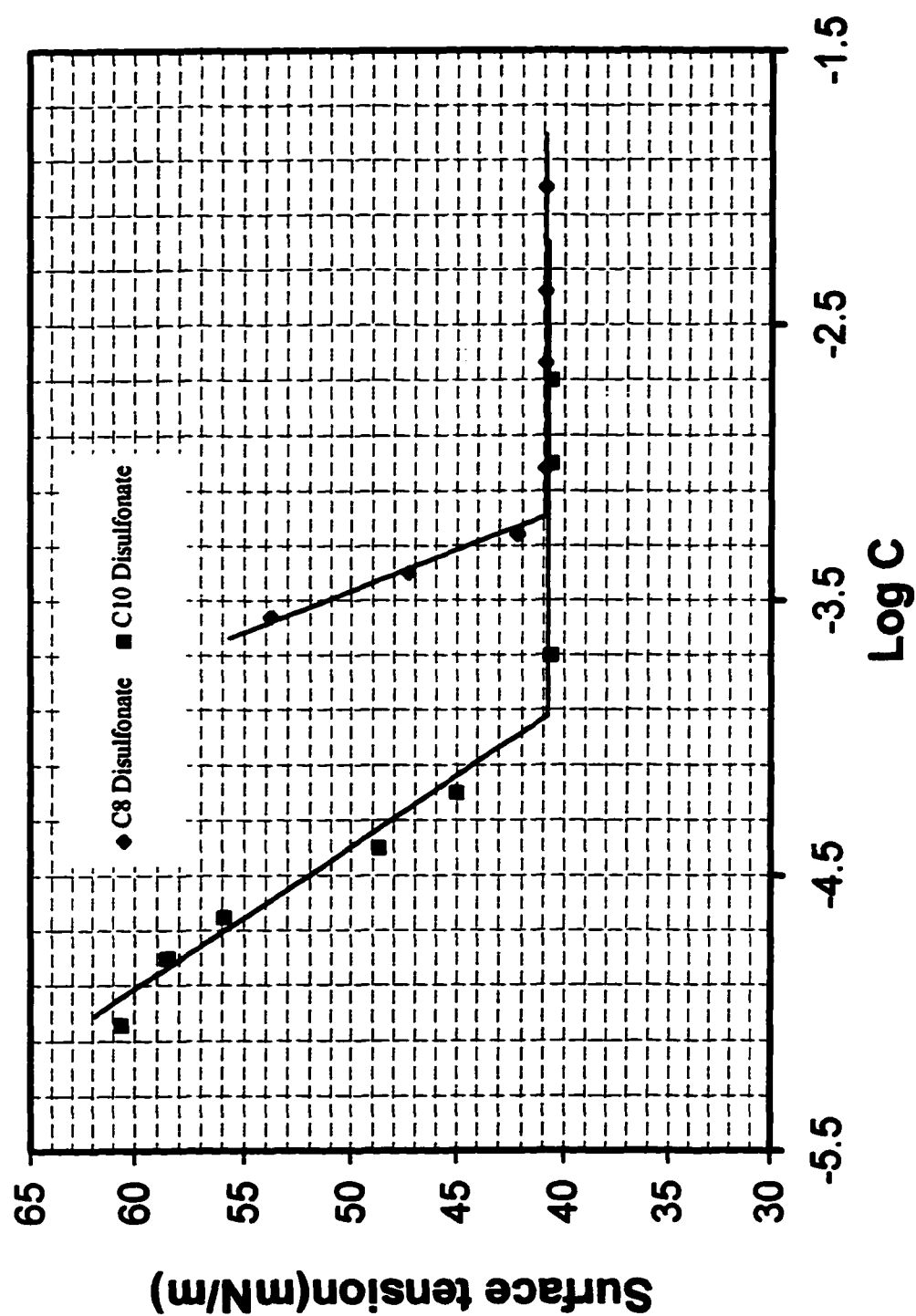


Figure 29: Surface Tension - Log C Plot of $(C_nSO_3Na)_2(CH_2)_2$ Disulfonate in H_2O at $25^\circ C$

