Order Number 9009796

The relation of synergism in binary mixtures of surfactants to microenvironmental factors

Utarapichart, Cheawchan, Ph.D.

City University of New York, 1989

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

The Relation of Synergism in Binary Mixtures of Surfactants to Microenvironmental Factors

By

Cheawchan Utarapichart

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

1989

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

8/24/89
date

Chairman of Examining Committee

8/28/89
date

Executive Officer

Michael P. Aronson
Supervisory Committee

The City University of New York

Abstract

The Relation of Synergism in Binary Mixtures of Surfactants to Microenvironmental Factors

by

Cheawchan Utarapichart

Advisor : Professor Milton J. Rosen

The degree of interaction between two surfactants in mixed monolayer at the aqueous solution/air interface or mixed micelle in aqueous solution can be measured by calculating the molecular interaction parameter, β^{σ} and β^{M}, respectively, from surface tension measurement, using nonideal solution theory.

Interaction between the two surfactants in polyoxyethylenated nonionic-anionic mixture decreases when the hydrophilic group in anionic is moved to a more central position. With increase in ionic strength of the solution, the values of β^{σ} and β^{M} go through maxima. This may be due to the complex formation between Na^{+} and some ether oxygens of the polyoxyethylene chain. Temperature increase in the 25^{o} - 40^{o} C range results in a decrease in the values of β^{σ} and β^{M}. Interaction between polyoxyethylenated anionic and alkyl sulfate or alkyl sulfonate increases with increase in the number of oxyethylene units in the polyoxyethylenated anionic.

Effects of surfactant structure, ionic strength of the solution, and temperature on synergism in surface tension reduction efficiency and mixed micelle formation in polyoxyethylenated nonionc - anionic mixtures have been investigated. Synergism and negative synergism in surface tension reduction effectiveness were also investigated in polyoxyethylenated anionic - anionic and polyoxyethylenated nonionic - anionic mixtures, respectively.

Measurements of [Na^+] at 25° C by use of a Na^+ selective electrode indicate that non-cyclic polyoxyethylenated(POE) nonionic surfactants,$C_{12}H_{25}(OC_2H_4)_XOH[C_{12}(EO)_X]$, in the absence of ionic surfactants and at concentrations more than one order of magnitude above their critical micelle concentrations, complex Na^+ weakly. In aqueous NaCl solutions of 0.004 M total ionic strength about 0.17 moles Na^+ are complexed per mole of $C_{12}(EO)_8$, 0.09 moles per mole of $C_{12}(EO)_4$. In the presence of an anionic surfactant, Na di (2- ethylhexyl) sulfosuccinate (AOT), the extent of complexation is considerably increased. The complexation constant, K, increases with increase in the AOT/$C_{12}(EO)_8$ molar ratio in the mixed micelle, with complexed Na^+ maintaining an approximately 1:1 molar ratio with AOT in the mixed micelle. K decreases when $C_{12}(EO)_8$ is replaced by $C_{12}(EO)_4$ or when AOT is replaced by its di - amyl analog. $C_{12}(EO)_8$ -$C_{14}N(CH_3)_3Br$ mixtures complex Na^+ even more weakly than in the absence of an anionic surfactant, indicating competition between cationic surfactant and Na^+ for the polyoxyethylene chain.

Dedication

To my parents

Acknowledgements

The author wishes to express his gratitude to Professor milton J. Rosen for his excellent guidence, encouragement, understanding and friendship throughout this work.

The author is also grateful to Dr. Michael P. Aronson and Professor P Gary Mennitt, the members of his supervisory committee for their time and advice.

Finally he would like to acknowledge Chemistry Department of Brooklyn College of The City University of New York, in providing a financial support.

Contents

TABLES

FIGURES

Chapter I

Introduction

1.1 General Aspects

In mixed surfactant systems, physical properties such as critical micelle concentration and surface tension may be substantially different from what would be expected based on the properties of the pure components. Such nonideal behavior is of both theoretical interest and industrial importance. For example, mixtures of different classes of surfactants often exhibit synergism (1-5) and this behavior can be utilized in practical applications (6).

Synergism is an area of major importance in the field of surfactants, because it has both theoretical and practical importance. From the theoretical view point , it affords insights into the nature and magnitude of interactions between different types of organic molecules, from the practical, it provides guidelines for the most efficient and effective use of surfactants in industrial applications.

Generally, synergistic effects seem to be negligible for mixtures of nonionic surfactants (7-9). Ionic-nonionic mixtures, on the other hand, do show appreciable synergism, which in some case can be described in terms of a nonideal solution model for the surfactant mixtures (10,11). Largest, however, are the synergistic effects in cationic-anionic mixtures. The total surfactant concentration required to give a certain surface tension lowering for a 1:1 mixture can be orders of magnitude smaller than it is for each of the component solution.

Qualitatively , this synergistic effect can be explained as follows (12): For individual oppositely-charged surfactants such as sodium dodecyl sulfate and dodecyl trimethyl ammonium bromide, the tendency of the long chain ions to adsorb is strongly reduced by the necessary presence in the surface of sodium or bromide counterions, which are essentially non- surface active. In their mixtures, electroneutral 1:1 combinations of the oppositely-charged long

chain ions are much more surface active than the individual long chain ions of the mixture , that is , they have a much greater partition coefficient between surface and bulk.

The conditions for the existence of synergism between two surfactants in the fundamental properties of mixed monolayer formation and mixed micelle formation have been derived (5,13,14). From the properties of the two individual surfactants and one mixture of them, we can predict whether or not synergism in these phenomena will exist, if so , the exact proportions of the two components that show maximum synergism. In this work , we have investigated the effect of change in the molecular structure of the surfactants or in such microenvironmental factors as electrolyte content, temperature, on their molecular or synergistic interaction.

The key to understanding molecular interaction between surfactant pairs and to predicting the existence of synergism between them is the determination of the molecular interaction parameters, β^{σ} and β^{M} for mixed monolayer formation at the aqueous solution/interface and for mixed micelle formation in aqueous solution, respectively. The experimental approach is to measure the surface tension of aqueous solutions of the individual surfactants and of at least one binary mixture of them in aqueous solution, as a function of the total concentration of surfactant.

1.2 Literature Survey On Molecular Interactions Between Surfactants In Aqueous Solution

An early attempt to measure quantitatively the effect of an additive on the surface properties of a surfactant system was an investigation by Hutchinson(15) into the interaction of *n*-octyl alcohol with sodium n-dodecyl sulfate. His approach was to measure the surface (excess) concentrations of the surface active species at the aqueous solution/ air interface by use of the Gibbs adsorption equation in the form

$$- d\gamma = 2.303RT [\Gamma_1 d\log a_1 + \Gamma_2 d\log a_2] \qquad [1]$$

where $d\gamma$ is the change in the surface tension in mNm^{-1}, R is 8.314 J $K^{-1}mol^{-1}$, T is the absolute temperature, and Γ_1 and Γ_2 are the surface excess concentrations of the two surface active species and a_1 and a_2 their respective activities in the aqueous bulk phase. From this relationship, we obtained

$$\Gamma_1 = \frac{1}{2.303RT} \left(\frac{-\partial\gamma}{\partial \log a_1} \right)_{T,a_2} \qquad [2]$$

and

$$\Gamma_2 = \frac{1}{2.303RT} \left(\frac{-\partial\gamma}{\partial \log a_2} \right)_{T,a_1} \qquad [3]$$

For highly surface active species, the surface excess concentration may be equated with the actual surface concentration without significant error. From two series of γ-log C curves, in one of which the bulk phase molar concentration of the surfactant was held at a fixed value while the bulk phase molar concentration of the cosurfactant was varied and in the second of which the bulk phase molar concentration of the cosurfactant was held at fixed values while the bulk phase molar concentration of the surfactant was varied, all at constant temperature, Hutchinson calculated surface (excess) concentrations of both surface active species in solutions of different composition.

From these concentrations and N, the Avogadro number, the average area A, per molecule $\left(= \frac{1}{N(\Gamma_1 + \Gamma_2)} \right)$ for the mixture at the interface was calculated. Plots of A versus surface pressure, π ($=\gamma_0 - \gamma$, where γ_0 is the surface tension of the pure solvent) for the two individual surface active species and their mixtures were used to indicate little interaction between the two materials.

Another approach was that of Goodrich (16) who calculated the excess free energy of mixing, G_{XS} of two surface active species of different polarity in insoluble monolayers spread over ammonium sulfate solution, by use of the relationship

$$G_{xs} = \int_0^{\pi} A_{12}\, d\pi - x_1 \int_0^{\pi} A_1\, d\pi - x_2 \int_0^{\pi} A_2\, d\pi \qquad [4]$$

where A_{12}, A_1, and A_2 are the area per molecule of surface active species in the mixed film and films of the pure components 1 and 2, respectively, and X_1 and X_2 the mole fraction of components 1 and 2, respectively, in the mixed film. The integrals were evaluated by plotting the π-A curves for the individual components and for the mixed film and integrating graphically. Plots of G_{XS} versus mole fraction of either of the components were used to show the extent of interaction between them. By this method, maximum interaction between long, straight-chain alcohols and straight-chain ionic surfactants was shown to occur when the two surface active materials were at 1:1 molar ratio in the surface film. Interaction increased with increase in the chain length of the hydrophobic groups of the two components and decreased markedly with the introduction of branching into the chain of one of the components.

Goddard (17) investigated the interaction between long-chain alcohols and sodium cetyl sulfate by the monolayer penetration technique. Molecular association was shown to be strongest when the alcohol possesses a straight hydrocarbon chain and can be weakened considerably by altering the configuration of the chain.

More recently, there have been a number of attempts to quantify the effect of a second surface active species on the process of micelle formation in aqueous media. Usually, ideal mixing in the micelle has been assumed(7,18,19). Clint(7) developed a theory that treats the mixed micelles as an ideal solution of the surfactants and predicts critical micelle concentration (CMC), micelle composition, and monomer concentration. The critical micelle concentration, C_{12}^M of the system containing the two surfactants calculated from the relationship

$$\frac{1}{C_{12}^M} = \frac{\alpha_1}{C_1^M} + \frac{(1-\alpha_1)}{C_2^M} \qquad [5]$$

where α_1 is the mole fraction of surfactant 1 in the total surfactant in the solution phase, and C_1^M and C_2^M are the critical micelle concentrations of surfactants 1 and 2, respectively. The same equation was derived by Lange and Beck (20). The data obtained indicate that this approach is valid for mixtures of homologous surfactants and for mixtures of of nonionic surfactants whose hydrophilic groups do not differ too widely in chemical structure, but is invalid for ionic-nonionic and anionic-cationic mixtures.

To overcome this limitation, Rubingh (21) used regular solution theory to calculate the composition of mixed micelles formed from mixtures of two surfactants, including mixtures of ionic with nonionic species.

The chemical potential, μ_1 of monomeric surfactant 1 in the solution phase in equilibrium with the mixed micelle is given by

$$\mu_1 = \mu_1^o + RT \ln C_1 \qquad [6]$$

where μ_1^o is the standard chemical potential of monomeric surfactant 1 when the unit of concentration is in mole/l, and C_1 is the concentration of monomeric surfactant 1. The chemical potential, μ_1^M of surfactant 1 in the mixed micelle is given by

$$\mu_1^M = \mu_1^{Mo} + RT \ln f_1^M X_1^M \qquad [7]$$

where μ_1^{Mo} is the chemical potential of surfactant 1 in the micelle containing only surfactant 1, f_1^M is the activity coefficient of surfactant 1 in the mixed micelle, and X_1^M is the mole fraction of surfactant 1 in the mixed micelle.

Using a simple phase separation model for micellization , we write for surfactant 1 in the micelle containing only surfactant 1,

$$\mu_1^{Mo} = \mu_1^{o} + RT \ln C_1^M \qquad [8]$$

Eqs.[6], [7], and [8] are combined with the relationship that at equilibrium $\mu_1 = \mu_1^M$ to yield

$$C_1 = X_1^M f_1^M C_1^M \qquad [9]$$

Similarly, for surfactant 2,

$$C_2 = (1 - X_1^M) f_2^M C_2^M \qquad [10]$$

where C_2 is the concentration of monomeric surfactant 2, f_2^M is the activity coefficient of surfactant 2 in the mixed micelle.

At concentration below the concentration of mixed micelle formation, the concentration of surfactant 1 in the solution phase is given by

$$C_1 = \alpha_1 C_{12} \qquad [11]$$

where C_{12} is the total concentration of surfactants 1 and 2,

and for surfactant 2,

$$C_2 = (1 - \alpha_1) C_{12} \qquad [12]$$

At the mixed CMC (C_{12}^M) these two relationships still hold. Combining Eqs. [11], [12], and Eqs.[9], and [10] yields

$$\alpha_1 C_{12}^M = X_1^M f_1^M C_1^M \qquad [13]$$

and

$$(1 - \alpha_1) C_{12}^M = (1 - X_1^M) f_2^M C_2^M \qquad [14]$$

X_1^M can be eliminated to give

$$\frac{1}{C_{12}^M} = \frac{\alpha_1}{f_1^M C_1^M} + \frac{(1-\alpha_1)}{f_2^M C_2^M} \qquad [15]$$

If $f_1^M = f_2^M = 1$ (the ideal approximation), the Eq.[15] reduces to Eq.[5]

Alternately, eliminate C_{12}^M, using Eqs.[13], and [14] to obtain

$$X_1^M = \frac{\alpha_1 f_2^M C_2^M}{\alpha_1 f_2^M C_2^M + (1-\alpha_1) f_1^M C_1^M} \qquad [16]$$

for the mole fraction of surfactant 1 in the mixed micelle at the CMC. Eqs.[15], and [16] although correct expressions, are not helpful without some relationship between activity coefficients in the micelle and micelle composition. It is here that the regular solution approximation can be introduced for the activity coefficient in the mixed micelle :

$$f_1^M = \exp\left[\beta^M (1 - X_1^M)^2\right] \quad [17]$$

$$f_2^M = \exp\left[\beta^M (X_1^M)^2\right] \quad [18]$$

The parameter β^M is related to the molecular interactions in the mixed micelle. Eqs.[13],[14],[17], and [18] are combined to yield

$$(X_1^M)^2 \ln\left[\alpha_1 C_{12}^M / X_1^M C_1^M\right] = (1 - X_1^M)^2 \ln\left[(1 - \alpha_1) C_{12}^M / (1 - X_1^M) C_2^M\right] \quad [19]$$

and

$$\beta^M = \frac{\ln\left[\alpha_1 C_{12}^M / X_1^M C_1^M\right]}{(1 - X_1^M)^2} \quad [20]$$

Eq.[19] can be solved iteratively for X_1^M for known values of C_{12}^M, C_1^M, C_2^M, and α_1. Eq.[20] can then be solved for β^M.