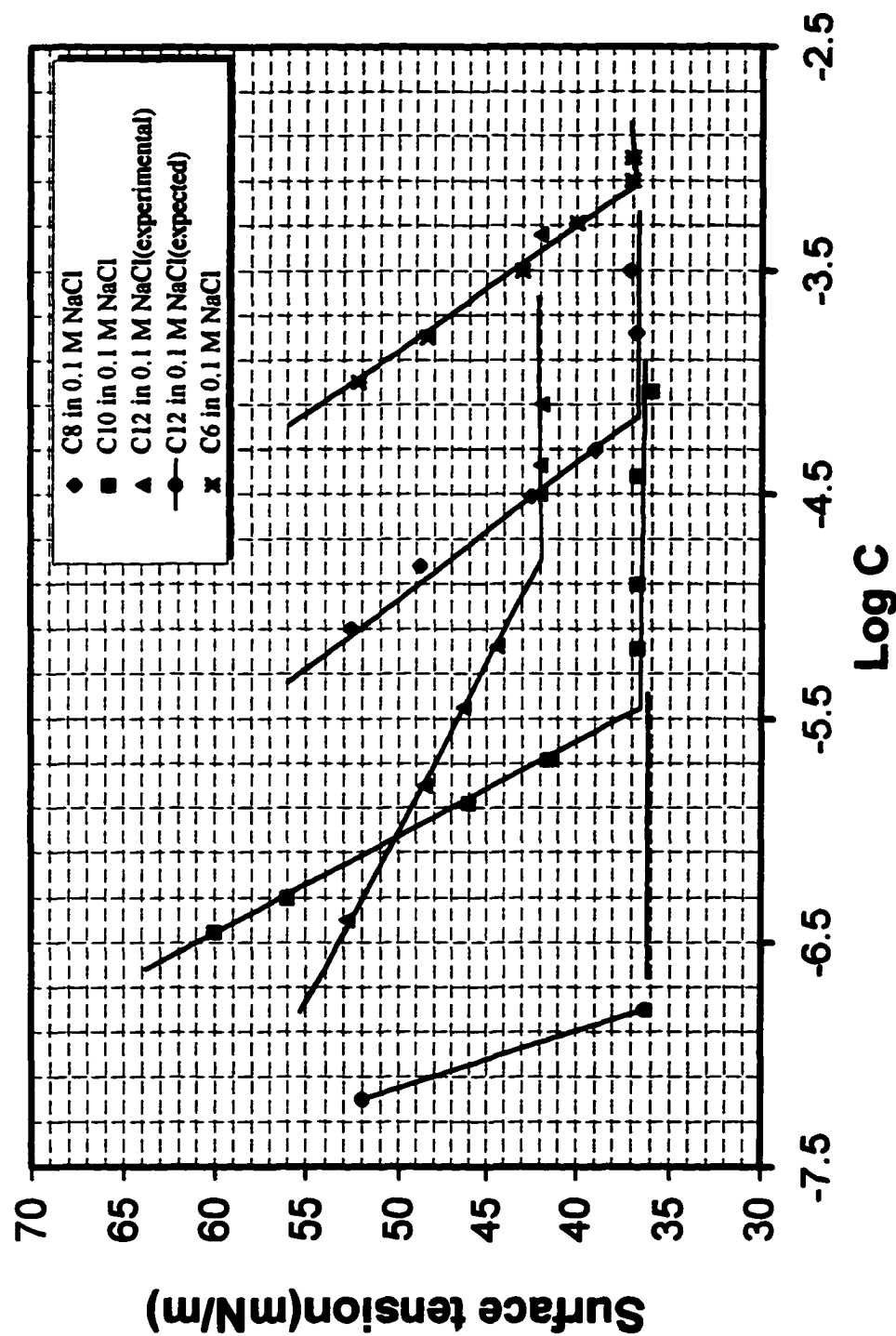


Figure 30: $(C_nSO_3Na)_2(CH_2)_2$, C_{12} (Expected) in 0.1 M NaCl at 25°C

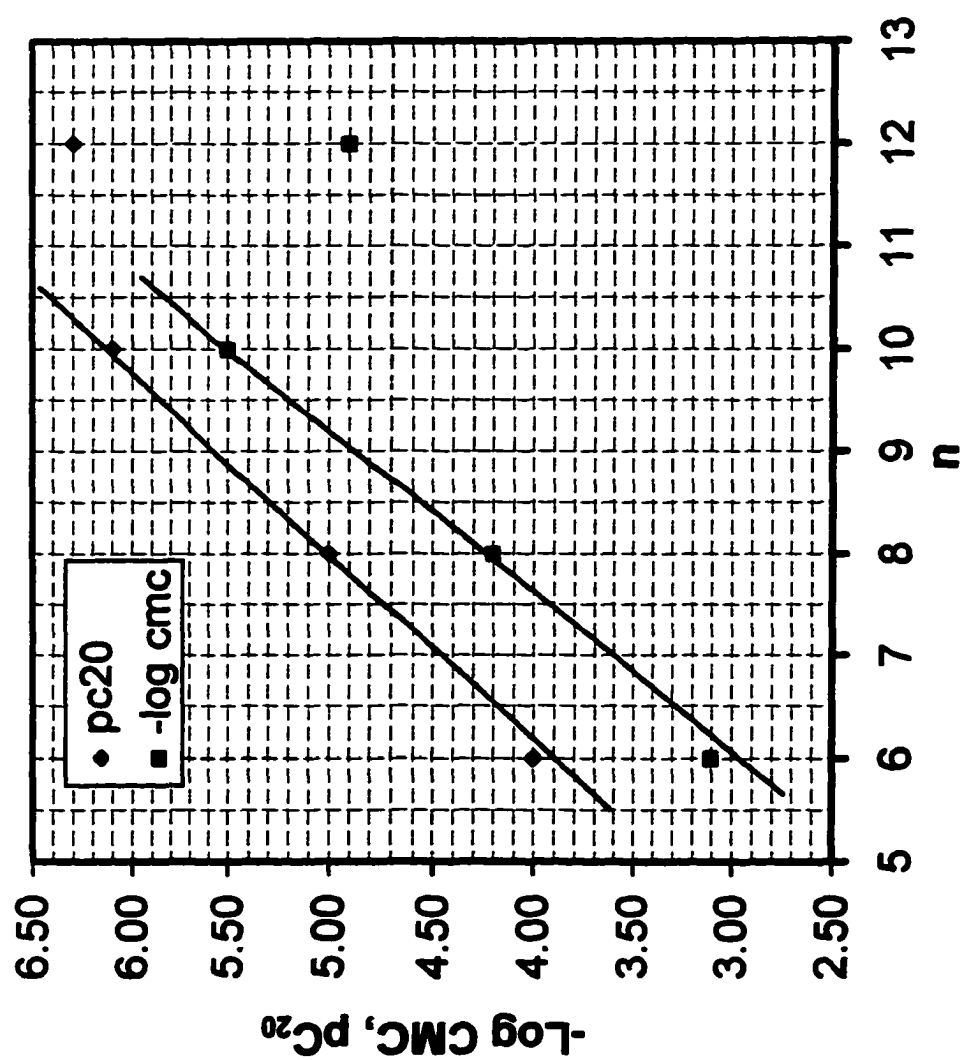


Figure 31: pc_{20} , $-\log \text{cmc}$ versus n plots of $(\text{C}_n\text{SO}_3\text{Na})_2(\text{CH}_2)_2$ series in 0.1 M NaCl at 25°C

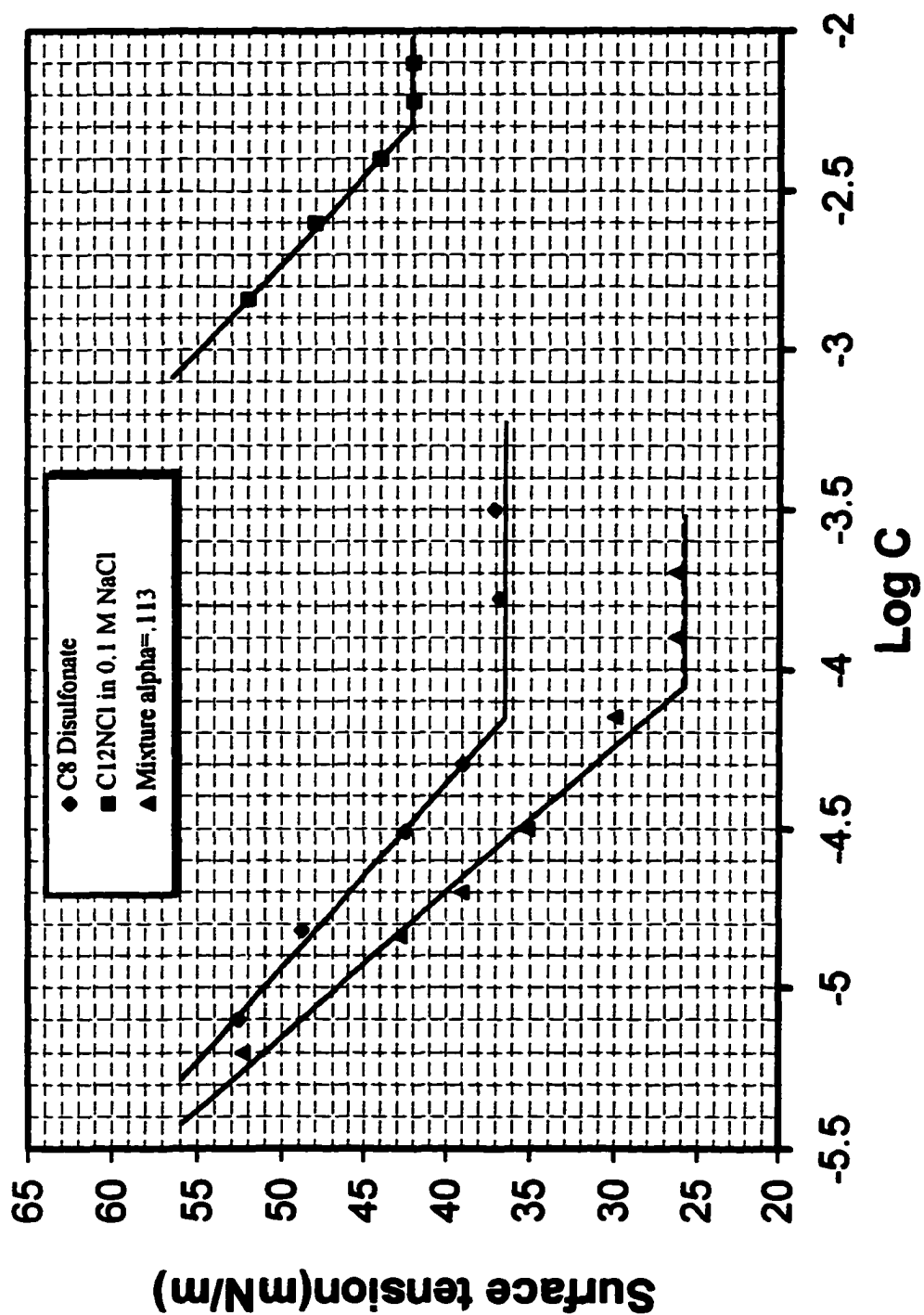
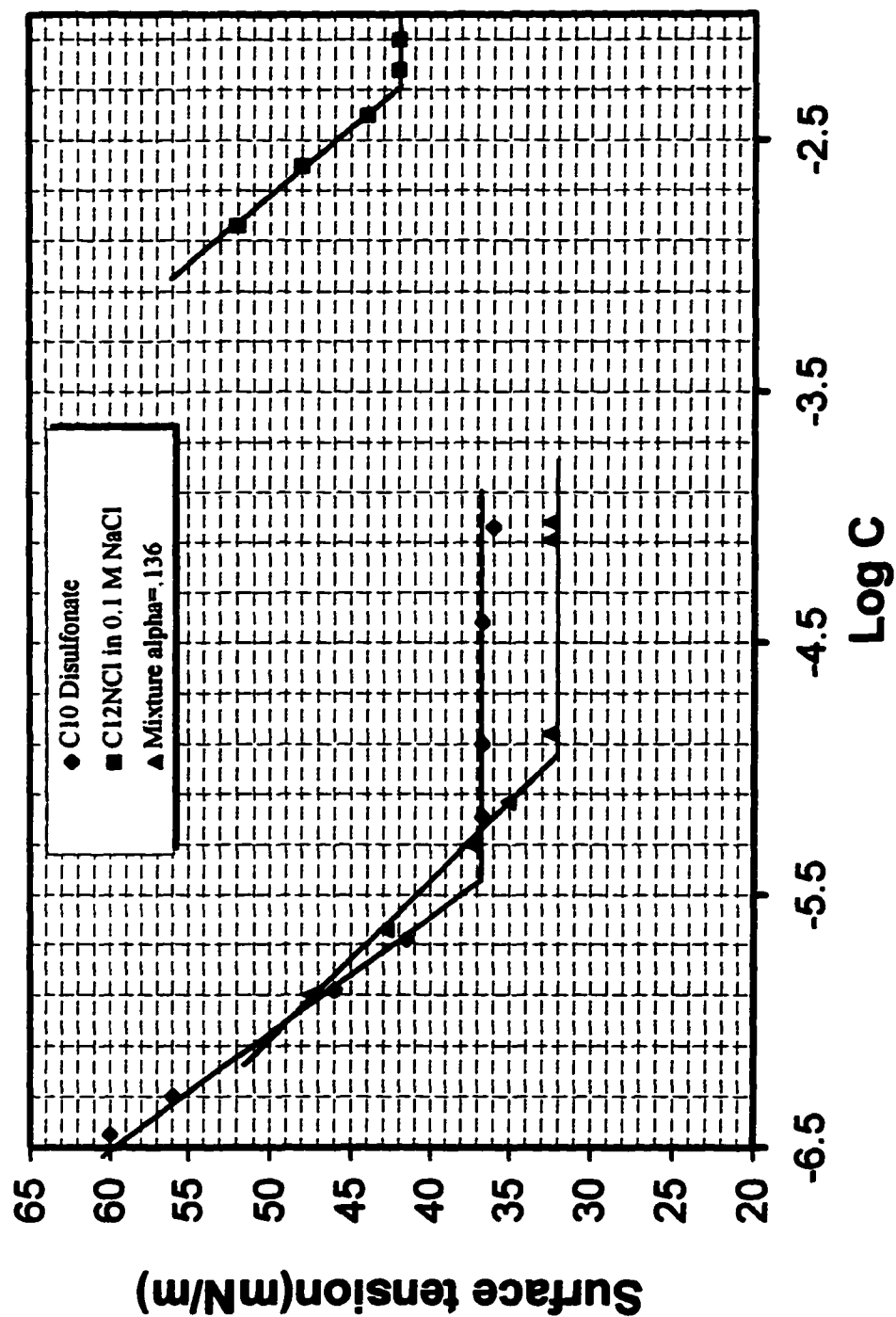