Based on the 2- dimensional gas model, the mixed monolayer at the surface phase can be considered as a mixture containing only the two different surfactants. The chemical potential, $\mu_{1,S}$, of surfactant 1 at the surface phase of an aqueous solution containing surfactants 1 and 2 can be written (22,23)

$$\mu_{1,S} = \mu^{o}_{1,S}(\pi) + RT \ln f_{1,S} X_1 - \gamma A_1 \qquad [21]$$

where $\mu^{o}_{1,S}(\pi)$ is the chemical potential of surfactant 1 at the surface phase of an aqueous solution of pure surfactant 1 and is a function of the surface pressure, π, $f_{1,S}$ is the activity coefficient of surfactant 1 at the surface phase, X_1 is the mole fraction of surfactant 1 at the surface phase, A_1 is the partial molar interfacial area of surfactant 1 in a mixture of surfactants 1 and 2, and γ is the surface tension.

The chemical potential, $\mu_{1,b}$, of surfactant 1 in the bulk phase of an aqueous solution containing surfactants 1 and 2 can be written

$$\mu_{1,b} = \mu^{o}_{1,b} + RT \ln C_1 f_1 \qquad [22]$$

where $\mu^{o}_{1,b}$ is the standard chemical potential of surfactant 1 (with the standard state defined as a 1 molar solution, but behaving ideally), f_1 is the activity coefficient of surfactant 1 in the bulk phase, and C_1 is the molar concentration of surfactant 1 in the bulk phase.

At equilibrium, $\mu_{1,b} = \mu_{1,S}$ and from Eqs.[21], and [22],

$$\mu^{o}_{1,S}(\pi) - \mu^{o}_{1,b} = RT \ln \left[C_1 f_1 / f_{1,S} X_1 \right] + \gamma A_1 \qquad [23]$$

For an aqueous solution of pure surfactant 1, but at the same surface pressure, π, as the aqueous solution containing surfactants 1 and 2,

$$\mu^{o}_{1,S}(\pi) - \mu^{o}_{1,b} = RT \ln C_1^{o} f_1^{o} + \gamma A_1^{o} \qquad [24]$$

where f_1^{o} is the bulk phase activity coefficient of pure surfactant 1, C_1^{o} is the molar concentration of pure surfactant 1 in the bulk phase, and A_1^{o} is the molar interfacial area occupied by pure surfactant 1. From Eqs.[23], and [24],

$$RT \ln \left[C_1 f_1 / f_{1,S} X_1 C_1^{o} f_1^{o} \right] = \gamma (A_1^{o} - A_1) \qquad [25]$$

When C_1 and C_1^o are small, $f_1/f_1^o = 1$ and Eq.[25] reduces to

$$\ln f_{1,S} = \ln \frac{C_1}{X_1 C_1^o} - \frac{\gamma(A_1^o - A_1)}{RT} \qquad [26]$$

In a similar fashion, we can obtain for surfactant 2 in the mixture,

$$\ln f_{2,S} = \ln \frac{C_2}{(1-X_1) C_2^o} - \frac{\gamma(A_2^o - A_2)}{RT} \qquad [27]$$

The activity coefficients $f_{1,S}$ and $f_{2,S}$ may be obtained from the second term of the Margules expansion approximations (the first term being equal to zero) (24):

$$\ln f_{1,S} = \beta^\sigma (1 - X_1)^2 \qquad [28]$$

$$\ln f_{2,S} = \beta^\sigma (X_1)^2 \qquad [29]$$

where β^σ is a measure of the deviation of the mixture from ideality and related to the molecular interactions between surfactants 1 and 2 in the mixed monolayer at the surface phase.

From Eqs. [26] and [28],

$$\beta^\sigma (1 - X_1)^2 = \ln \frac{C_1}{X_1 C_1^o} - \frac{\gamma(A_1^o - A_1)}{RT} \qquad [30]$$

and from Eqs.[27] and [29],

$$\beta^\sigma (X_1)^2 = \ln \frac{C_2}{(1-X_1) C_2^o} - \frac{\gamma(A_2^o - A_2)}{RT} \qquad [31]$$

$$\text{Let} \quad B_1 = \frac{\gamma(A_1^o - A_1)}{RT}$$

$$\text{and} \quad B_2 = \frac{\gamma(A_2^o - A_2)}{RT}$$

$$\text{Thus,} \quad \beta\sigma = \frac{\ln(C_1/C_1^o X_1) - B_1}{(1 - X_1)^2} \qquad [32]$$

$$\text{and} \quad \beta\sigma = \frac{\ln[C_2/C_2^o(1 - X_1)] - B_2}{(X_1)^2} \qquad [33]$$

From Eqs. [32] and [33],

$$\frac{(X_1)^2[\ln(C_1/C_1^o X_1) - B_1]}{(1 - X_1)^2[\ln(C_2/C_2^o(1 - X_1) - B_2]} = 1 \qquad [34]$$

There are two assumptions for the molar area of surfactant (25), the first assumption is that the area occupied by a mole of surfactant in the mixed monolayer of the mixture is not significantly different from that in a monolayer of the individual surfactant, i.e., $A_1 \approx A_1^o$ and $A_2 \approx A_2^o$, thus $B_1 = B_2 = 0$

Eqs.[32],[33], and [34] then become

$$\beta\sigma = \frac{\ln[C_1/C_1^o X_1]}{(1 - X_1)^2} \qquad [35]$$

$$\beta\sigma = \frac{\ln[C_2/C_2^o(1 - X_1)]}{(X_1)^2} \qquad [36]$$

and $$\frac{(X_1)^2 \ln (C_1/C_1^o X_1)}{(1 - X_1)^2 \ln [C_2/C_2^o (1 - X_1)]} = 1 \qquad [37]$$

The second assumption is that the ratio of the partial molar areas of the two surfactants in the mixed monolayer equals that of the two individual surfactants at the same surface tension, i.e.,

$$A_1/A_2 = A_1^o/A_2^o \qquad [38]$$

Eq.[38] implies that A_1 is some fraction, k, of A_1^o, due to the reduction of the repulsion between the ionic head groups and that A_2 is the same fraction of A_2^o, because of the mutual neutralization of charge by the oppositely - charged head groups in the mixed monolayer. That is $A_1 = k A_1^o$ and $A_2 = k A_2^o$.

We have the relationship

$$X_1 A_1 + (1 - X_1) A_2 = A_{av} \qquad [39]$$

From Eqs.[38] and [39],

$$A_1 = \frac{A_{av} A_1^o}{X_1 A_1^o + (1 - X_1) A_2^o}$$

and

$$A_2 = \frac{A_{av} A_2^o}{X_1 A_1^o + (1 - X_1) A_2^o}$$

From these,

$$B_1 = \frac{\gamma (A_1^o - A_1)}{RT} = \frac{\gamma A_1^o \left[1 - \frac{A_{av}}{X_1 A_1^o + (1 - X_1) A_2^o} \right]}{RT} \qquad [40]$$

and

$$B_2 = \frac{\gamma(A_2^o - A_2)}{RT} = \frac{\gamma A_2^o \left[1 - \dfrac{A_{av}}{X_1 A_1^o + (1 - X_1) A_2^o}\right]}{RT} \quad [41]$$

Eqs.[32] and [34] then become

$$\beta^\sigma = \frac{\ln \dfrac{C_1}{C_1^o X_1} - \dfrac{\gamma A_1^o}{RT}\left[1 - \dfrac{A_{av}}{X_1 A_1^o + (1 - X_1) A_2^o}\right]}{(1 - X_1)^2} \quad [42]$$

and

$$\frac{X_1^2\left[\ln (C_1/C_1^o X_1) - \dfrac{\gamma A_1^o}{RT}\left[1 - \dfrac{A_{av}}{X_1 A_1^o + (1 - X_1) A_2^o}\right]\right]}{(1-X_1)^2\left[\ln (C_2/C_2^o(1-X_1) - \dfrac{\gamma A_2^o}{RT}\left[1 - \dfrac{A_{av}}{X_1 A_1^o + (1-X_1) A_2^o}\right]\right]} = 1 \quad [43]$$

Since C_1, C_1^o, C_2, C_2^o, A_1^o, A_2^o and A_{av} can be obtained from experimental data , X_1 can be solved numerically from Eq.[43]. Substituting X_1 into Eq.[42], the interaction parameter, β^σ, can be obtained.

It is apparent from a comparison of Eqs.[35] and [37] with Eqs.[42] and [43] that as the quantity $1 - A_{av}/[X_1 A_1^o + (1-X_1) A_2^o]$, which we shall call the " packing deviation factor ", decreases, the two sets of equations become more and more similar and that when the quantity equal zero, the two sets of equations are the same. When the " packing deviation factor " is positive, then β^σ obtained from Eq.[42] will be more negative than that obtained from Eq.[35],when it is negative, then β^σ obtained from Eq.[42] will be more positive or less negative than that obtained from Eq.[35].

Kolp, et al (26) investigated the interaction of dimethyl dodecylamine oxide (DMDAO) with sodium dodecylbenzenesulfonate (NaDBS). By studies of pH, light transmission, and diffusion coefficient, DMDAO and NaDBS have been found to interact in aqueous solution in the following ways : (1) Below the CMC of the mixture, the protonated form of the amine oxide and the dodecylbenzene precipitated metathetically . This consumption of the protonated form results in protonation of additional amine oxide, which results in an increase in pH, the pK_{SP} of the precipitate is 10.8 , (2) Above the CMC, the phenomenon of mixed micelle formation is added to the metathetical interaction. The CMC of the system containing a 2:3 mole ratio of NaDBS to DMDAO is 0.706 X 10^{-3} mole/l (NaDBS + DMDAO), lower than the CMC of either of the surfactant alone . The molar ratio in the mixed micelle is about 1:2 NaDBS : DMDAO.

Rosen, et al (27) investigated the interaction of dimethyl dodecylamine oxide(DMDAO) with potassium dodecanesulfonate ($KDSO_3$) in dilute aqueous solution by surface tension study below the CMC of either solute. It was shown that the protonated dimethyl dodecylamine oxide cation, formed by the reaction of DMDAO with water, reacts with the dodecanesulfonate anion to form a salt, $C_{12}H_{25}N(CH_3)_2OH^{+}-O_3SC_{12}H_{25}$ (B). The infrared spectrum of this salt indicates that the cation and anion are strongly hydrogen bonded via the ionizable hydrogen. They developed equations for calculating the activity of B in aqueous solutions containing B as the only solute and in aqueous mixtures of DMDAO and $KDSO_3$. The coincidence of the γ – activity of B curve for solutions containing B as the only solute with that for aqueous $KDSO_3$ –DMDAO mixtures indicates that the activity of B determines the γ of these mixtures. The slope of the γ – activity of B curve indicates a close – packed arrangement of the hydrocarbon chains of B at the solution/air interface.

NMR investigations on micellar systems have been undertaken in the past decade by several authors (28 –43). This method has been used predominantly to measure the CMC and aggregation, and associate equilibrium constants. Chemical shifts, line widths and relaxation times of the nuclei (H^1, and occasionally F^{19}) of the surfactant molecules at various concentrations had been measured to obtain the information about the micellar properties. However, most of these measurements have been done on single surfactant compounds and not on mixed micellar systems, probably because of complication of these systems.

The NMR technique is thought to be one of the powerful tools to investigate the intermolecular interaction of two different surfactants in their mixed micelles and it will give us some information of this interaction which may not be obtained by means of other techniques (44-46).

Tokiwa and Tsujii (44) studied the interaction between anionic and nonionic surfactants in their mixed micelles by NMR technique. In this study, the NMR spectra of aqueous solutions of nonionic surfactant, dodecyl polyether ($C_{12}POE$) with different number of oxyethylene units, have been measured in the presence of anionic surfactants, sodium dodecyl sulfate ($NaC_{12}S$) and sodium p - octylbenzene-sulfonate (NaC_8BS), at different molar ratios of anionic/nonionic surfactant. When NaC_8BS is added to $C_{12}POE$ solutions, the peak due to protons of the polyoxyethylene chain of $C_{12}POE$ shifts to a higher magnetic field and becomes broader, the extent of the upfield shift depending on the polyoxyethylene chain length of $C_{12}POE$ and the mixing ratio of $NaC_8BS/C_{12}POE$. However, this peak remains at the same position and shows no remarkable change on addition of $NaC_{12}S$. The upfield shift of the polyoxyethylene peak caused by addition of NaC_8BS is ascribed to an interaction between the polyoxyethylene chain of $C_{12}POE$ and the benzene ring of NaC_8BS in their mixed micelle, since the only difference between the two anionic surfactants is whether they have a benzene ring in the molecule or not. Incidentally on mixing $C_{12}POE$ with NaC_8BS, the peak due to phenyl protons of NaC_8BS near to the alkyl chain shifts to a lower field to the extent of 3 - 4 cps.