Figure 32: Interaction of $(C_8SO_3Na)_2(CH_2)_2$ with $C_{12}NCl$ in 0.1 M NaCl at 25°C



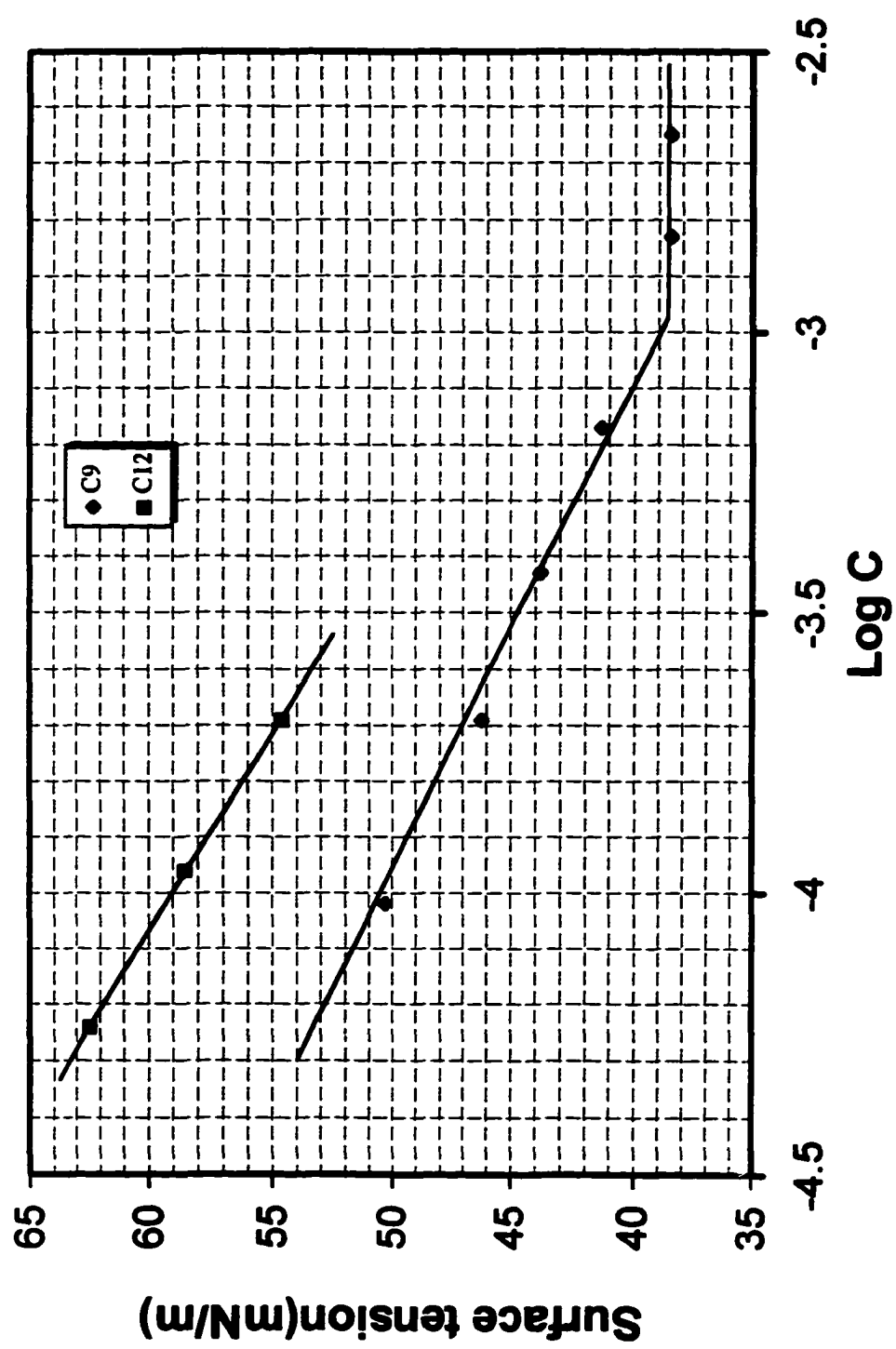


Figure 34: Surface Tension - Log C Plot of $(C_nArSO_3Na)_2CH_2$ in H_2O at $25^\circ C$

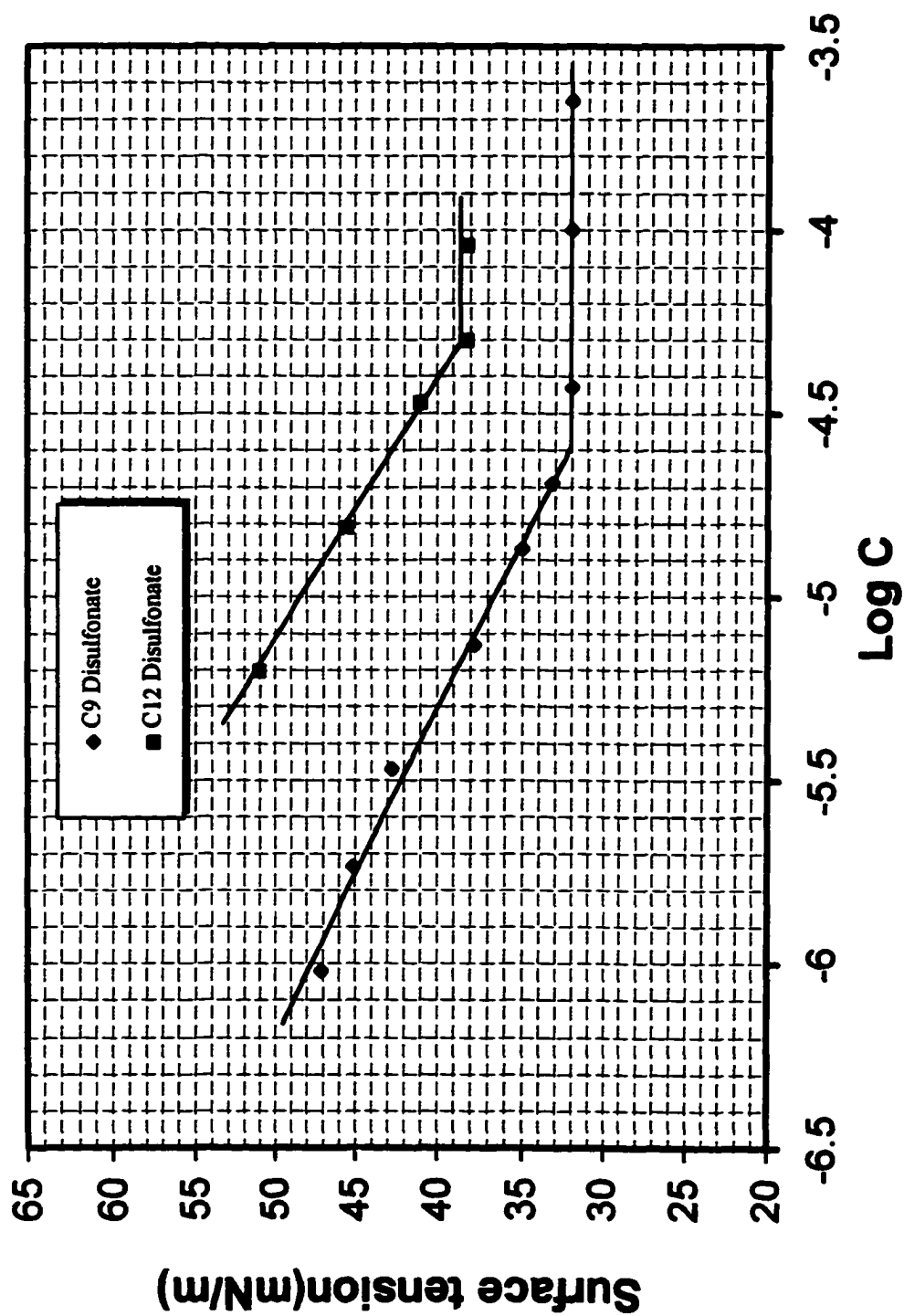


Figure 35: Surface Tension - Log C Plot of $(C_n\text{ArSO}_3\text{Na})_2\text{CH}_2$ in 0.1 M NaCl at 25°C