This interaction has been discussed in relation to the polyoxyethylene chain length of $C_{12}POE$ and the mixing ratio of $NaC_8BS/C_{12}POE$. In the mixed micelle, the number of $C_{12}POE$ molecules influenced by one NaC_8BS molecule was calculated to be 0.6 - 1.6, depending on the polyoxyethylene chain length and nearly constant for $C_{12}POE$ with oxyethylene units larger than about 9. The number of oxyethylene units influenced by the benzene ring of NaC_8BS was estimated to be about 9. In any study of the interaction between nonionics and ionics, the concentrations of the two species could be expected to be important in governing the nature, extent, and mechanism of the interaction. Such anionic - nonionic interaction would therefore be a sensitive function of the molar ratio of anionic to nonionic.

The curves of upfield shift Δv vs concentration C for C_{12}POE with different p (the number of oxyethylene units per molecule) are shown in Figure 1, where C is the concentration of NaC_8BS expressed by the molar ratio of $NaC_8BS/C_{12}POE$, the concentration of $C_{12}POE$ is being kept constant. When one compares the value of Δv at constant C, it decreases with increasing number of p. This suggests that , in the mixed micelle, the influence of the benzene ring of NaC_8BS on the polyoxyethylene protons cannot extend to the whole polyoxyethylene chain when the chain is sufficiently long.

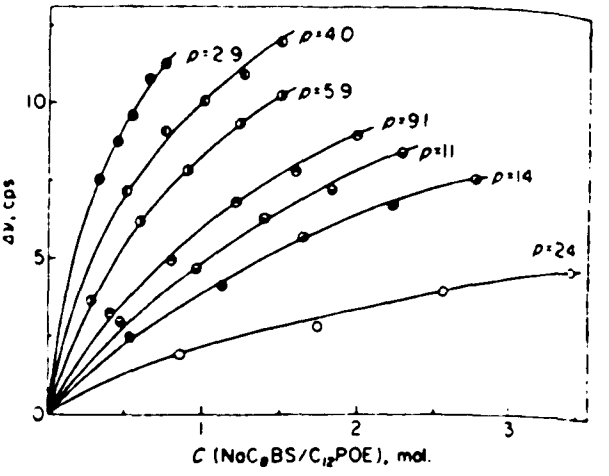


Figure 1. The upfield shift, Δv, of the polyoxyethylene proton signal plotted against the concentration, C, of added NaC_8BS for C_{12}POE-p with different p.

Bansal, et al (47) also studied anionic - nonionic surfactant interaction in the mixed micelle by the NMR technique. In this study, the anionic surfactant is sodium dodecylbenzenesulfonate (NaDBS) and the nonionic surfactants are tripropylene glycol monomethyl ether (PPG - 3) and tetrapropylene glycol monomethyl ether (PPG - 4). In the mixed micelle involving propylene glycol monomethyl ether (PPG) and NaDBS, it is likely that protons of PPG that are packed facing the benzene ring will experience the ring current paramagnetism and will be shifted upfield and it was found that the aromatic protons of NaDBS undergo a very small , almost negligible downfield shift. The changes in the chemical shift values and the integration values of the polypropylene protons and benzene protons was interpreted

in terms of mixed micelle formation with simultaneous presence of highly fluid mixed micelles of varying compositions. Kalibabchuk (48) investigated the interaction of cetyl pyridinium bromide with oxyethylated alcohols in aqueous medium. In this investigation, the NMR spectra show that (OCH_2CH_2) groups interact with the aromatic rings of cetyl pyridinium bromide in mixed micelles. Only 0.39 - 0.77 polyether mol interacts with 1 cetyl pyridinium bromide mol.

In surface and interfacial monolayers, two or more components often interact with another. Corkill, et al (49) investigated monolayer formed by mixtures of anionic and cationic surface-active agents. The study was made of the monolayers formed by salts of the type alkyl trimethylammonium alkyl sulfate at the air/solution interface. Insoluble monolayers were examined on a Langmuir trough. Although the substrate or the particular molecular species involved has some effect , maximum interaction invariably occurs at a 1: 1 ratio of long chain cation to anion. The composition of the surface layers of the soluble members was measured by radiotracer techniques. When the long chain cation and anion have the same chain length, an equimolar surface composition is obtained.

Hendrikx (50) studied interactions in mixed films of docosyl trimethylammonium bromide and sodium dodecyl sulfate. In this study, films of docosyl trimethylammonium bromide, sodium dodecyl sulfate, and mixtures of both constituents spread on aqueous solutions (pH= 5.5) have been investigated. The results give evidence of electrostatic interaction taking place in the mixed films. The effect of cetyl alcohol upon the equimolar films (A) of cationic and anionic surfactants has also been studied. The cetyl alcohol and " A mixture " are in 1: 1 ratio. From surface pressure and surface potential measurements, it appears that there is no interaction between cetyl alcohol and the equimolar " A mixture ". There is either an ideal mixture or two nonmiscible compounds. From the surface potential measurements, he has deduced the values of permanent dipole moments of cetyl alcohol and docosyl trimethylammonium bromide molecules. As a matter of fact, the surface potential of the mixed films, with a surface density higher than the collapse density, decreases as a function of the salt activity in the substrate, namely $CaCl_2$

Yoshio, et al (51) investigated the interaction between sulfobetaine type surfactants and ionic surfactant in aqueous solution. They found that the CMC of 3- dodecyl dimethyl ammoniopropane-1-sulfonic acid(I) - dodecyl trimethylammonium chloride mixtures indicated that the two surfactants behaved as homologs. In sodium dodecyl sulfate (II) - I mixtures, the CMC were smaller than those for I or II alone and indicated that I was a cationic surfactant. The conductance of I-II mixtures depends anomalously on the I : II ratio, and the phenomenon was explained by association - dissociation of counterions to (or from) the comicelles of I and II.

Mukhayer, et al (52) studied the interaction of benzyltriphenylphosphonium chloride (BTPC) and sodium dodecyl sulfate (SDDS) in aqueous solution, a model system for large organic ions of opposite charge by using the conductimetric titration method (53). This revealed three regions of interaction. In the first region, the interaction is the formation of the soluble ion - pairs ($BTP^+ DDS^-$). A approach derived from Job' s continuous variation method (54) was applied to the conductivity data to determine the ion - pair association constant ($K_{ion\text{-}pair} = 156$) . The second region occurs when the two ions interact to form an insoluble complex. The complex was defined by the solubility product for a 1:1 salt ($K_s = 9.97X10^{-8}$). A quadratic relationship was used for predicting the free and complexed BTP^+ and DDS^- ions in the solution. The values predicted by this relationship were in qualitative agreement with the experimentally calculated complexed ions determined from conductivity measurements. The experimental values were corrected for the presence of ion - pairs and obstruction effect due to the complex. The third region is characterized by the micellar solubilization of the complex.

Davis, et al (55) investigated the effect of ionic strength, temperature and urea on the interaction between sodium dodecyl sulfate(SDDS) and benzyltriphenylphospho - nium chloride (BTPC). In this study, they found that the interaction between SDDS and BTPC in aqueous solution results in the formation of an insoluble complex (DDSBTP). The solubility of this complex can be altered by changes in ionic strength and temperature and the addition of urea. An increased ionic strength increases the solubility of the complex (i.e., it is salted in). The calculated mean activity coefficient lies close to the Debye - Huckel line for a 1 : 1 electrolyte until the

ionic strength reaches about 0.1. Above this point the activity coefficient decreases rapidly and the solubility of the complex increases due to the formation of mixed micellar aggregates of DDS^- species with BTP^+ species as counter ions. The solubility of the complex also changes with an increase in temperature, an increase in temperature from 10 - 60 ^oC gives rise first to a reduced solubility and then to an increased solubility. The decrease in solubility with increased temperature at lower temperature is attributed to the increased interaction between the hydrophobic moieties of the interacting species. At higher temperature the solubility increases since increased temperature not only affects water structure but also the dielectric constant of the medium and thus electrostatic interaction between the two ions. Added urea brings about an increased solubility of the complex through its well known effect on hydrogen - bonded water and in turn its destabilizing effect on hydrophobic interactions. It is concluded that complex formation between two large organic ions of opposite charge such as BTP^+ and DDS^- is a twofold process, the coulombic interaction between the two centers of opposite charge and hydrophobic interaction between the two bulky nonpolar portions of the ions.

Mukhayer, et al (56) investigated the effect of alkyl chain length on the interaction between sodium alkyl sulfates (anions) and various phosphonium compounds (cations) by conductimetric titration. The logarithm of the stoichiometric solubility product (log K_s') is linearly related to alkyl chain length and the free energy of transfer (ΔG_F^o) of a CH_2 group from aqueous environment to the complex is found to be - 3.2 kJ mol^{-1} for alkyl groups attached to the anion but only - 1.0 k J mol^{-1} for groups attached to the cation. The thermodynamic quantities ΔH_F^o and ΔS_F^o have been derived from studies on the temperature variation of log K_s'. The derived data support the view that the separated phase resulting from anion - cation interaction is liquid - like in nature (a coacervate).

Mukhayer, et al (57) also investigated the effect of various substituents in the benzyl moiety on the interaction between benzyltriphenylphosphonium chloride and sodium dodecyl sulfate by conductimetric titration at a range of temperature. Calculated functional group contributions to the thermodynamics of complexation ($\Delta\Delta G_F$, $\Delta\Delta H_F$, $\Delta\Delta S_F$) are considered in terms of a twofold interaction process, electrostatic interaction between charged centers reinforced by hydrophobic interaction between nonpolar functions.

Lange and Beck (20) investigated the effect of oxyethylene group on β^M values of polyoxyethylenated nonionic - anionic systems in aqueous solution at 25 ^{o} C. The values of β^M are -3.1 for the system $C_{12}SO_4Na$ - C_8 (EO)$_4$, -3.4 for the system $C_{12}SO_4Na$ - C_8 (EO)$_6$, and - 4.1 for the system $C_{12}SO_4Na$ - C_8 (EO)$_{12}$. From this data, it is apparent that the interaction between an alkyl sulfate and a polyoxyethylenated nonionic increases with increasing the number of oxyethylene units in the nonionic. This may be due to the greater complexing of Na^+ with the ether oxygens of polyoxyethylene chain with increasing the number of oxyethylene units, giving the nonionic a greater amount of cationic character, leading to the stronger interaction with an alkyl sulfate.

There have been many studies on the interactions of nonionic and anionic surfactants in aqueous solutions (58 - 68), in which the mixed micelle formation of mixtures has been studied by measuring the surface tension and by solubilization methods. Recently, Meguro, et al (69) investigated the interaction between sodium tetradecyl sulfate and a series of homogeneous polyoxyethylene glycol- n -dodecyl ethers. In this study, the surface tensions of a mixed system of sodium tetradecyl sulfate (STS) and a series of polyoxyethylene glycol-n-dodecyl ether (nED, n =5-8) were measured at temperature of 30 ^{o} and 40 ^{o} C, respectively. When the STS concentration was fixed, the surface tension curves of the mixed systems showed a flat portion in the range of which the mixed micelle would be formed. The appearance of the flat portion on the surface tension curves suggests the existence of interaction between STS and nED. With a decrease of the added STS concentration , the length of the flat portion in these curves decreased gradually, and finally disappeared in the presence of 0.05 mM STS. Furthermore , when the concentration of STS was fixed at 1.0 mM, which is below the CMC, the flat portion length in the surface tension curves decreased with decreasing oxyethylene chain length in nED and with increasing temperature. The influence of increment of temperature was comparable to that for reducing the length of oxyethylene chain in nED.

On the other hand, sodium - di - 2 - ethyl hexyl sulfosuccinate (AOT) is an important practical anionic surfactant widely used in nonaqueous as well as in aqueous solutions. Although the micelle formation and solution behavior of AOT in water have been studied by several workers (70 - 73), there are a few studies of interaction of AOT with other surfactants, Chang, et al (74) studied the surface properties of mixtures of AOT and nonionic surfactants by measuring their surface

tensions and by calculating the interaction parameter between them. In this investigation, the surface tensions of the mixed systems consisting of AOT and homogeneous polyoxyethylene glycol -n - dodecyl ether (nED, n = 5 - 8) were measured in the absence and presence of NaCl by modified Wilhelmy plate method. In the case of the system containing nED and AOT, the nED concentrations were fixed at various amounts, and all the surface tension curves approached 32 or 33 mNm^{-1} as the concentration of AOT approached $1x10^{-3}$ mol/l . On the other hand, when the AOT concentration was fixed at $1x10^{-3}$ mol/l , the surface tension curves for the mixed system showed a flat portion in the range where mixed micelle in the solution and the two dimensional ones on the water surface were formed. In the case of the system containing 6ED, AOT and NaCl, the surface tension curves show inflection points shifted to higher concentration of AOT as the concentration of 6ED increased.

In systems containing constant concentration of AOT ($9.66x10^{-4}$ mol/l), the average values of β^{σ} are -0.9 for the 5ED - AOT system, -1.2 for the 6ED - AOT system, -1.5 for the 7ED - AOT system, and -2.6 for the 8ED - AOT system. These results for nED - AOT systems suggest that deviation from the ideal increases with increasing the length of oxyethylene chain of nonionic surfactant and that the interaction of nonionic surfactant and AOT increases with increasing the length of oxyethylene chain of nED.

Further, in systems containing constant concentration of nED, the average values of β^{σ} are -1.2 for the 5ED - AOT system, -1.2 for the 6ED - AOT system , -2.1 for the 7ED - AOT system, and -2.3 for the 8ED - AOT system. The magnitude of β^{σ} with oxyethylene chain length of nonionic surfactants shows tendency similar to that described above. Additionally, they found that the absolute value of β^{σ} for the system containing constant concentration of 6ED increases with increasing AOT concentration, suggesting the stronger interaction of 6ED and AOT with increasing AOT concentration.