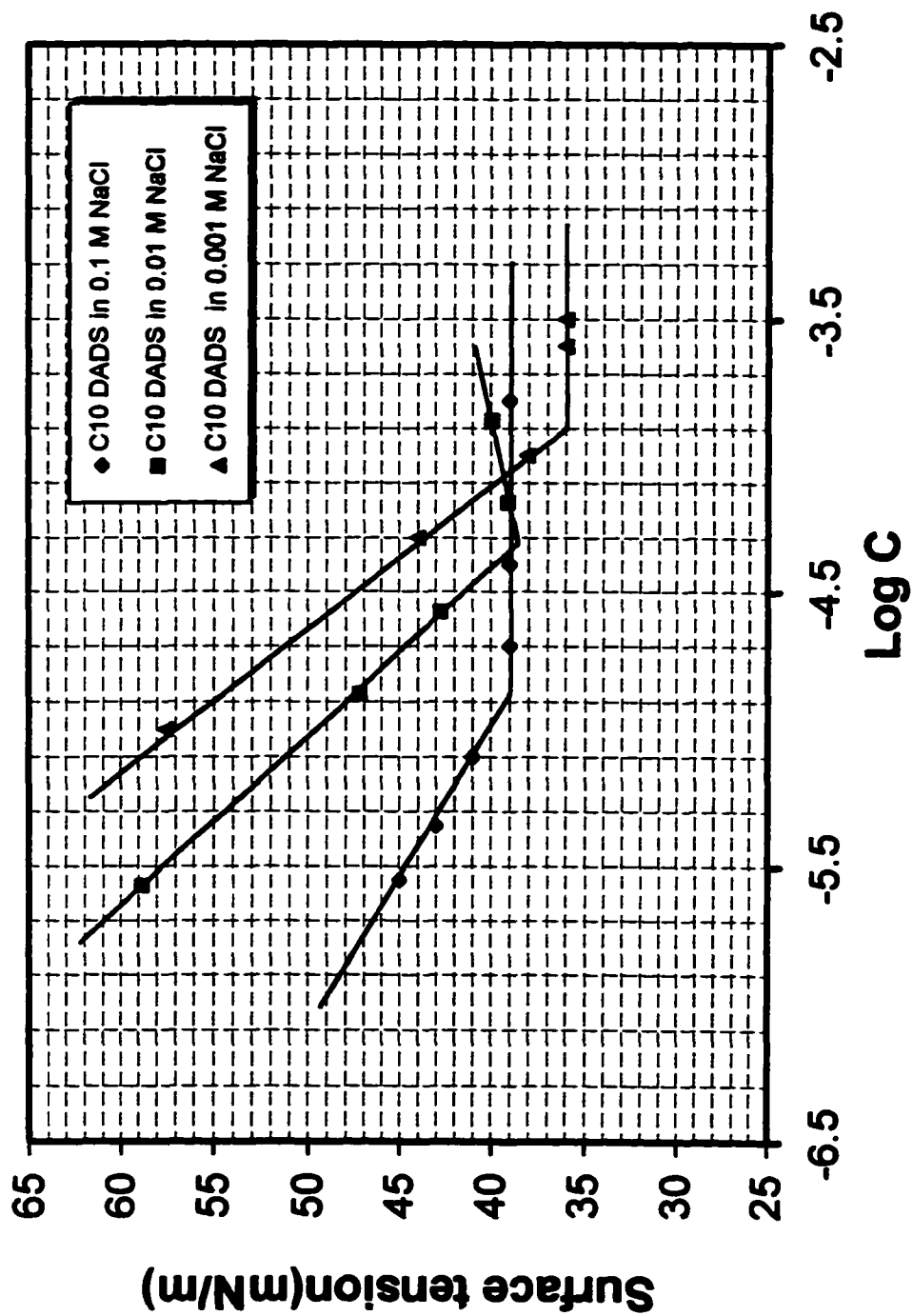


Figure 36: Surface Tension versus $\log C$ plots of $C_{10}DADS$ in NaCl at 25°C:

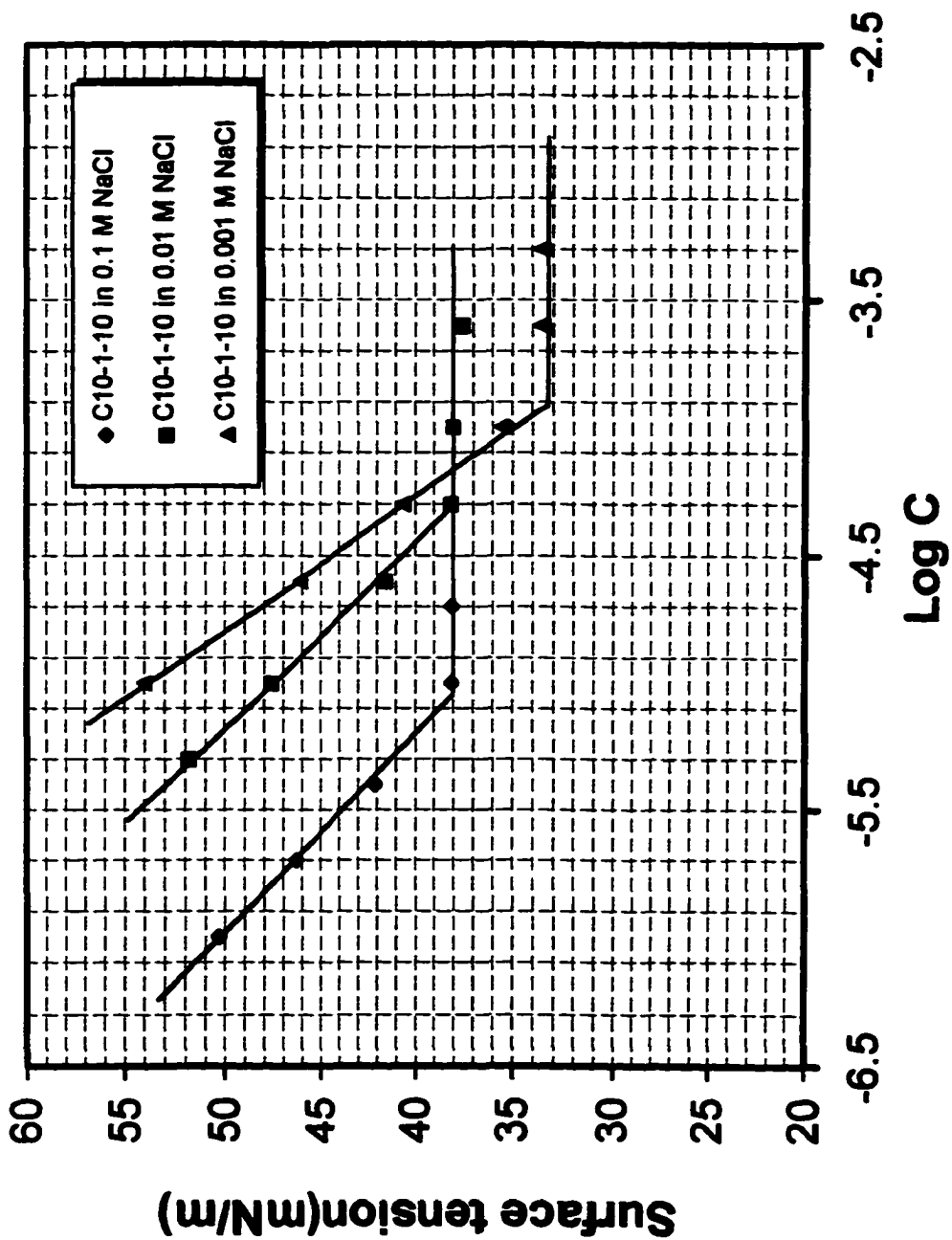


Figure 37: Surface Tension versus log C plots of C₁₀₋₁₋₁₀ in NaCl at 25°C:

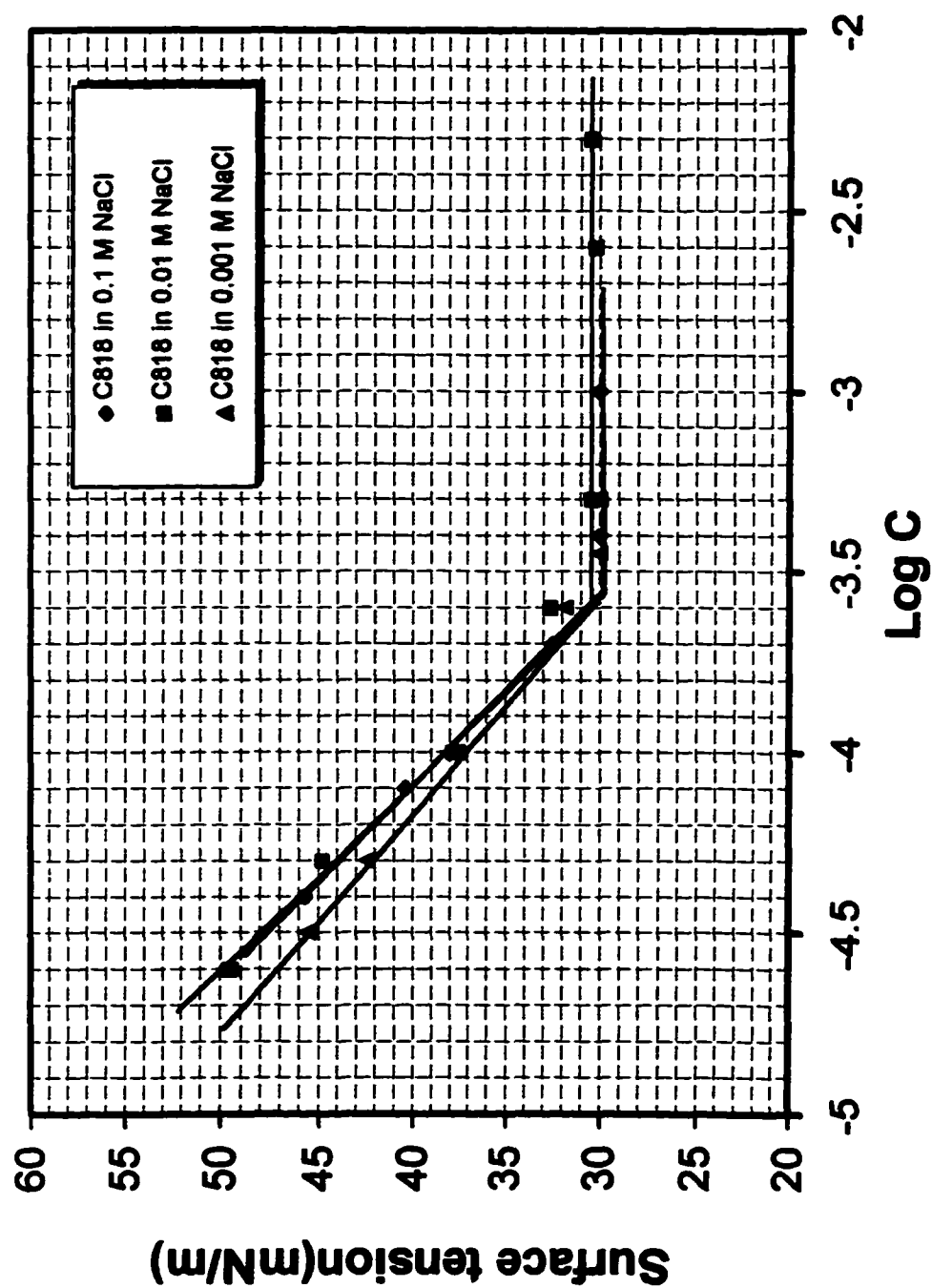


Figure 38: Surface Tension versus log C plots of C₈₋₁₋₈ in NaCl at 25°C

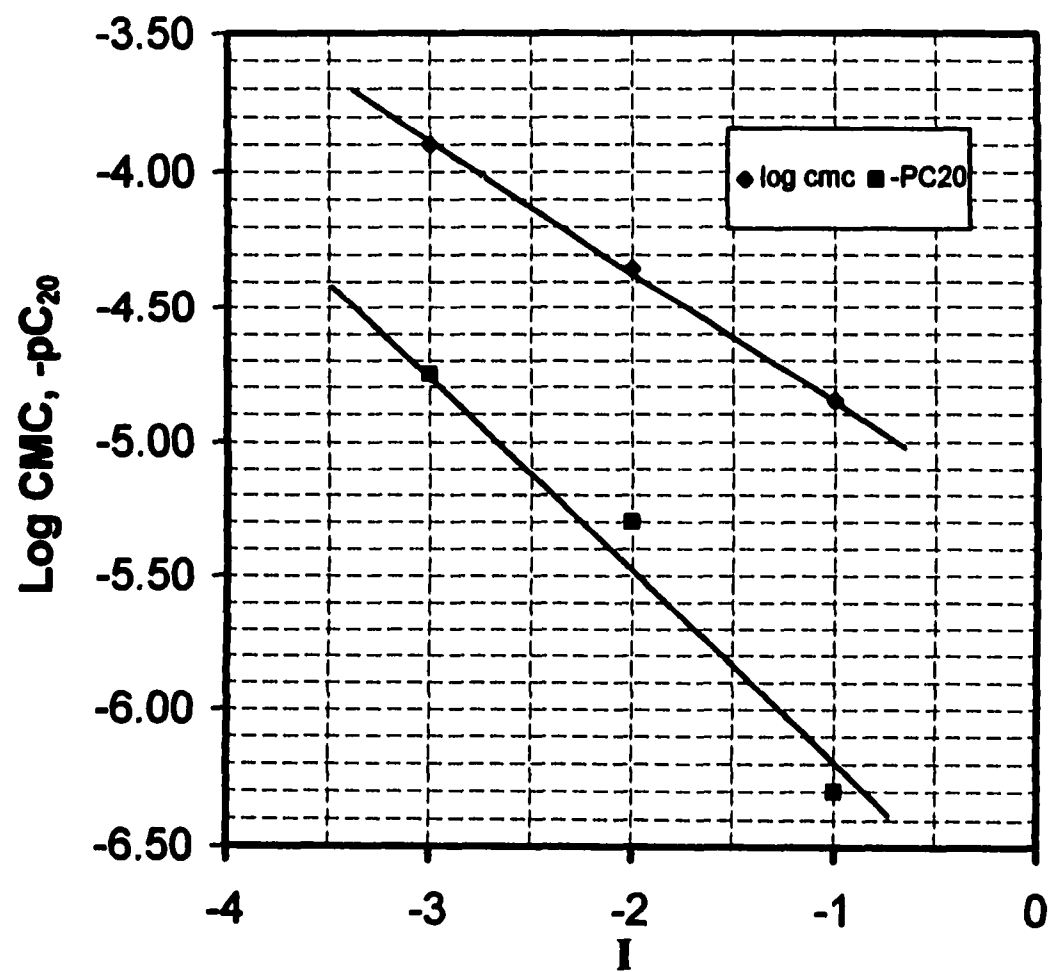


Figure 39: Log cmc, -pC₂₀ versus log I (ionic strength) plots of C₁₀DADS in NaCl at 25°C

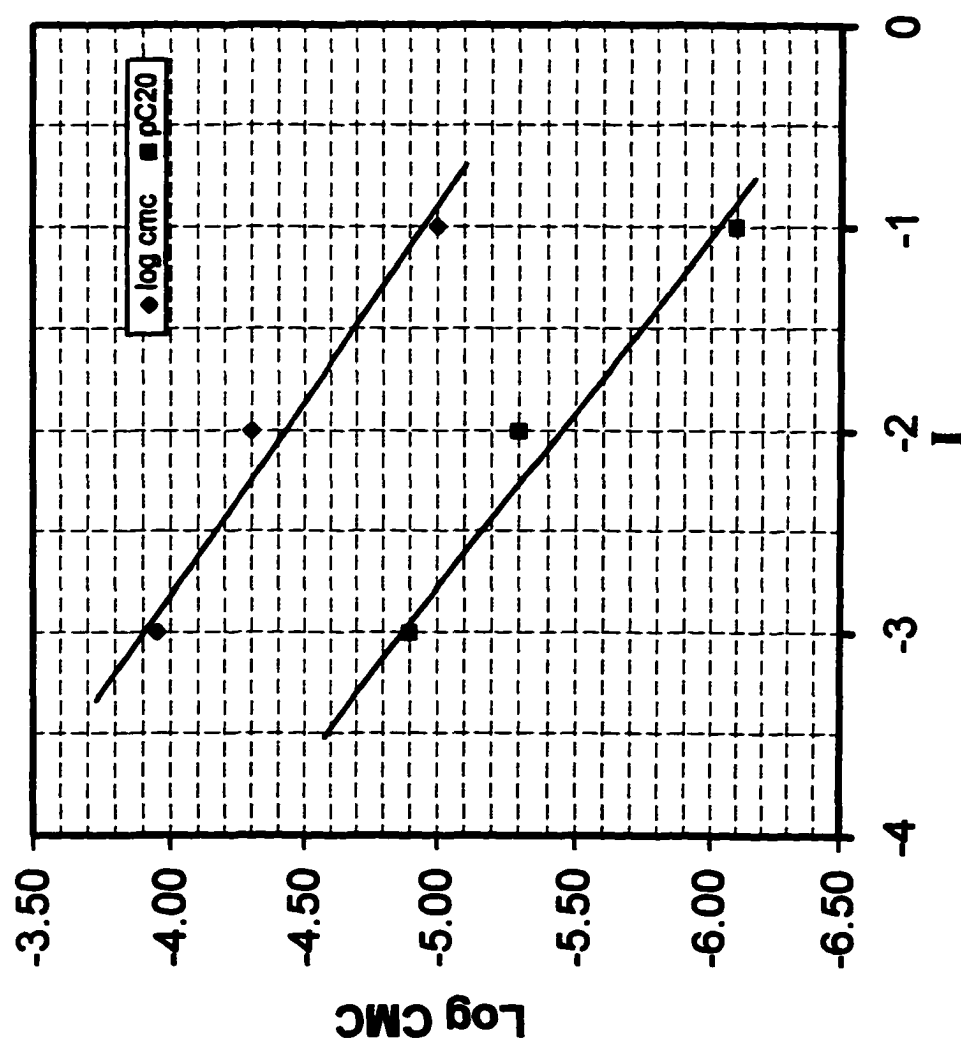


Figure 40: Log cmc, -pC20 versus log I (ionic strength) plots of $C_{10-1-10}$ in NaCl at 25°C

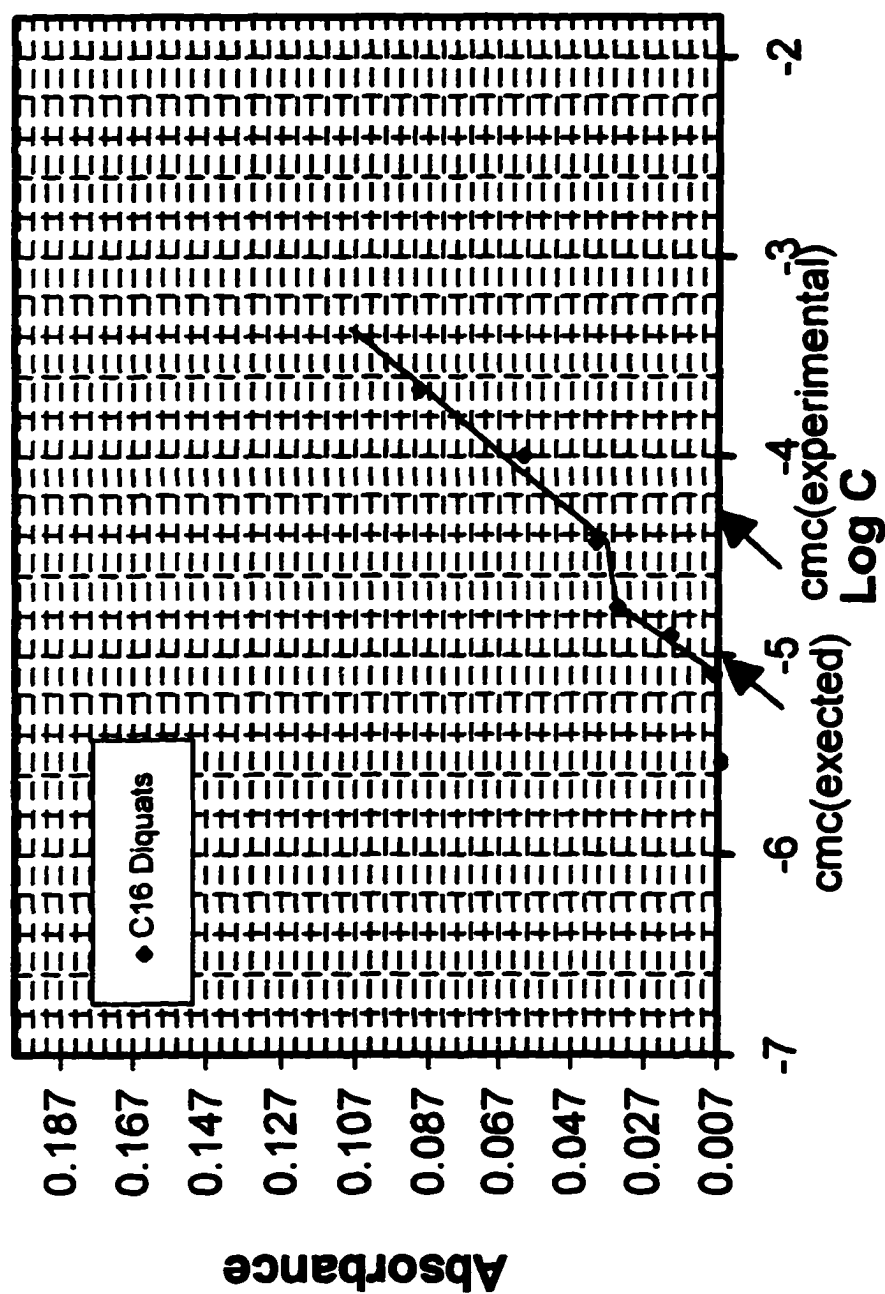


Figure 41. Vls. Absorbance of $(C_{16}N)_2(OH)_2$ vs. log C plot at 473 nm

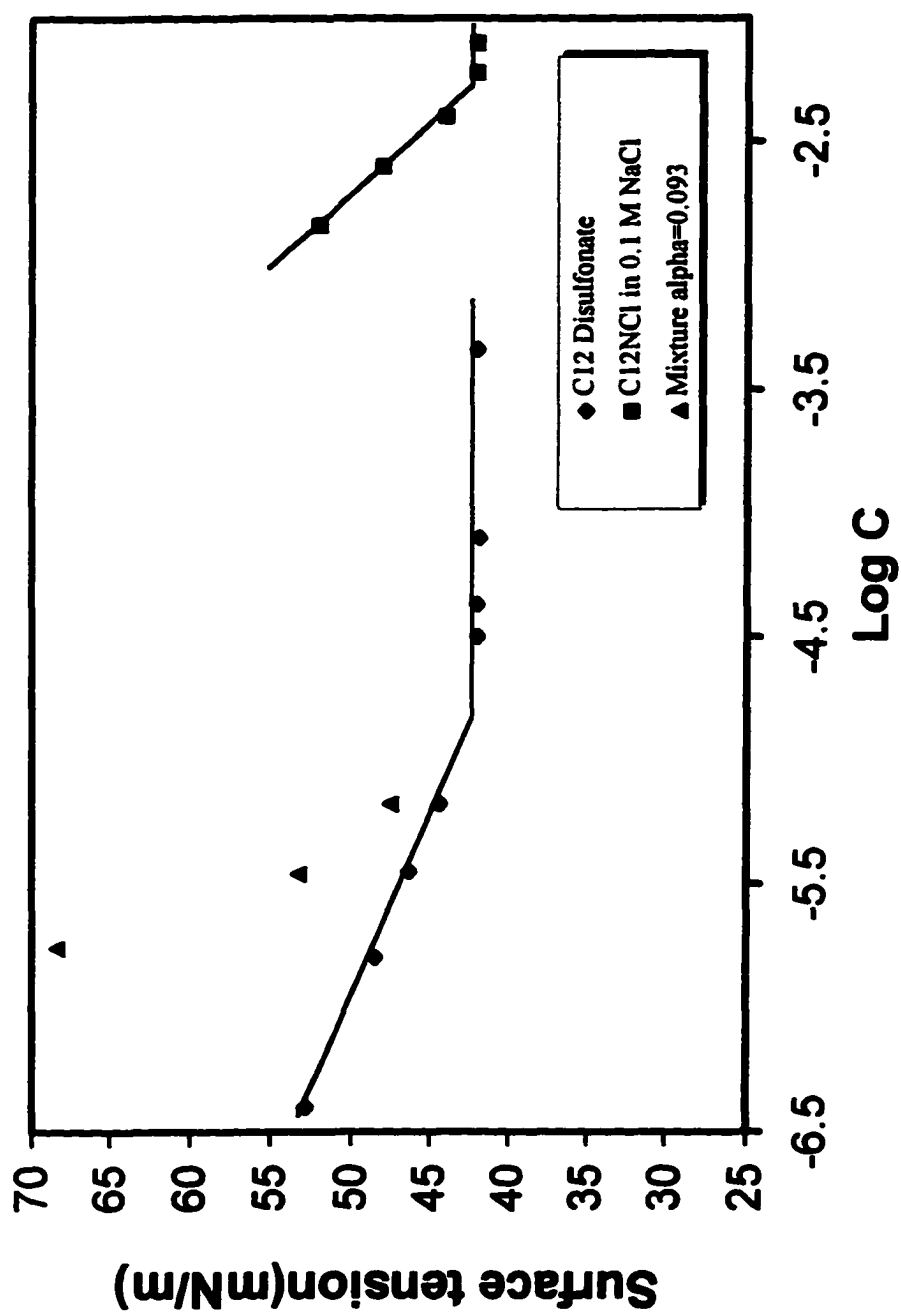


Figure 42. Interaction of $(C_{12}SO_3Na)_2(CH_2)_2$ with $C_{12}NCl$ in 0.1 M NaCl at 25°C