Rosen and Hua (75) studied molecular interactions at aqueous solution/air interface in binary mixtures of surfactants. Three systems were investigated : $C_{12}(EO)_3$ - $C_{12}(EO)_8$, $C_{12}SO_3Na$ - $C_{12}(EO)_8$, and $C_{12}pyrBr$ - $C_{12}(EO)_8$. The surface molecular interaction parameter β^{σ} for the system $C_{12}(EO)_3$ - $C_{12}(EO)_8$ has an average value of - 0.17, indicating an almost ideal mixture in the surface. For the system $C_{12}SO_3Na$ - $C_{12}(EO)_8$, the average value of β^{σ} is - 2.5, indicating significantly stronger interaction between $C_{12}SO_3$ and $C_{12}(EO)_8$ than between $C_{12}(EO)_3$ and $C_{12}(EO)_8$. For the system $C_{12}pyrBr$ -$C_{12}(EO)_8$, β^{σ} has an average value of - 0.79, which appears to indicate that the interaction between a cationic and polyoxyethylenated nonionic is somewhat greater than that between two polyoxyethylenated nonionics, but significantly less than that between an anionic and polyoxyethylenated nonionic. A possible explanation is that protonation of some ether oxygens in polyoxyethylene chain causes the nonionic to act as a weakly cationic material in the presence of the anionic surfactant. This is consistent with the known tendency of polyoxyethylenated nonionic to show weakly cationic character at reduced pH in the presence of large anions (76) and we can conclude that , for surfactants containing the same hydrophobic group, the order of molecular interaction in aqueous solution with polyoxyethylenated nonionic is anionic > cationic > nonionic.

From the previous work of Rosen and Hua (75), the interaction between polyoxyethylenated nonionic surfactants and anionic surfactants is believed to be due mainly to the weakly cationic character of the polyoxyethylene chain. In order to test this hypothesis , Rosen and Zhao (77) investigated the interaction between $C_{12}(EO)_8$ and $C_{12}SO_3Na$ at 25 ^{o} C in NaCl solution of 0.1 M total ionic strength (T.I.S.) at pH 3.1_0, 5.8_5, and 10.1_0. The values of β^{σ} are - 2.64 at pH 3.1_0, -2.55 at pH 5.8_5, and - 2.47 at pH 10.1_0. The decrease in the absolute value of β^{σ} with increasing pH is consistent with the hypothesized weakly cationic character of the polyoxyethylene chain.

Rosen and Zhao (77) studied the effect of relative number of carbon atoms in the two hydrophobic groups on β^{σ}, three sets of systems were investigated at 25 ^{o} C , all in NaCl solution at 0.1 M T.I.S. :

(1) $C_{12}(EO)_8$ mixtures with sodium alkyl sulfates of C_{10}, C_{12} and C_{14} chain length

(2) $C_{12}(EO)_8$ mixtures with sodium alkanesulfonates of C_{10}, C_{12} and C_{14} chain length

(3) 1,2 - dodecanediol (C_{12} diol) mixtures with sodium alkanesulfonates of C_{10}, C_{12} and C_{14} chain length .

The values of β^{σ} for these systems are listed in table 1

Table 1 Effect of relative number of carbon atoms in the two hydrophobic groups on β^{σ}

System	β^{σ}
$C_{12}(EO)_8$ - $C_{10}SO_4Na$	-3.2
$C_{12}(EO)_8$ - $C_{12}SO_4Na$	-3.5
$C_{12}(EO)_8$ - $C_{14}SO_4Na$	-3.2
$C_{12}(EO)_8$ - $C_{10}SO_3Na$	-2.2
$C_{12}(EO)_8$ - $C_{12}SO_3Na$	-2.6
$C_{12}(EO)_8$ - $C_{14}SO_3Na$	-2.3
C_{12} diol - $C_{10}SO_3Na$	-2.4
C_{12} diol - $C_{12}SO_3Na$	-3.2
C_{12} diol - $C_{14}SO_3Na$	-2.6

From the data in table 1, we can see that maximum interaction occurs when the two different surfactants have alkyl chains with the same number of carbon atoms. The data also indicate that interaction of sodium alkanesulfonates with C_{12} diol is somewhat stronger than that with $C_{12}(EO)_8$. This may be due, at least , in part, to the smaller area occupied at the aqueous solution/air interface by C_{12} diol (0.2 nm^2)

(78) than by $C_{12}(EO)_8$ (0.66 nm^2) (79), permitting closer approach of the former to alkanesulfonates .

Rosen and Zhao (77) also investigated the effect of ionic strength of solution on the interaction between polyoxyethylenated nonionic and ionic surfactants, the systems studied are $C_{12}(EO)_8$ - C_{12}pyrCl, $C_{12}(EO)_8$ - $C_{12}SO_4Na$, and $C_{12}(EO)_8$ - $C_{12}SO_3Na$. The values of β^σ are shown in table 2

Table 2 Effect of ionic strength of solution on β^σ at 25 °C

System	Medium	β^σ
$C_{12}(EO)_8$ - C_{12}PyrCl	H_2O	-2.8
$C_{12}(EO)_8$ - C_{12}PyrCl	0.1 M T.I.S (NaCl)	-2.2
$C_{12}(EO)_8$ - C_{12}PyrCl	0.5 M T.I.S (NaCl)	-1.5
$C_{12}(EO)_8$ - $C_{12}SO_4Na$	H_2O	-2.7
$C_{12}(EO)_8$ - $C_{12}SO_4Na$	0.1 M T.I.S (NaCl)	-3.5
$C_{12}(EO)8$ - $C_{12}SO_4Na$	0.5 M T.I.S (NaCl)	-3.1
$C_{12}(EO)_8$ - $C_{12}SO_3Na$	H_2O	-1.5
$C_{12}(EO)_8$ - $C_{12}SO_3Na$	0.1 M T.I.S (NaCl)	-2.6
$C_{12}(EO)_8$ - $C_{12}SO_3Na$	0.5 M T.I.S (NaCl)	-2.0

C_{12}PyrCl = n - dodecyl pyridinium chloride

From the data in table 2, we can see that the interaction between nonionic $C_{12}(EO)_8$ and cationic C_{12}PyrCl decreases monotonously with increasing the ionic strength of the solution, indicating that the nature of the interaction between nonionic and cationic is probably electrostatic (since increase in the ionic strength of the solution decreases electrostatic interactions). However, an increase in the ionic strength of the solution produces first an increase, and then a decrease, in the interaction between nonionic and anionic surfactants. The explanation for this initial

increase is that, in the presence of anionic surfactant, there is complexing of Na^+ with the ether oxygens of polyoxyethylene chain, giving the nonionic a small amount of cationic character, with the results that its interaction with the anionic increases. The decrease in the interaction between nonionic and anionic with increasing ionic strength of the solution to 0.5 M is then the usual decrease in electrostatic interaction with increase in the ionic strength of the solution.

Rosen and Zhu (4) studied the interactions of zwitterionic with nonionic, cationic and anionic. In the four systems investigated, three are binary mixtures of betaine, $C_{12}H_{25}N^+(CH_2C_6H_5)CH_3CH_2COO^-$ ($C_{12}BMG$), with an anionic, $C_{12}SO_3Na$, with a nonionic, $C_{12}(EO)_8$, and with a cationic, $C_{12}NMe_3Br$, the fourth is a binary mixture of the sulfobetaine,$C_{10}H_{21}N^+(CH_2C_6H_5)CH_3CH_2CH_2$- SO_3^- ($C_{10}BMT$) with the anionic, $C_{12}SO_3Na$. The values of β^σ and β^M for these systems are shown in table 3

Table 3 Values of β^σ and β^M for systems investigated at 25 ° C

System	β^σ	β^M
$C_{12}BMG$ - $C_{12}(EO)_8$	- 0.6	- 0.9
$C_{12}BMG$ - $C_{12}NMe_3Br$	- 1.3	- 1.3
$C_{12}BMG$ - $C_{12}SO_3Na$, pH = 5.0	- 6.9	- 5.4
$C_{12}BMG$ - $C_{12}SO_3Na$, pH = 5.85	- 5.7	- 5.0
$C_{12}BMG$ - $C_{12}SO_3Na$, pH = 6.7	- 4.9	- 4.4
$C_{10}BMT$ - $C_{12}SO_3Na$, pH = 6.6	- 2.5	-

It is apparent from the data in table 3 that the betaine interacts much more strongly with the anionic than with the cationic or nonionic surfactant. Since the hydrophobic groups in all three cases are of similar structure and chain length, the different in β values reflect differences in the interaction between the two different hydrophilic groups in each binary system. On comparison of the system $C_{12}BMG$ - $C_{12}SO_3Na$, pH =6.7 and the system $C_{10}BMT$ - $C_{12}SO_3Na$, pH = 6.6 , the first system contains a zwitterionic (a betaine) capable of readily accepting a proton to become a cationic

species, the second system contains a zwitterionic (a sulfobetaine) of similar structure that is much less capable of accepting a proton (the sulfonate ion is a much weaker base than the carboxylate ion). The greater ability of the first system to accept a proton, with the resulting strong anionic - cationic interaction, gives it a significantly greater negative β^{σ} value than the second system, at similar pH. Note also the increase in the negative values of both β^{σ} and β^{M} with decrease in pH, as would be expected for an interaction involving acceptance of a proton.

Zhao and Zhu (80) investigated molecular interaction in mixed solution of fluorocarbon and hydrocarbon surfactants. The systems studied are $C_7F_{15}COONa$ (C_7FNa) - $C_{10}SO_4Na$, C_7FNa - $C_{12}SO_4Na$, $C_8H_{17}SOCH_3$ - C_7FNa , $C_8N(CH_3)Br$- C_7FNa, and $C_{10}F_{19}O(C_2H_4O)_9H$ -t- $C_8H_{17}C_6H_4O(C_2H_4O)_{10}H$. In mixed anionic - anionic systems C_7FNa - $C_{10}SO_4Na$ and C_7FNa - $C_{12}SO_4Na$, in NaCl solution of 0.1 M T.I.S at 30 ^{o} C the values of β^{σ} are all positive, which is to say, the activity coefficient of surfactants in the surface phase are greater than 1, clearly indicating the mutual phobicity between FC- and HC- chains of the surfactants. However, the positive values of β^{σ} are considerably small (0.5 -0.8), showing a rather weak mutual phobic interaction. For the nonionic -nonionic system, $C_{10}F_{19}O(C_2H_4O)_9H$ - t -$C_8H_{17}C_6H_4O(C_2H_4O)_{10}H$, β^{σ} has a small positive value (0.6), it once again clearly shows the mutual phobic interaction between FC- and HC- chains of the surfactants. For the cationic - anionic system, $C_8N(CH_3)Br$ - C_7FNa in NaBr solution of 0.1 M T.I.S at 30 ^{o} C the values of β^{σ} at various mole ratio of $C_8N(CH_3)Br$ and C_7FNa are negative and rather large (-12 - -15) indicating the strong molecular interactions due to the strong coulombic attraction between the two opposite charged surface active ions. For the nonionic - anionic system, $C_8H_{17}SOCH_3$ - C_7FNa in NaBr solution of 0.1 M T.I.S at 25 ^{o} C, the rather great value of β^{σ} (- 5 − - 6) shows the strong molecular interaction between the two components ' polar groups , since the two hydrophobic chains would be mutual - phobic. Considerably strong molecular interaction between $C_8H_{17}SOCH_3$ and C_7FNa may be probably attributed to the strong polarity of $\rangle$S=O group which

would gain a proton in the aqueous solution to become slightly positive charge (i.e., $C_8H_{17}SOCH_3 + H^+$ <-------> $C_8H_{17}S^+(OH)CH_3$) and thus a strong interaction takes place between $C_8H_{17}S^+(OH)CH_3$ and C_7F^- due to the coulombic attraction. This is evidenced by the fact that pH of the aqueous solution of $C_8H_{17}SOCH_3$ becomes higher than water and the absolute value of β^σ for C_8H_{17} - $SOCH_3$ - $C_8N(CH_3)Br$ system is much smaller than that for $C_8H_{17}SOCH_3$ - C_7F-Na system. The weak mutual phobic interaction between FC- and HC- chains has been clearly revealved in the anionic - anionic and nonionic - nonionic systems as indicated by the positive β^σ values. In the systems with considerable molecular interactions between the two surfactant components, such as $C_{18}N(CH_3)Br$-C_7FNa and $C_8H_{17}SOCH_3$ - C_7FNa systems, the mutual phobic interaction can be concealed certainly and there are large negative β^σ values for these systems.

1.3 Synergism In Binary Mixtures Of Surfactants

In most cases, when different types of surfactants are purposely mixed, what is sought is synergism, the condition when the properties of the mixture are better than those attainable with the individual components by themselves (81).

Rosen and Hua have used the treatment of Rubingh (21) for mixed micelle formation and their treatment of mixed monolayer formation (13) to derive equations showing the relationship of the interaction parameters β^{σ} and β^{M} to the existence of synergism in binary mixtures of surfactants.

1.3.1 Synergism In Surface Tension Reduction Efficiency

The efficiency of surface tension reduction by a surfactant is defined (82) as the solution phase concentration required to produce a given surface tension (reduction). Synergism in this respect is present when a binary mixture of surfactants can yield a given surface tension (reduction) at a total concentration lower than that required of both individual surfactants.

The point of maximum synergism is where the lowest total concentration of mixed surfactants is required to attain a given surface tension (reduction).