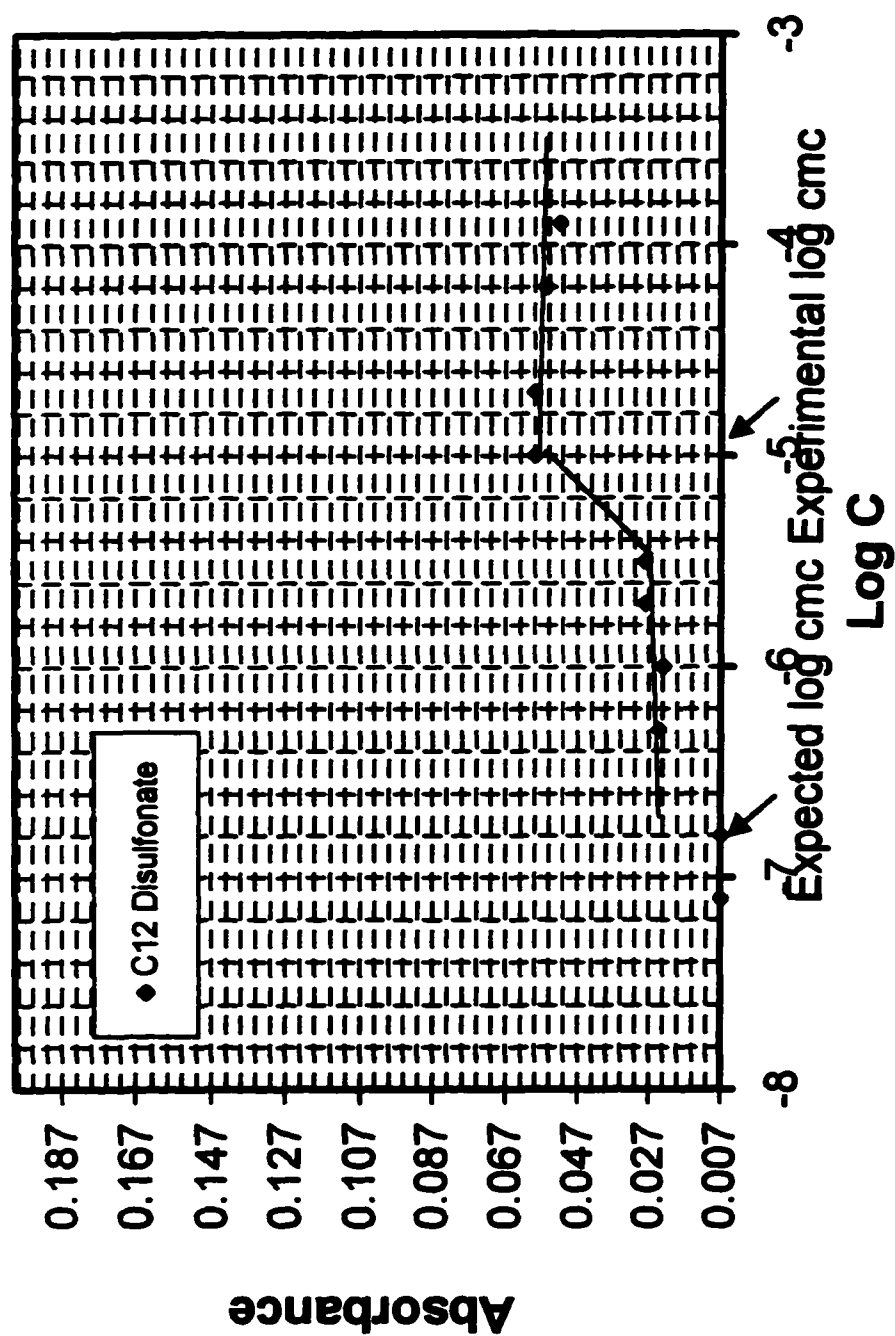


Figure 43. Vis. Absorbance of $(C_{12}SO_3Na)_2(CH_2)_2$ vs. log C plot at 604 nm

REFERENCES

- 1 Adamson, A. W., *Physical Chemistry of Surfaces*, 2nd Edition, Interscience Publishers, New York, 1967. P. 72.
- 2 Aveyard, R., Haydon, D. A., *An Introduction to the preinciples of Surface Chemistry*, Cambridge London, London, 1973. P. 3.
- 3 Mukerjee, P., *Advan. Colloid Interface Sci.*, 1, 241(1967).
- 4 Fendler, E.; Fendler, J., *Catalysis in Micellar and Macromolecular Systems*, Academic, NY., 1975. pp. 271-397.
- 5 Shinoda, K.; Nakagawa, T.; Tamamushi, B.; Isemura, T., *Colloidal Surfactants*, Academic press, New York, 1963, P. 1-80.
- 6 Mukerjee, P.; Mysels, K. J., *Critical micelle concentration of aqueous surfactant systems*, NSRDS-NBS 36, U. S. Dept. of Commence, Washington D. C., 1971.
- 7 Lange, H., in *Solvent Properties of Surfactant Solution*, K. Shinoda (Ed.), Dekker, New York, 1967, Chap. 4.
- 8 Schwartz, A. M., in *Surface and Colloid Science*, E. Matijevic (Ed.), Wiley, New York, 1972, Vol. 5, pp. 195-244.
- 9 Cutler, W. G. and Kissa (Ed.), *Detergency: Theory and Technology*, Dekker, New York, 1986.
- 10 Crofoot, R. B. and Cheng, Y. C., *J. Appl. Phys.*, 50, 6583(1979).
- 11 Croucher, M. D., Drappel, S., Duff, J., Lok, K. and Wong, R., *Colloid and Surfaces*, 11, 303(1984).
- 12 Neidleman, S. L. and Geigert, J., *J. Am. Oil Chem. Soc.* 61, 290-297(1984).
- 13 Rosen, M. J., *J. Am. Oil Chem. Soc.*, 51, 461(1974).

- 14 Rosen, M. J., *J. Colloid Interface Sci.*, 56, 320(1976).
- 15 Deinega, Y.; Ul'berg, Z. R.; Marochko, L. G.; Rudi, V. P.; Denisenko, V. P. *Kolloid. Zh.* 36, 649(1974).
- 16 Karabini, S., K. Esselink, P. A. J. Hilbers, B. Smit, J. Karthaus, N. M. van Os, and R. Zana, *Science* 266, 254-256(1994)
- 17 Okahara, M.; Masuyama, A.; Sumida, Y.; Zhu, Y-P. *J. Jpn. Oil Chem. Soc., (Yukagaku)* 37, 716(1988).
- 18 Zhu, Y-P.; Masuyama, A.; Okahara, M. *J. Am. Oil Chem. Soc.*, 67, 459(1990)
- 19 Zhu, Y-P.; Masuyama, A.; Nagata, T.; Okahara, M. *J. Jpn. Oil Chem. Soc., (Yukagaku)* 40, 473(1991).
- 20 Zhu, Y-P.; Masuyama, A.; Okahara, M. *J. Am. Oil Chem. Soc.*, 68, 268(1991)
- 21 Zhu, Y-P.; Masuyama, A.; Kirito, Y-I.; Okahara, M. *J. Am. Oil Chem. Soc.*, 68, 539(1991)
- 22 Gao, T. and M. J. Rosen, *J. Am. Oil Chem. Soc.* 71, 771-776(1994).
- 23 Rakshit, A. K.; Zograf, G.; Jalal, I. M.; Gunstone, F. D. *J. Colloid Interface Sci.* 80, 46 (1981).
- 24 Fahey, D.; Small, D. M., *Langmuir*, 4, 589 (1988).
- 25 Menger, F. M.; Littau, C. A., *J. Amer. Chem. Soc.*, 113, 1451(1991).
- 26 Menger, F. M., Littau, C. A., *J. Am. Chem. Soc.*, 115, 10083-10090(1993).
- 27 Rosen, M., *Chemtech* 3, 30(1993).
- 28 Zana, R. and Talmon, Y., *Nature*, 362, 228(1993).
- 29 Alami, E.; Beinert, G.; Marie, P.; Zana, R., *Langmuir*, 9, 1465(1993).

- 30 Frindi, M.; Michels, B.; Zana, R. *Langmuir* 10, 1140 (1994).
- 31 Kern, F.; Lequeux, F.; Zana, R.; Candau, S. J., *Langmuir*, 10, 1714 (1994).
- 32 Song, L-D.; Rosen, M. J., *Langmuir*, 12, 1149 (1996).
- 33 Rosen, M. J.; Liu, L., *J. Am. Oil Chem. Soc.*, accepted for publication 1996.
- 34 M. J. Rosen, L. Liu, and L. D. Song, "Normal and Abnormal Properties of Gemini Surfactants", **4th World Surfactants Congress**, Barcelona, June, 1996.
- 35 Devisky, F.; Masarova, L.; Lacko, I. *J. Colloid Interface Sci.*, 105, 235(1985)
- 36 Devisky, F.; Lacko, I.; Bittererova, F. and Tomeckova, L. *J. Colloid Interface Sci.*, 114, 314(1986)
- 37 Devinski, F.; Lacko, I.; Tanweerul, I. *J. Colloid Interface Sci.*, 143, 336 (1991).
- 38 Zana, R.; Benrraou, M. and Rueff, R. *Langmuir*, 7, 1072(1991)
- 39 Alami, E.; Levy, H. and Zana, R. *Langmuir*, 9, 940(1993)
- 40 Masuyama, A., Hirono, T., Zhu, Y-P., Okahara, M., and Rosen, M.J., *J. Jpn. Oil Chem. Soc. (Yukagaku)* 41, 301 (1992).
- 41 Masuyama, A., T. Kawano, Y-P. Zhu, T. Kida, and Y. Nakatsuji, *Chem Letters, (Chem. Soc. Japan)* 2053-2056(1993).
- 42 Zhu, Y-P., A. Masuyama, Y. Kobata, Y. Nakatsuji, M. Okahara, and M. J. Rosen, *J. Colloid Interface Sci.* 158, 40-45(1993).
- 43 Zhu, Y.-P.; Masuyama A.; Nakatsuji Y. and Okahara M. *J. Jpn. Oil Chem. Soc. (Yukagaku)* 42, 86-94(1993).