With the assumption that $A_1 = A_1^{o}$, Eq.[26] becomes

$$C_1 = X_1 C_1^{o} f_{1,S} \qquad [44]$$

From Eqs.[44] and [28], we obtain

$$\alpha_1 C_{12} = X_1 C_1^{o} \exp\left[\beta^{\sigma} (1 - X_1)^2 \right] \qquad [45]$$

With the assumption that $A_2 \simeq A_2^o$, Eq.[27] becomes

$$C_2 = (1 - X_1) C_2^o f_{2,S} \qquad [46]$$

From Eqs.[46] and [29], we obtain

$$(1 - \alpha_1) C_{12} = (1 - X_1) C_2^o \exp\left[\beta^\sigma (X_1)^2\right] \qquad [47]$$

From Eq.[45],

$$\ln C_{12} - \ln C_1^o = \ln X_1 - \ln \alpha_1 + \beta^\sigma (1 - X_1)^2 \qquad [48]$$

For synergism to exist, $C_{12} < C_1^o$, the condition for synergism, therefore, is

$$\ln X_1 - \ln \alpha_1 + \beta^\sigma (1 - X_1)^2 < 0 \qquad [49]$$

When synergism exist, there will be a minimum in the C_{12} versus $\alpha_1$curve and maximum synergism will be attained where the C_{12} versus $\alpha_1$curve shows a minimum , mathematically, that

$$\frac{d C_{12}}{d \alpha_1} = 0$$

From Eq.[48],

$$\frac{d \ln C_{12}}{d \alpha_1} = \frac{1}{X_1} \cdot \frac{d X_1}{d \alpha_1} - \frac{1}{\alpha_1} - 2\beta^\sigma (1 - X_1) \frac{d X_1}{d \alpha_1} \qquad [50]$$

$$\frac{d C_{12}}{d \alpha_1} = C_{12} \left[\frac{1}{X_1} \cdot \frac{d X_1}{d \alpha_1} - \frac{1}{\alpha_1} - 2\beta^\sigma (1 - X_1) \frac{d X_1}{d \alpha_1} \right] \qquad [51]$$

Since C_{12} can never be 0, $\frac{d C_{12}}{d \alpha_1}$ will be o when

$$\frac{1}{X_1} \cdot \frac{d X_1}{d \alpha_1} - \frac{1}{\alpha_1} - 2\beta\sigma(1 - X_1) \frac{d X_1}{d \alpha_1} = 0 \qquad [52]$$

or

$$\frac{d X_1}{d \alpha_1} = \frac{X_1}{\alpha_1[1 - 2\beta\sigma X_1(1 - X_1)]} \qquad [53]$$

From Eqs.[45] and [47],

$$\frac{\alpha_1}{(1- \alpha_1)} = \frac{X_1 C_1^o \exp [\beta\sigma (1-X_1)^2]}{(1-X_1) C_2^o \exp [\beta\sigma(X_1)^2]} \qquad [54]$$

Rearranging and taking logs,

$$\ln X_1 - \ln (1- X_1) + \ln (1 - \alpha_1) - \ln \alpha_1 + \ln (C_1^o/C_2^o) + \beta\sigma(1-2X_1) = 0$$

From which,

$$\frac{1}{X_1} \cdot \frac{d X_1}{d \alpha_1} + \frac{1}{(1-X_1)} \cdot \frac{d X_1}{d \alpha_1} - \frac{1}{(1-\alpha_1)} - \frac{1}{\alpha_1} - 2\beta\sigma \cdot \frac{d X_1}{d \alpha_1} = 0$$

$$\frac{d X_1}{d \alpha_1} = \frac{X_1(1-X_1)}{\alpha_1(1- \alpha_1) [1 - 2\beta\sigma X_1(1-X_1)]} \qquad [55]$$

Combine Eqs.[53] and [55],

$$X_1 = \alpha_1^* \qquad [56]$$

where α_1^* is the mole fraction of surfactant 1 in the total surfactant in the solution phase at the point of maximum synergism.

Relation [56] states that for a minimum or maximum to exist in the C_{12} versus α_1 curve, the mole fraction of either surfactant in the total surfactant in the surface phase must equal its mole fraction in the total surfactant in the solution phase.

Combine Eqs.[56] and[49] and recalling that $(1-X_1)^2$ is always a positive number, we conclude that , for synergism to exist, β^σ must be negative.

Since $\alpha_1 = X_1$ at the minimum, Eq.[54] reduces to

$$\frac{C_1^o \exp [\, \beta^\sigma (1-X_1)^2 \,]}{C_2^o \exp [\, \beta^\sigma (X_1)^2 \,]} = 1,$$

From which, $$\ln (C_1^o/C_2^o) = - \beta^\sigma (1 - 2X_1) \qquad [57]$$

Since $0 < X_1 < 1$ and β^σ must be negative for synergism to exist, relationship [57] states that a second condition for synergism is that

$$| \ln (C_1^o/C_2^o) | \quad \text{must be} \quad < \quad | \beta^\sigma |$$

When surfactant 1 is more surface active than surfactant 2, i.e., $C_1^o < C_2^o$, then α_1^* and X_1 will be > 0.5 at the point of maximum synergism, when surfactant 1 is less surface active than surfactant 2, α_1^* and X_1 will be < 0.5 at that point.

The minimum total mixed surfactant concentration in the solution phase, $C_{12,min}$, required to produce a given surface tension (reduction) , and the individual solution phase concentrations of surfactants 1 and 2, C_{S1} and C_{S2},

respectively, at the point of maximum synergism in surface tension reduction efficiency, can be calculated from Eqs.[48] and [57].

Since $\alpha_1^* = X_1$ at that point, Eq.[48] reduces to

$$\ln C_{12,min} = \ln C_1^o + \beta^\sigma (1 - X_1)^2 \qquad [58]$$

From Eq.[57],

$$X_1 = \frac{\ln (C_1^o/C_2^o) + \beta^\sigma}{2\beta^\sigma} = \alpha_1^* \qquad [59]$$

From Eqs.[58] and [59],

$$\ln C_{12,min} = \ln C_1^o + \beta^\sigma \left[\frac{\beta^\sigma - \ln (C_1^o/C_2^o)}{2\beta^\sigma} \right]^2 \qquad [60]$$

Or

$$C_{12,min} = C_1^o \exp \left[\beta^\sigma \left[\frac{\beta^\sigma - \ln (C_1^o/C_2^o)}{2\beta^\sigma} \right]^2 \right] \qquad [61]$$

$$C_{S1} = \alpha_1^* C_{12,min} \qquad [62]$$

and

$$C_{S2} = C_{12,min} - C_{S1} \qquad [63]$$

In summary, the conditions for synergism in surface tension reduction efficiency are

(1) β^σ must be negative

(2) $|\ln (C_1^o/C_2^o)|$ must be $< |\beta^\sigma|$

1.3.2 Synergism In Mixed Micelle Formation

Synergism in mixed micelle formation is present when CMC of the mixture is lower than that of the individual pure surfactants.

From Eqs.[13] and [17],

$$\alpha_1 C_{12}^M = X_1^M C_1^M \exp[\beta^M (1-X_1^M)^2 \quad [64]$$

From Eqs.[14] and [18],

$$(1-\alpha_1) C_{12}^M = (1-X_1^M) C_2^M \exp[\beta^M (X_1^M)^2 \quad [65]$$

From Eqs.[64] and [65], relationships analogous to those derived for synergism in surface tension reduction efficiency can be obtained for synergism in mixed micelle formation.

The conditions for synergism in this respect are

(1) β^M must be negative

(2) $|\ln (C_1^M/C_2^M)| < |\beta^M|$

At the point of maximum synergism in mixed micelle formation, i.e., when the CMC of the mixture is at its minimum value, $C_{12}^M{}_{,min}$,

$$\alpha_1^{*,M} = X_1^M = \frac{\ln (C_1^M/C_2^M) + \beta^M}{2\beta^M} \quad [66]$$

The minimum CMC of the mixture at the point of maximum synergism, $C_{12}^M{}_{,min}$, i.e., the minimum total mixed surfactant concentration in the solution phase required for mixed micelle formation, is given by the relationship :

$$C_{12}^M{}_{,min} = C_1^M \exp\left[\beta^M \left[\frac{\beta^M - \ln (C_1^M/C_2^M)}{2\beta^M}\right]^2\right] \quad [67]$$

The solution phase concentration of surfactant 1 at the point of maximum synergism in mixed micelle formation, C_{S1}^{M}, is given by

$$C_{S1}^{M} = \alpha_1^{*,M} C_{12}^{M,min} \quad [68]$$

and for surfactant 2,

$$C_{S2}^{M} = C_{12}^{M,min} - C_{S1}^{M} \quad [69]$$

1.3.3 Synergism In Surface Tension Reduction Effectiveness

The effectiveness of surface tension reduction has been defined(83) as the surface tension reduction attained at the CMC. Synergism in this respect is present when the mixture of surfactants of its CMC reaches a lower surface tension than that obtained at the CMC of either component of the mixture by itself.

Rosen and Zhu (5) and Hua and Rosen (14) have derived equations for the conditions under which synergism in surface tension effectiveness will exist at the CMC in binary mixtures of surfactants.

The basic equations of the nonideal solution theory (13) for adsorption at the liquid/air interface from a solution of two surfactants at its CMC (C_{12}^{M}) are

$$\frac{\alpha_1 C_{12}^{M}}{C_1^{o,cmc}} = X_1 f_{1,S} = X_1 \exp[\beta\sigma(1-X_1)^2] \quad [70]$$

$$\frac{(1-\alpha_1) C_{12}^{M}}{C_2^{o,cmc}} = (1-X_1) f_{2,S} = (1-X_1) \exp[\beta\sigma (X_1)^2] \quad [71]$$

where $C_1^{o,cmc}$ and $C_2^{o,cmc}$ are the solution phase molar concentrations of individual surfactants 1 and 2, respectively, required to yield a surface tension equal to γ_{CMC}, the surface tension of the mixture at its CMC

The linear portion of the γ - ln C plot of each individual surfactant at its CMC can hypothetically be extended to concentration values above the CMC to yield surface tension values equal to the surface tension γ_{cmc} of the mixture at its CMC (9,11), yielding the relationships :

$$\gamma_{cmc} = K_1' + K_1 \ln C_1^{o,cmc} \quad [72]$$

$$\gamma_{cmc} = K_2' + K_2 \ln C_2^{o,cmc} \quad [73]$$

From Eq.[70],

$$\ln C_1^{o,cmc} = \ln \alpha_1 + \ln C_{12}^{M} - \ln X_1 - \beta\sigma(1 - X_1)^2 \quad [74]$$

While Eq.[71] yields

$$\ln C_2^{o,cmc} = \ln (1- \alpha_1) + \ln C_{12}^{M} - \ln (1-X_1) - \beta\sigma(X_1)^2 \quad [75]$$

Substituting Eq.[74] into Eq.[72] yields

$$\gamma_{cmc} = K_1' + K_1[\ln(\alpha_1 C_{12}^{M}/X_1) - \beta\sigma(1- X_1)^2] \quad [76]$$

When synergism in surface tension reduction effectiveness exists, there will be a minimum in the γ_{cmc} versus α_1 curve, i.e.,

$$\frac{d\gamma_{cmc}}{d\alpha_1} = K_1[\frac{1}{\alpha_1} + \frac{d\ln C_{12}^{M}}{d\alpha_1} - \frac{1}{X_1}\cdot\frac{dX_1}{d\alpha_1} + 2\beta\sigma(1-X_1)\frac{dX_1}{d\alpha_1}] = 0 \quad [77]$$

Or

$$\frac{d\ln C_{12}^M}{d\alpha_1} = \left[\frac{1}{X_1} - 2\beta\sigma(1-X_1) \right] \frac{dX_1}{d\alpha_1} - \frac{1}{\alpha_1} \qquad [78]$$

Similarly, from Eqs.[75] and [73]

$$\frac{d\ln C_{12}^M}{d\alpha_1} = \left[\frac{1}{1-X_1} + 2\beta\sigma X_1 \right] \frac{dX_1}{d\alpha_1} - \frac{1}{1-\alpha_1} \qquad [79]$$

The basic equations of the nonideal solution theory (21) for mixed micelle formation in a solution of two surfactants are

$$\frac{\alpha_1 C_{12}^M}{C_1^M} = X_1^M f_1^M = X_1^M \exp[\beta^M (1-X_1^M)^2] \qquad [80]$$

$$\frac{(1-\alpha_1) C_{12}^M}{C_2^M} = (1-X_1^M) f_2^M = (1-X_1^M) \exp[\beta^M (X_1^M)^2] \qquad [81]$$

From Eq.[80],

$$\ln C_{12}^M = \ln C_1^M - \ln \alpha_1 + \ln X_1^M + \beta^M (1-X_1^M)^2 \qquad [82]$$

and from Eq.[81],

$$\ln C_{12}^M = \ln C_2^M - \ln (1-\alpha_1) + \ln (1-X_1) + \beta^M (X_1^M)^2 \qquad [83]$$

Differentiating Eqs.[82] and [83] with respect to α_1 yields

$$\frac{d\ln C_{12}^M}{d\alpha_1} = -\frac{1}{\alpha_1} + \left[\frac{1}{X_1^M} - 2\beta^M (1-X_1^M) \right] \frac{dX_1^M}{d\alpha_1} \qquad [84]$$

and

$$\frac{d\ln C_{12}^{M}}{d\alpha_1} = -\frac{1}{1-\alpha_1} - \left[\frac{1}{1-X_1^{M}} - 2\beta^{M} X_1^{M}\right]\frac{dX_1^{M}}{d\alpha_1} \qquad [85]$$

Combining Eqs.[84] and [78] yields

$$\left[\frac{1}{X_1} - 2\beta^{\sigma}(1-X_1)\right]\frac{dX_1}{d\alpha_1} = \left[\frac{1}{X_1^{M}} - 2\beta^{M}(1-X_1^{M})\right]\frac{dX_1^{M}}{d\alpha_1} \qquad [86]$$

While combining Eqs.[85] and [79] yields

$$\left[\frac{1}{1-X_1} - 2\beta^{\sigma}X_1\right]\frac{dX_1}{d\alpha_1} = \left[\frac{1}{1-X_1^{M}} - 2\beta^{M}X_1^{M}\right]\frac{dX_1^{M}}{d\alpha_1} \qquad [87]$$

Dividing Eq.[86] by [87] yields

$$\frac{(1/X_1) - 2\beta^{\sigma}(1-X_1)}{(1/1-X_1) - 2\beta^{\sigma}X_1} = \frac{(1/X_1^{M}) - 2\beta^{M}(1-X_1^{M})}{(1/1-X_1^{M}) - 2\beta^{M}X_1^{M}}$$

Which reduces to

$$X_1 = X_1^{M} \qquad [88]$$

Relationship [88] states that , for either a minimum or a maximum in the γ_{cmc} versus α_1 curve to exist, the composition of the mixed surface layer must equal that of the mixed micelle.

Combining Eqs.[74], [82], and [88], we obtain

$$\ln C_1^{M} - \ln C_1^{o,cmc} = (\beta^{\sigma} - \beta^{M})(1 - X_1)^2 \qquad [89]$$

While combining Eqs.[75], [83], and [88] yields

$$\ln C_2^M - \ln C_2^{o,cmc} = (\beta^\sigma - \beta^M)(X_1)^2 \qquad [90]$$

Substituting Eq.[72] into Eq.[89] yields

$$K_1 \ln C_1^M + K_1' - \gamma_{cmc} = K_1(\beta^\sigma - \beta^M)(1- X_1)^2 = \gamma^o_{cmc1} - \gamma_{cmc} \qquad [91]$$

While substituting Eq.[73] into Eq.[90] yields

$$K_2 \ln C_2^M + K_2' - \gamma_{cmc} = K_2(\beta^\sigma - \beta^M)(X_1)^2 = \gamma^o_{cmc2} - \gamma_{cmc} \qquad [92]$$

where γ^o_{cmc1} and γ^o_{cmc2} are the surface tension values at their CMC's of individual surfactants 1 and 2, respectively.

Conditions For the Existence of Synergism and Negative Synergism in Surface Tension Reduction Effectiveness

Synergism in surface tension reduction effectiveness exists when $\gamma_{cmc} < \gamma^o_{cmc1}, \gamma^o_{cmc2}$

In Eqs.[91] and [92] we know that K_1 and K_2 (the slope of the γ - ln C plots of the individual surfactants 1 and 2, respectively.) are always negative and terms $(1-X_1)^2$ and $(X_1)^2$ are always positive. The necessary condition for synergism in this respect, i.e., $\gamma_{cmc} < \gamma^o_{cmc1}, \gamma^o_{cmc2}$, is then

$$\beta^\sigma - \beta^M < 0$$

The necessary condition for negative synergism in this respect, i.e., $\gamma_{cmc} > \gamma^o_{cmc1}, \gamma^o_{cmc2}$, is

$$\beta^\sigma - \beta^M > 0$$

Combining Eqs.[74] and [75], we obtain

$$\ln C_1^{o,cmc} - \ln \alpha_1 + \ln X_1 + \beta^\sigma(1-X_1)^2$$

$$= \ln C_2^{o,cmc} - \ln (1- \alpha_1) + \ln (1-X_1) + \beta^\sigma(X_1)^2 \qquad [93]$$

Combining Eqs.[82] and [83], we obtain

$$\ln C_1^M - \ln \alpha_1 + \ln X_1^M + \beta^M (1-X_1^M)^2$$

$$= \ln C_2^M - \ln (1- \alpha_1) + \ln (1-X_1^M) + \beta^M (X_1^M)^2 \qquad [94]$$

Combining Eqs.[93], [94], and [88], we obtain

$$\ln[(C_1^{o,cmc}/C_2^{o,cmc})(C_2^M/C_1^M)] = (\beta^\sigma - \beta^M)(2X_1 - 1) \qquad [95]$$

From Eq.[95], since $2X_1 - 1 < 1$, then the condition for either a minimum or a maximum to exist in the γ_{cmc} versus α_1 curve is

$$\left| \beta^\sigma - \beta^M \right| > \left| \ln[(C_1^{o,cmc}/C_2^{o,cmc})(C_2^M/C_1^M)] \right|$$

In summary, the conditions for the existence of synergism in this respect are

(1) $\beta^\sigma - \beta^M < 0$

(2) $\left| \beta^\sigma - \beta^M \right| > \left| \ln[(C_1^{o,cmc}/C_2^{o,cmc})(C_2^M/C_1^M)] \right|$

The conditions for the existence of negative synergism in this respect are

(1) $\beta^\sigma - \beta^M > 0$

(2) $\beta^\sigma - \beta^M > \left| \ln[(C_1^{o,cmc}/C_2^{o,cmc})(C_2^M/C_1^M)] \right|$

Conditions at the Point of Maximum Synergism

The different between the surface tension of the mixed solution at its CMC and that of the individual surfactants 1 and 2 at their CMC's when $X_1^* = X_1^{M,*}$ are

$$\gamma^o_{cmc1} - \gamma^*_{cmc} = K_1 (\beta^\sigma - \beta^M)(1 - X_1^*)^2 \qquad [96]$$

$$\gamma^{o}_{cmc2} - \gamma^{*}_{cmc} = K_2 (\beta^{\sigma} - \beta^{M})(X_1^{*})^2 \qquad [97]$$

where γ^{*}_{cmc} is γ_{cmc} at a minimum or maximum in the γ_{cmc} versus $\alpha_1$curve, X_1^{*} is X_1 corresponding to a minimum or maximum in the γ_{cmc} versus $\alpha_1$curve, and $X_1^{M,*}$ is X_1^{M} corresponding to a minimum or maximum in the γ_{cmc} versus $\alpha_1$curve.

From Eqs.[96] and [97], we obtain

$$\frac{\gamma^{o}_{cmc1} - K_1(\beta^{\sigma} - \beta^{M})(1 - X_1^{*})^2}{\gamma^{o}_{cmc2} - K_2(\beta^{\sigma} - \beta^{M})(X_1^{*})^2} = 1 \qquad [98]$$

Eq.[98] is solved numerically for X_1^{*}. From Eq.[94], we obtain

$$\ln (\alpha_1/1- \alpha_1) = \ln (C_1^{M}/C_2^{M}) + \ln (X_1^{M}/1- X_1^{M}) + \beta^{M}(1- 2X_1^{M})$$

From which

$$\alpha_1 = \frac{(C_1^{M}/C_2^{M})(X_1^{M}/1- X_1^{M}) \exp[\beta^{M}(1- 2X_1^{M})]}{1 + (C_1^{M}/C_2^{M})(X_1^{M}/1- X_1^{M}) \exp[\beta^{M}(1- 2X_1^{M})]} \qquad [99]$$

Substituting the value of $X_1^{*} = X_1^{M}$ into Eq.[99],

$$\alpha_1^{*} = \frac{(C_1^{M}/C_2^{M})(X_1^{*}/1- X_1^{*})\exp[\beta^{M}(1- 2X_1^{*})]}{1 + (C_1^{M}/C_2^{M})(X_1^{*}/1- X_1^{*})\exp[\beta^{M}(1- 2X_1^{*})]} \qquad [100]$$

where α_1^{*} is the mole fraction of surfactant 1 in the total surfactant in the solution phase at the point of maximum synergism or negative synergism.

Substituting the value of X_1^{*} and α_1^{*} into Eq.[82] or [83] we obtain, respectively,

$$\ln C_{12}^{M,*} = \ln C_1^{M} - \ln \alpha_1^{*} + \ln X_1^{*} + \beta^{M}(1- X_1^{*})^2 \qquad [101]$$

or

$$\ln C_{12}^{M,*} = \ln C_2^M - \ln (1- \alpha_1^*) + \ln (1- X_1^*) + \beta^M(X_1^*)^2 \qquad [102]$$

where $C_{12}^{M,*}$ is the CMC of the mixture at the point of maximum synergism or negative synergism.

Substituting the value of X_1^* into Eq.[96] or [97], we obtain, respectively,

$$\gamma^*_{cmc} = \gamma^o_{cmc1} - K_1(\beta^\sigma - \beta^M)(1- X_1^*)^2 \qquad [103]$$

or

$$\gamma^*_{cmc} = \gamma^o_{cmc2} - K_2 (\beta^\sigma - \beta^M)(X_1^*)^2 \qquad [104]$$

Chapter II

Experimental

2.1 Materials

2.1.1 Surface Active Agents

Sodium dodecyl sulfate, $C_{12}H_{25}SO_4Na$ ($C_{12}SO_4Na$) and sodium dodecyl sulfonate, $C_{12}H_{25}SO_3Na$ ($C_{12}SO_3Na$) were purchased from Research plus, Inc, Bayonne, N.J., > 98 % purity. Sodium dodecyl polyoxyethylene sulfate, $C_{12}H_{25}$-$(OC_2H_4)_XSO_4Na$ [$C_{12}(EO)_XSO_4Na$] where X = 2-4, were obtained from Henkel, West Germany, courtesy of Dr. M. Schwuger.

Sodium di - 2 ethylhexyl sulfosuccinate (AOT) and sodium di amyl sulfosuccinate (AAY) were obtained from American Cyanamid company, Wayne, N.J. n - Tetradecyl ammonium bromide,$C_{14}H_{29}N^+(CH_3)_3Br^-$ [$C_{14}NBr$] was synthesized in our laboratory.

Octaethyleneglycol mono n - dodecyl ether, $C_{12}H_{25}(OC_2H_4)_8OH[C_{12}(EO)_8]$ and tetraethyleneglycol mono n - dodecyl ether, $C_{12}H_{25}(OC_2H_4)_4OH[C_{12}(EO)_4]$ were purchased from Nikko Chemical Co, Tkyo, Japan. The purity is > 98 %.

$C_{12}H_{25}$ - 2 - $C_6H_4SO_3Na$ (2^o LAS) and $C_{12}H_{25}$ - 4-$C_6H_4SO_3Na$ (4^o LAS) were research samples obtained from Conoco Inc, Oklahoma.

2.1.2 Water and Inorganic Salt

The water used for the preparation of surfactant solutions was deionized first and distilled twice (the last distillation being from alkaline $KMnO_4$ solution, through a 3 feet high Vigreaux column with quartz condenser and receiver). The specific conductance of the quartz condensed water is $1.1x10^{-6}$ mho cm^{-1} at 25 ^{o} C and the pH is about 5.8.

Sodium chloride (100 % standard, Thom Smith Chemist, Beulah,MI.), used to adjust ionic strength of the solutions , was baked over 6 hours in a porcelain

casserole at red heat to remove traces of organic compounds. The surface tension of aqueous solution of the baked NaCl was measured to ensure the absence of traces of surface-active impurities. Magnesium carbonate was purchased from J.T. Baker Chemical Co, N.J.

2.2 Purification and Concentration Determination in Aqueous Surfactant Solution

Before being used for surface tension measurement, aqueous solutions of the surfactants which were prepared with quartz distilled water were further purified by repeated passage through minicolumns of octadecylsilanized silica gel (SEP - PAK C_{18} Cartridge, Water Assoc, Milford, Mass)(84) to remove any traces of impurities more surface active than the parent compound, until the surface tension versus log concentration curve of the material showed no minimum in the vicinity of the CMC and, in addition, reached equilibrium value of surface tension within one hour.

The concentrations of $C_{12}(EO)_8$ and $C_{12}(EO)_4$ solutions were determined from standard curves of surface tension versus log concentration of pure $C_{12}(EO)_8$ and $C_{12}(EO)_4$ in this lab (85). The concentration of sodium di - amyl sulfosuccinate (AAY) solution was determined by accurately weighing the chemical (dried in vacuo over phosphorus pentoxide to constant weight) and preparing the solution in a volumetric flask.

Two - phase titration using mixed indicator (86) was used to determine the concentrations of the other ionic surfactant solutions, after passage through the SEP - PAK column first. The titration is based upon the transfer of dye - anionic surfactant complex between aqueous phase and organic phase. The organic - soluble complex of an anionic surfactant with a basic dye is destroyed by the cationic surfactant and the dye is released into the water phase and the complex of anionic and cationic surfactants enters the organic phase (chloroform).

To 10 ml of anionic surfactant of unknown concentration (approximately 2×10^{-3} M) in a 200 ml glass - stopped conical flask, 15 ml of chloroform ,10 ml of water and 10 ml of acidic mixed indicator were added. This solution was titrated against the cationic surfactant solution, Hyamine 1662, of known concentration until

the pink color was discharged from the chloroform layer. After each addition of Hyamine 1662, the mixture was vigorous shaken and then the layers are allowed to separate. At the end point, the lower layer has a gray color with no traces of pink color. The procedure used to determine the concentration of $C_{14}N(CH_3)Br$ was the same as that used for the anionic surfactant solution, except that the anionic surfactant ($C_{12}SO_3Na$) of known concentration was used to check the $C_{14}N(CH_3)Br$ solution of unknown concentration.

The standard cationic surfactant solution used to titrate the anionic surfactant solutions, was prepared by using diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride (Hyamine 1662) (98 % purity, Rohm and Hass. Co, PA). The purity of Hyamine 1662 was determined by titrating against sodium dodecyl sulfate (BDH Chemical, Ltd, Poole, England). On the basic of this, the molar absorptivity of the sample of Hyamine 1662 was determined to be 1266 $L \cdot mol^{-1} cm^{-1}$ at wavelength of 269.5 nm. The concentration of all subsequent Hyamine solutions were checked by ultraviolet absorbance and the above value of the molar absorptivity was used.

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) (87,88). Weigh 0.5 $\pm$ 0.005 g of dimidium bromide into a 50 ml beaker and weigh disulphine blue V, 0.25 $\pm$ 0.005 g, into another 50 ml beaker. Add 25 ml of hot 10 % (volume) 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 hot 10 % ethanol solution. This solution was saved as a 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 volumetric flask and shake it well, then dilute to 500 ml with distilled water. This is the acidic mixed indicator used for the two - phase titration of cationic or anionic surfactant solutions.

2.3 Surface Tension Measurement

All surface tension measurements were made by Wilhelmy vertical plate technique (89), using a rectangle platinum plate of approximately 5 cm perimeter(0.1 mm thickness), sandblasted to be completely wetted(zero contact angle) by all solutions. The plate was calibrated against quartz distilled water each day that a measurement was made. The correction of densities was ignored in the present work because the weight per cent of surfactant in all solutions was less than 1 %, therefore, the densities of surfactant solutions were considered to be that of the quartz distilled water.

The surface tension apparatus consists of a circular dial - type torsion balance with a maximum capacity of 500 mg, readable to 0.2 mg. One of the arms was tared to approximately balance the platinum plate (and the cotton string supporting it) on the end of the other arm. The whole balance rests on a metal covered wood platform over a constant temperature bath. The platform can be raised and lowered accurately by a machine - threaded hydraulic device.