- 44 Zhu, Y.-P., Masuyama A.; Kirito Y.-C., Okahara M.; and Rosen M. *J. J. Am. Oil Chem. Soc.* 69, 626-632(1992).
- 45 Masuyama, A.; Yokota, M.; Zhu, Y-P.; Kida, T. and Nakatsuji. Y. *J. Chem. Soc., Chem. Commun.*, 1435-1436(1994).
- 46 Aronson, M. P., Gum, M. L. and Goddard, E. D. *J. Am. Oil Chem. Soc.* 60, 1333 (1983).
- 47 Bourrel, M., Bernard, D. and Graciaa, A. *Tenside Detergents* 21, 311 (1984).
- 48 Rosen, M. J. "*Surfactants and Interfacial Phenomena*", 2nd Edition, Wiley, New York, 1989
- 49 Rosen M. J., Zhu, Z-H., and Gao, T., *J. Colloid Interface Sci.*, 157, 254-259(1993).
- 50 Rosen, M. J., Gao, T., Nakatsuji, Y., Masuyama, A., *Colloids and Surfaces*, 88A(1994) 1-11.
- 51 Liu, L. and Rosen, M. J. *J. Colloid Interface Sci.*, 179, 454-459 (1996).
- 52 Rosen, M. J., *Langmuir*, 7, 885(1991).
- 53 Gibbs, J. W., *The Collect Work of J. W. Gibbs Longmans, Green, New York, Vol. I; P. 219*(1930).
- 54 Adam, N. K., *The Physics and Chemistry of Surfaces*, Oxford University Press, London and New York, 1967.
- 55 Payens, T. A. P., *Proc. 2nd Int. Cong. Surf. Activ.*, 1, 61 (1957) (London).
- 56 Van Voorst Vader, F., *Trans. Faraday Soc.*, 57,2253(1961).
- 57 Webb, D. A.; Danielli, J. F., *Nature*, 146, 197(1940).
- 58 Sasaki, J.; Tajima, K.; Sasaki, T., *Bull. Chem. Soc. Jap.*, 45, 348(1972).

- 59 Lange, H.; Schwuger, M. J., *Kolloid - Z. Z. Polym.*, 243, 120(1971).
- 60 Schwuger, M. J., *Kolloid - Z. Z. Polym.*, 243, 129(1971).
- 61 Hua, H. Y.; Chao, K. H., *Acta Chimica Sinica*, 30, 441(1964).
- 62 Sanoda, K., *Colloidal Surfactants*, Academic Press, New York, Chapter 1, 1963.
- 63 Lange, H., *Kolloid - Z. Z. Polym.*, 13, 96(1953).
- 64 Shinoda, K., *J. Phys. Chem.*, 58, 541(1954).
- 65 Shedlovsky, L.; Jakob, C. W.; Epstein, M. B., *J. Phys. Chem.*, 67, 2075(1963).
- 66 Iwadare, Y., *Bull. Chem. Soc. Jpn.*, 43, 3364(1970).
- 67 Moro, Y.; Motomura, K.; Matuura, R., *J. Colloid Interface Sci.*, 46, 111(1974).
- 68 Clint, J. H., *J. C. S. Faraday I*, 71, 1327(1975).
- 69 Ingram, B. T.; Luckhurst, A. H. W., *Surface Active Agents*, The Society of Chemical Faraday, London, P. 89, 1979.
- 70 Rubingh, D. N. *In Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum: New York, 1979; Vol. I, p 337.
- 71 Ingram, B. T., *Colloid Polym. Sci.*, 25, 191(1980).
- 72 Scamehorn, J. F.; Schechter, R. S.; Wade, W.H., *J. Disp. Sci. Tech.*, 3, 26(1982).
- 73 Holland, P. M.; Rubingh, D. N., *J. Phys. Chem.*, 87, 1984(1983).
- 74 Kamrath, R. F.; Franses, E. T., *Ind. Eng. Chem. Fundam.*, 22, 230(1983).
- 75 Hall, D. G.; Huddleston, R. W., *Colloid Surfaces*, 13, 209(1985).
- 76 Osborne-Lee, I. W.; Schechter, R. S.; Wade, W. H.; Barakat, Y., *J. Colloid Interface Sci.*, 108, 60(1985).

- 77 Rosen, M. J.; Hua, X. Y. *J. Colloid Interface Sci.*, 86,164(1982).
- 78 Rosen, M. J., in *Phenomena in Mixed surfactant Systems*, Scamehorn, J. F., Ed., American Chemical Society, Washington, DC, 1986; ACS Symposium Series Vol. 311; P. 144.
- 79 Rosen, M. J.; Hua, X. Y., *J. Colloid Interface Sci.*, 90, 212(1982).
- 80 Rosen, M. J.; Zhao, F., *J. Colloid Interface Sci.*, 95, 443(1983).
- 81 Zhu, B. Y.; Rosen, M. J., *J. Colloid Interface Sci.*, 99, 435(1984).
- 82 Rosen, M. J.; Murphy, D., *J. Colloid Interface Sci.*, 101, 224(1986).
- 83 Rosen, M. J.; Gu, B., *Colloids and Surfaces*, 23, 119(1987).
- 84 Rosen, M. J. *Langmuir*, 7, 885-888(1991).
- 85 Rosen, M. J.; Murphy, D. S. *J. Colloid Interface Sci.* 110,224(1986).
- 86 Rosen, M. J.; Gu, B. *Colloid Surf.* 23, 119(1987).
- 87 Hua,X. Y.; Rosen, M. J., *Colloid Interface Sci.* 90,212(1982).
- 88 Hua,X. Y.; Rosen, M. J., *J. Colloid Interface Sci.* 125,730(1988).
- 89 Rosen, M. J. ; Zhao, F. *J. Colloid Interface Sci.* 95,443(1983).
- 90 Zhu, B.Y. and Rosen, M. J. *J. Colloid Interface Sci.* 99,435(1984).
- 91 Rosen, M. J.; Zhu, B. Y., *J. Colloid Interface Sci.* 99, 427(1984).
- 92 Rosen M. J.; Zhu, Z. H. *J. Am. Oil Chem. Soc.* 65, 663(1988).
- 93 Rosen, M. J.; Friedman, D.; Gross, M. J. *Phys. Chem.* 68,3219(1964).
- 94 Rosen, M. J.; Gu, B.; Murphy, D. S.; Zhu, Z. H. *J. Colloid Interface Sci.* 129, 468(1989).
- 95 Zhu, Z. H.; Yang, D.; Rosen, M. J., *J. Am. Oil Chem. Soc.* 66, 998(1989).
- 96 Gu, B., and Rosen, M. J., *J. Colloid Interface Sci.*, 129(1989)537.
- 97 Rosen, M. J., *Progr. Colloid & Polym. Sci.* (1994) 95:39-47.

- 98 Reid, V. W., Longman, G. F., and Heinerth, E., *Tenside*, **4**(1967)
292.
- 99 Rosen, M. J., and Goldsmith, H. A., "*Systematic Analysis of surface-active Agents*", 2nd Edition, Wiley-Interscience, New York, 1972, p. 427.
- 100 Rosen, M. J.; *J. Colloid and Interface Sci.* **79**(2),587(1981).
- 101 Rosen, M. J.; Dahanayake, M.; and Cohen, A. W., *Colloids and Surfaces* **5**, 159(1982).
- 102 Dahanayake, M, *Ph. D. Thesis*, the City University of New York, P. 70, 1985.
- 103 Rosen, M. J., *J. Colloid Interface Sci.*, **79**,587(1981).
- 104 Dahanayake, M.; Rosen, M. J., in *structure/Performance Relationships in Surfactants*, Rosen, M. J., Ed., ACS symposium Series 253, Amer. Chem. Soc., Washington, DC, 1984.
- 105 Reid, V. M.; Alston.; Heinerth, E., *Tenside*, **4**, 292(1967).
- 106 Li, Z. P. and Rosen, M. J., *J. Anal. Chem.* **53**, 1516(1981).
- 107 Rosen, M. J.; and Goldsmith, H. A., *Systematic Analysis of Surface-Active Agents*, 2nd Ed., Wiley-Interscience New York, 1972, P. 427.
- 108 Wihelmy, L., *Ann. Phys.*, **119**, 177(1863).
- 109 Draves, C. Z., *Am. Dyestuff Rep.* **28**, 425(1939).
- 110 Ross, J.; Miles, G. D., Am. Soc. For Testing Materials, Method D1173-53, Philadelphia, PA, 1953, *Oil and Soap* **18**, 99(1941).
- 111 Devinsky, F., Personal communication, 1994.
- 112 Zana, R. *Langmuir* **12**,1209 (1996).
- 113 Devinsky, F.; Lacko, I.; Bittererova, F. and Tomeckova, L. *J. Colloid Interface Sci.*, **114**, 314(1986).

- 114 Rosen, M. J., *Progr. Colloid & Polym. Sci.* (1994) 95:39-47.
- 115 Rosen, M. J., *J. Colloid Interface Sci.*, 95(1983) 443.

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