The solution to be tested was kept in a 200 ml dish partially immersed in a constant temperature bath at the desired temperature $\pm$ 0.02 ^{o} C.

The procedure for measuring surface tension by the Wilhelmy plate technique is as follows:

(1) The temperature of the bath was adjusted to the desired temperature.

(2) The 200 ml dish containing approximately 50 ml of the surfactant solution was placed in the water bath and equilibrated to the bath temperature.

(3) The platinum plate was rinsed with quartz distilled water, and was flamed the outer portion with a Bunsen burner flame until it was red, holding the plate vertically by a pair of tweezers.

(4) The plate was suspended from the cotton thread suspended from the locked balance. The balance was unlocked and adjusted to read zero.

(5) The balance was locked and lowered slowly until the lower edge of the plate almost reached its image reflected from the surface of the solution. The plate was checked and adjusted, if necessary, to lie parallel to the surface of the solution. The stirrer of the constant temperature bath was shut off, the balance was unlocked and the assembly lowered until the plate was just pulled under the surface of the solution. The stirrer of the constant temperature bath was turned on.

(6) The samples were aged at least for 15 minutes before readings were taken.

(7) The readings were taken as follows: The stirrer of the constant temperature bath was shut off and the plate was restored to it's original position in space by moving the arm of the torsion balance until the pointer reached the zero position. The plate was immersed again and left for 10 to 15 minutes before the next measurement was made. Five successive readings were taken without detaching the plate from the surface of the solution.

2.4 Determination of [Na^+] of Single and Mixed Surfactant Systems

[Na^+] of single and mixed surfactant systems were measured by a sodium ion selective electrode Cat.No. 13-639-20 (Fisher Scientific Co. Pittsburgh, Pa.) equipped with pH meter (model 135 A, Delta - matic) at pH 5.2, 25 ^{o} C. A saturated KCl - calomel electrode was used as a reference. The calibration curves of [Na^+] versus mV are shown in figures 23 - 27. Uncertainty in reading mV = 0.5 mV = 0.5×10^{-4} M Na^+. In these measurements, the number of readings = 9.

Chapter III

Results and Discussion

3.1 Effect of Surfactant Structure and Molecular Environment on Values of β^{σ} and β^{M}

3.1.1 Effect of LAS Structure on Values of β^{σ} and β^{M}

Systems $C_{12}(EO)_8$ - 4 ° LAS and $C_{12}(EO)_8$ - 2 ° LAS were investigated at 25 ° C in distilled water and in NaCl solutions of 0.005 and 0.01 M total ionic strength (T.I.S.). Values of β^{σ} and β^{M} are listed in table 4. Plots of surface tension (γ) versus logarithm of total surfactant concentration (log C_{12}) for $C_{12}(EO)_8$, 2 ° LAS and their mixtures in water and in NaCl solutions of 0.005 and 0.01 M T.I.S. are shown in figures 8, 9, and10, respectively. Plots of γ versus log - C_{12} for $C_{12}(EO)_8$, 4 ° LAS and their mixtures in water and in NaCl solutions of 0.005 and 0.01 M T.I.S. are shown in figures 11, 12, and 13, respectively.

Table 4 Effect of LAS Structure on Values of β^{σ} and β^{M} at 25 ° C

System	Medium	β^{σ}	β^{M}
$C_{12}(EO)_8$ - 4 ° LAS	H_2O	- 2.4	- 5.0
$C_{12}(EO)_8$ - 2 ° LAS	H_2O	- 3.0	- 5.3
$C_{12}(EO)_8$ - 4 ° LAS	0.005 M T.I.S.(NaCl)	- 3.8	- 5.4
$C_{12}(EO)_8$ - 2 ° LAS	0.005 M T.I.S.(NaCl)	- 4.0	- 5.7
$C_{12}(EO)_8$ - 4 ° LAS	0.01 M T.I.S.(NaCl)	- 3.9	- 4.7
$C_{12}(EO)_8$ - 2 ° LAS	0.01 M T.I.S.(NaCl)	- 4.3	- 5.4

From the data in table 4, it is apparent that the system $C_{12}(EO)_8$ - 2 ° LAS has greater absolute values of β^{σ} and β^{M} than the system $C_{12}(EO)_8$ - 4 ° LAS, indicating the stronger interactions between the two surfactants in mixed monolayer and in mixed micelle in the system $C_{12}(EO)_8$ - 2° LAS than in the system $C_{12}(EO)_8$- 4 ° LAS. This is because 2 ° LAS has a more linear structure than 4 ° LAS, therefore permitting more lateral chain - chain interaction with $C_{12}(EO)_8$ by the former. And the stronger interaction of 2 ° LAS, compared to 4 ° LAS, with C_{12} - $(EO)_8$ in the mixed monolayer may be due, at least in part, to the smaller area occupied at the aqueous solution/air interface by 2 ° LAS (64.9, 51.8, and 47 A^{o2} in H_2O , 0.005 and 0.01 M T.I.S.(NaCl), respectively.) than by 4 ° LAS (69 , 56, and 51 A^{o2} in H_2O, 0.005 and 0.01 M T.I.S.(NaCl), respectively), permitting closer approach of 2 ° LAS to $C_{12}(EO)_8$.

3.1.2 Effect of Ionic Strength of the Solution on Values of β^{σ} and β^{M}

The system $C_{12}(EO)_8$ - 4 ° LAS was investigated in distilled water and in NaCl solutions of 0.005, 0.01, 0.025, 0.05, and 0.1 M T.I.S. at 25 ° C, and the systm $C_{12}(EO)_8$ - AOT was investigated in distilled water and in NaCl solutions of 0.01, 0.025, and 0.05 M T.I.S. at 25 ° C. Values of β^{σ}, β^{M}, and A_{av} are listed in table 5. Plots of γ versus log C_{12} for $C_{12}(EO)_8$, 4 ° lAS and their mixtures in water and in NaCl solutions of 0.005, 0.01, 0.025, 0.05, and 0.1 M T.I.S. are shown in figures 11,12,13,14,15, and 16, respectively. Plots of γ versus log C_{12} for $C_{12}(EO)_8$, AOT and their mixtures in water and in NaCl solutions of 0.01,0.025, and 0.05 M T.I.S. are shown in figures 17, 18, 19, and 20, respectively.

Table 5 Effect of Ionic Strength of the Solution on Values of β^{σ} and β^{M} at 25° C

System	Medium	β^{σ}	β^{M}	A_{av}, A^{o2}
$C_{12}(EO)_8$ - 4 ° LAS	H_2O	- 2.4	- 5.0	70.0
$C_{12}(EO)_8$ - 4 ° LAS	0.005 M T.I.S.(NaCl)	- 3.8	- 5.4	57.0
$C_{12}(EO)_8$ - 4 ° LAS	0.01 M T.I.S.(NaCl)	- 3.9	- 4.7	56.0
$C_{12}(EO)_8$ - 4 ° LAS	0.025 M T.I.S.(NaCl)	- 3.8	- 4.6	54.3
$C_{12}(EO)_8$ - 4 ° LAS	0.05 M T.I.S.(NaCl)	- 3.7	- 4.2	51.0
$C_{12}(EO)_8$ - 4 ° LAS	0.1 M T.I.S.(NaCl)	- 3.5	- 3.9	50.0
$C_{12}(EO)_8$ - AOT	H_2O	- 2.4	- 2.0	73.0
$C_{12}(EO)_8$ - AOT	0.01 M T.I.S.(NaCl)	- 2.8	- 4.2	63.0
$C_{12}(EO)_8$ - AOT	0.025 M T.I.S.(NaCl)	- 2.4	- 3.9	61.7
$C_{12}(EO)_8$ - AOT	0.05 M T.I.S.(NaCl)	- 1.7	- 3.6	59.5

From the data in table 5, it is apparent that the interaction between $C_{12}(EO)_8$ and 4 ^{o} LAS in the mixed monolayer at the aqueous solution /air interface increases with increase in the ionic strength of the solution to 0.01 M, followed by a decrease with further increase in the ionic strength to 0.1 M, and there is an increase in the interaction between the two surfactants in the mixed micelle with increase in the ionic strength of the solution to 0.005 M, followed by a decrease with further increase in the ionic strength to 0.1 M.

The electrostatic component of the attractive interaction between the surfactant molecules in the mixed monolayer and in the mixed micelle would be expected to decrease with increase in the ionic strength of the solution due to compression of the electrical double layer surrounding the charged head groups.

The reason for the initial increase in the strength of the interaction between the two surfactants with increase in the ionic strength to 0.005 M is that, in the presence of anionic surfactant, there is complexing of the Na^+ with some of the ether oxygens in the polyoxyethylene chain of the polyoxyethylenated nonionic, $C_{12}(EO)_8$, in a manner similar to their interaction with crown ethers (90), giving the nonionic a small amount of cationic character, with the result that its interaction with the anionic increases. Alkali - metal cations have been shown to be capable of complexing with polyoxyethylenated nonionics in the presence of anionic surfactants and other large anions (91), and these complexes have been used as a basis for the analysis of this type of nonionic (92, 93).

As the ionic strength of the solution is further increased to 0.1 M, the interaction between the two surfactants decreases. This is because the usual decrease in electro - static interaction between the two surfactants as a result of an increase in the ionic strength of the solution overcomes the increase in the interaction due to the increase in complexation (Once a given Na^+ concentration is reached, complexation increases only slightly with the increase in Na^+ concentration).

The values of the average area, A_{av}, per surfactant molecule in the mixed monolayer at the aqueous solution/air interface are consistent with the results. It is apparent from the data in table 5 that, as the ionic strength of the solution increases to 0.005 M the value of A_{av} decreases significantly. This is because the formed complex increases the interaction with the anionic surfactant and the increasing ionic strength of the solution lowers the repulsion between remaining charge of similarly

charged surfactant molecules. The A_{av} value is decreased only slightly with further increase in the ionic strength to 0.1 M. This is because the major repulsive force between the surfactant molecules having similar charged head groups has already been decreased by the increase in the ionic strength to 0.005 M.

The results for the system $C_{12}(EO)_8$ - AOT are similar to those of the system $C_{12}(EO)_8$ - 4 ^{o} LAS.

3.1.3 Effect of Temperature on Values of β^σ and β^M

The system $C_{12}(EO)_8$ - 2 ^{o} LAS was investigated in NaCl solution of 0.01 M T.I.S. at 25 ^{o}, 35 ^{o}, and 40 ^{o} C, respectively. Values of β^σ, β^M, and $\beta^\sigma - \beta^M$ are listed in table 6. Plots of γ versus log C_{12} for $C_{12}(EO)_8$, 2 ^{o} LAS, and their mixtures in NaCl solution of 0.01 M T.I.S. at 25 ^{o}, 35 ^{o}, and 40 ^{o} C are shown in figures 10, 21, and 22, respectively.

Table 6 Effect of Temperature on Values of β^σ and β^M
System : $C_{12}(EO)_8$ - 2 ^{o} LAS, 0.01 M T.I.S.(NaCl)

Temp.(^{o} C)	β^σ	β^M	$\beta^\sigma - \beta^M$	A_{av} (A^{o2})
25	- 4.3	- 5.4	1.1	59.3
35	- 3.7	- 4.3	0.6	60.5
40	- 3.4	- 3.8	0.4	61.2

From the data in table 6, it is apparent that as temperature increases, the absolute values of β^{σ} and β^{M} decrease, indicating a decrease in strength of interaction between the two surfactants with increase in temperature. This is due to the fact that the area occupied by both of interacting surfactant molecules increase with increase in temperature in the range investigated, with consequent increase in the intermolecular distance, leading to the weaker interaction between them. The surface area per molecule for $C_{12}(EO)_8$ in 0.01 M T.I.S.(NaCl) are 65, 66.5, and 67 A^{o2} at 25 °, 35 °, and 40 ° C, respectively, and the surface area per molecule for 2 ° LAS in 0.01 M T.I.S.(NaCl) are 47, 48.3, and 49 A^{o2} at 25 °, 35 °, and 40 ° C, respectively. The values of A_{av} are consistent with the result. The values of β^{σ}- β^{M} also decrease with increase in temperature, this is because there is a larger decrease in interaction between surfactant molecules in the mixed micelle than in the mixed monolayer at the aqueous solution/air interface with temperature increase in this range.

3.1.4 Effect of $-SO_4^-$ VS $-SO_3^-$ Group on Value of β^{σ} in Presence of Mg^{2+}

Four systems were investigated in 1.95×10^{-3} M Mg^{2+} solution at 25 ° C : $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_3Na$, $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$, $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_3Na$, and $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$. Plots of γ versus log C_{12} for these systems are shown in figures 4,5,6, and 7. Values of β^{σ} for these systems are listed in table 7.

Table 7 Effect of $-SO_4^-$ VS $-SO_3^-$ Group on Values of β^σ in Presence of Mg^{2+} at 25 °C.

System	Medium	β^σ
$C_{12}(EO)_3SO_4Na$ - $C_{12}SO_3Na$	$1.95x10^{-3}$ M Mg^{2+}	- 0.44
$C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$	$1.95x10^{-3}$ M Mg^{2+}	- 2.1
$C_{12}(EO)_4SO_4Na$ - $C_{12}SO_3Na$	$1.95x10^{-3}$ M Mg^{2+}	- 0.71
$C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$	$1.95x10^{-3}$ M Mg^{2+}	- 3.7

From the data in table 7, it is apparent that the absolute value of β^σ for the system $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ is greater than that for the system $C_{12}(EO)_3$-SO_4Na - $C_{12}SO_3Na$. This means that interaction in the mixed monolayer at the aqueous solution/air interface between $C_{12}(EO)_3SO_4Na$ and $C_{12}SO_4Na$ is significantly stronger than that between $C_{12}(EO)_3SO_4Na$ and $C_{12}SO_3Na$. And the data also indicate that interaction in the mixed monolayer at the aqueous solution/air interface between $C_{12}(EO)_4SO_4Na$ and $C_{12}SO_4Na$ is significantly stronger than that between $C_{12}(EO)_4SO_4Na$ and $C_{12}SO_3Na$.

Some of the ether oxygens in polyoxyethylene chain of polyoxyethylenated anionics, $C_{12}(EO)_XSO_4Na$ (X = 3 and 4) complex with Mg^{2+}, therefore the polyoxyethylene chain has some cationic character. In polyoxyethylenated anionics, the negative charge of the surfactant ion should increase the tendency of the ether

oxygens to complex with Mg^{2+}. Since the interaction between polyoxyethylenated anionic surfactants and anionic surfactants is believed to be due mainly to the weakly cationic character of the polyoxyethylene chain, the significantly stronger interaction of $C_{12}SO_4Na$, compared to $C_{12}SO_3Na$, with polyoxyethylenated anionics may indicate greater polarizability of the sulfate group than the sulfonate group , due to the oxygen atom between carbon and sulfur.

3.1.5 Effect of Oxyethylene Group on Values of β^{σ} and β^{M} in Presence of Mg^{2+}

Five systems were investigated in $1.95x10^{-3}$ M Mg^{2+} solution at 25 °C : $C_{12}(EO)_2SO_4Na$ - $C_{12}SO_3Na$, $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_3Na$, $C_{12}(EO)_4SO_4Na$- $C_{12}SO_3Na$, $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$, and $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$. Plots of γ versus log C_{12} for these systems are shown in figures 3,4,5,6, and 7, respectively. Values of $\beta^{\sigma}$and β^{M} for the systems investigated are listed in table 8.

Table 8 Effect of Oxyethylene Group on Values of β^{σ} and β^{M} in Presence of Mg^{2+} at 25 °C

System	Medium	β^{σ}	β^{M}
$C_{12}(EO)_2SO_4Na$ - $C_{12}SO_3Na$	$1.95x10^{-3}$ M Mg^{2+}	- 0.16	-
$C_{12}(EO)_3SO_4Na$ - $C_{12}SO_3Na$	$1.95x10^{-3}$ M Mg^{2+}	- 0.44	-
$C_{12}(EO)_4SO_4Na$ - $C_{12}SO_3Na$	$1.95x10^{-3}$ M Mg^{2+}	- 0.71	-
$C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$	$1.95x10^{-3}$ M Mg^{2+}	- 2.1	- 1.2
$C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$	$1.95x10^{-3}$ M Mg^{2+}	- 3.7	- 1.8

From the data in table 8, it is apparent that the strength of interactions between polyoxyethylenated anionics and $C_{12}SO_3Na$ or $C_{12}SO_4Na$ in mixed monolayer or in mixed micelle increases with increase in the number of oxyethylene groups in polyoxyethylenated anionics. This may be due to the greater complexing of Mg^{2+} with polyoxyethylene chain with increase in the number of oxyethylene groups, giving the polyoxyethylene chain a greater amount of cationic character, leading to the stronger interactions with $C_{12}SO_3Na$ or $C_{12}SO_4Na$. The complexing efficiency of Mg^{2+} to the polyoxyethylene chain depends on the fit of Mg^{2+} in the polyoxyethylene chain. It has been shown that the binding of cation to a crown ether depends on both the size of the crown ring and the ionic diameter of the cation (94).

3.2 Synergism in Surface Tension Reduction Efficiency

The system $C_{12}(EO)_8$ - 2 ^{o} LAS was investigated in NaCl solution of 0.005 M T.I.S. at 25 ^{o} C and 0.01 M T.I.S. at 25 ^{o}, 35 ^{o}, and 40 ^{o} C, respectively. The system $C_{12}(EO)_8$ - 4 ^{o} LAS was investigated in NaCl solutions of 0.005, 0.01, 0.025, and 0.05 M T.I.S. at 25 ^{o} C. The system $C_{12}(EO)_8$ - AOT was investigated in NaCl solutions of 0.01, 0.025, and 0.05 M T.I.S. at 25 ^{o} C. And systems $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$, and $C_{12}(EO)_4Na$ - $C_{12}SO_4Na$ were investigated in $1.95x10^{-3}$ M Mg^{2+} solution at 25 ^{o} C. The experimental data for these systems are shown in tables 9 -15. From the data in these tables, it is apparent that the calculated values of C_{12},min (Eq.61), the minimum total mixed surfactant concentration in the solution phase required to produce a given surface tension (reduction) are very close to the experimental values.

Table 9 Synergism in Surface Tension Reduction Efficiency at 25 °C

System	Medium	α_1	X_1	C_{12}, mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - 2° LAS	0.005 M T.I.S (NaCl)	0	0	26.3×10^{-5}	-
		0.675	0.730	2.69×10^{-5}	-3.9
		0.764	0.759	2.60×10^{-5}	-4.1
		1.0	1.0	3.31×10^{-5}	-

$\gamma = 42$ mNm^{-1} α_1^*(calcd) = 0.760

ln (C_1^o/C_2^o) = -2.07, C_{12},min (calcd) = 2.59×10^{-5} mol dm^{-3}, β^σ_{av} = -4.0

System	Medium	α_1	X_1	C_{12}, mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - 2° LAS	0.01 M T.I.S. (NaCl)	0	0	18.20×10^{-5}	-
		0.6002	0.67	2.32×10^{-5}	-4.2
		0.7576	0.72	2.21×10^{-5}	-4.4
		1.0	1.0	3.31×10^{-5}	-

$\gamma = 42$ mNm^{-1} α_1^*(calcd) = 0.69

ln (C_1^o/C_2^o) = -1.70, C_{12},min (calcd) = 2.28×10^{-5} mol dm^{-3}, β^σ_{av} = -4.3

Table 10 Synergism in Surface Tension Reduction Efficiency at 35 °C and 40 °C

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - 2° LAS at 35 °C	0.01M T.I.S. (NaCl)	0	0	14.10×10^{-5}	-
		0.6797	0.722	1.84×10^{-5}	-3.7
		0.7608	0.749	1.78×10^{-5}	-3.8
		1.0	1.0	2.29×10^{-5}	-

$\gamma = 42$ mNm^{-1} α_1^*(calcd) = 0.752

ln (C_1^o/C_2^o) = -1.82, C_{12},min (calcd) = 1.78×10^{-5} mol dm^{-3}, β^σ_{av} = -3.7

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - 2° LAS at 40 °C	0.01 M T.I.S (NaCl)	0	0	13.5×10^{-5}	-
		0.6797	0.740	1.74×10^{-5}	-3.4
		0.7562	0.770	1.70×10^{-5}	-3.4
		1.0	1.0	2.00×10^{-5}	-

$\gamma = 42$ mNm^{-1} α_1^*(calcd) = 0.782

ln (C_1^o/C_2^o) = -1.91, C_{12},min (calcd) = 1.70×10^{-5} mol dm^{-3}, β^σ_{av} = -3.4

Table 11 Synergism in Surface Tension Reduction Efficiency at 25 °C

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - 4° LAS	0.005 M T.I.S. (NaCl)	0	0	38.0×10^{-5}	-
		0.3992	0.647	4.62×10^{-5}	-3.8
		0.7686	0.770	3.70×10^{-5}	-3.9
		1.0	1.0	4.57×10^{-5}	-

$\gamma = 40$ mNm^{-1} α_1^*(calcd) = 0.780

$\ln (C_1^o/C_2^o) = -2.12$, C_{12},min = 3.72×10^{-5} mol dm^{-3}, $\beta^\sigma_{av} = -3.8$

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - 4° LAS	0.01 M T.I.S. (NaCl)	0	0	25.1×10^{-5}	-
		0.02824	0.374	9.55×10^{-5}	-3.9
		0.1331	0.515	5.01×10^{-5}	-4.0
		0.7566	0.763	2.70×10^{-5}	-3.8
		1.0	1.0	3.31×10^{-5}	-

$\gamma = 42$ mNm^{-1} α_1^*(calcd) = 0.762

$\ln (C_1^o/C_2^o) = -2.05$, C_{12},min (calcd) = 2.69×10^{-5} mol dm^{-3}, $\beta^\sigma_{av} = -3.9$

Table 12 Synergism in Surface Tension Reduction Efficiency at 25 °C

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^{σ}
$C_{12}(EO)_8$ - 4° LAS	0.025 M T.I.S. (NaCl)	0	0	11.40×10^{-5}	-
		0.4571	0.569	2.63×10^{-5}	-3.8
		0.6275	0.630	2.54×10^{-5}	-3.7
		1.0	1.0	4.27×10^{-5}	-

$\gamma = 40$ mNm^{-1} α_1^{*}(calcd) = 0.629

$\ln (C_1^{o}/C_2^{o}) = -0.98$, C_{12},min (calcd) = 2.57×10^{-5} mol dm^{-3}, $\beta^{\sigma}_{av} = -3.8$

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^{σ}
$C_{12}(EO)_8$ - 4° LAS	0.05 M T.I.S. (NaCl)	0	0	6.31×10^{-5}	-
		0.4365	0.512	2.09×10^{-5}	-3.7
		0.5534	0.553	2.00×10^{-5}	-3.7
		1.0	1.0	4.27×10^{-5}	-

$\gamma = 40$ mNm^{-1} α_1^{*}(calcd) = 0.553

$\ln (C_1^{o}/C_2^{o}) = -0.39$, C_{12},min (calcd) = 2.02×10^{-5} mol dm^{-3}, $\beta^{\sigma}_{av} = -3.7$

Table 13 Synergism in Surface Tension Reduction Efficiency at 25 °C

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - 4° LAS	0.1 M T.I.S. (NaCl)	0	0	3.39×10^{-5}	-
		0.4365	0.464	1.53×10^{-5}	-3.4
		0.5372	0.501	1.50×10^{-5}	-3.6
		1.0	1.0	3.89×10^{-5}	-

$\gamma = 40$ mNm^{-1} α_1^*(calcd) = 0.52

ln (C_1^o/C_2^o) = -0.14, C_{12},min (calcd) = 1.52×10^{-5} mol dm^{-3}, β^σ_{av} = -3.5

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - AOT	0.01 M T.I.S. (NaCl)	0	0	11.5×10^{-5}	-
		0.4443	0.611	3.09×10^{-5}	-2.6
		0.7346	0.725	2.63×10^{-5}	-2.9
		1.0	1.0	3.31×10^{-5}	-

$\gamma = 42$ mNm^{-1} α_1^*(calcd) = 0.742

ln (C_1^o/C_2^o) = -1.24, C_{12},min (calcd) = 2.60×10^{-5} mol dm^{-3}, β^σ_{av} = -2.8

Table 14 Synergism in Surface Tension Reduction Efficiency at 25 °C

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - AOT	0.025 M T.I.S. (NaCl)	0	0	6.03×10^{-5}	-
		0.4363	0.548	2.46×10^{-5}	-2.4
		0.6322	0.630	2.24×10^{-5}	-2.5
		1.0	1.0	3.16×10^{-5}	-

$\gamma = 42$ mNm^{-1} α_1^*(calcd) = 0.628

ln $(C_1^o/C_2^o) = -0.64$, C_{12},min (calcd) = 2.20×10^{-5} mol dm^{-3}, $\beta^\sigma_{av} = -2.4$

System	Medium	α_1	X_1	C_{12},mol dm^{-3}	β^σ
$C_{12}(EO)_8$ - AOT	0.05 M T.I.S. (NaCl)	0	0	4.47×10^{-5}	-
		0.3974	0.449	2.95×10^{-5}	-1.6
		0.5190	0.516	2.75×10^{-5}	-1.8
		1.0	1.0	4.27×10^{-5}	-

$\gamma = 40$ mNm^{-1} α_1^*(calcd) = 0.515

ln $(C_1^o/C_2^o) = -0.046$, C_{12},min (calcd) = 2.76×10^{-5} mol dm^{-3}, $\beta^\sigma_{av} = -1.7$

Table 15 Synergism in Surface Tension Reduction Efficiency at 25 °C

System : $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ in 1.95×10^{-3} M Mg^{2+} solution

α_1	X_1	C_{12}, mol dm^{-3}	β^σ
0	0	12.2×10^{-4}	-
0.1407	0.494	4.47×10^{-4}	-1.9
0.6202	0.804	2.57×10^{-4}	-1.4
0.952	0.910	1.95×10^{-4}	-2.9
1.0	1.0	2.09×10^{-4}	-

$\gamma = 39$ mNm^{-1} α_1^*(calcd) = 0.954

ln $(C_1^o/C_2^o) = -1.76$, C_{12},min (calcd) = 1.95×10^{-4} mol dm^{-3}, $\beta^\sigma_{av} = -2.1$

System: $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$ in 1.95×10^{-3} M Mg^{2+} solution

α_1	X_1	C_{12}, mol dm^{-3}	β^σ
0	0	12.2×10^{-4}	-
0.1373	0.481	3.35×10^{-4}	-3.4
0.2408	0.544	2.57×10^{-4}	-3.5
0.7216	0.696	1.51×10^{-4}	-4.3
1.0	1.0	2.37×10^{-4}	-

$\gamma = 39$ mNm^{-1} α_1^*(calcd) = 0.737

ln $(C_1^o/C_2^o) = -1.64$, C_{12},min (calcd) = 1.52×10^{-4} mol dm^{-3}, $\beta^\sigma_{av} = -3.7$

3.2.1 Effect of Ionic Strength of the Solution on Synergism in Surface Tension Reduction Efficiency

The system $C_{12}(EO)_8$ - 2° LAS was investigated in NaCl solutions of 0.005 and 0.01 M T.I.S., the system $C_{12}(EO)_8$ - 4° LAS was investigated in NaCl solutions of 0.005, 0.01, 0.025, 0.05, and 0.1 M T.I.S, and the system $C_{12}(EO)_8$ - AOT was investigated in NaCl solutions of 0.01, 0.025, and 0.05 M T.I.S., all at 25 ° C. Values of β^{σ}, ln (C_1^{o}/C_2^{o}), α_1^{*}, and 1 - $C_{12,min}/C_1^{o}$ are listed in table 16.

Table 16 Effect of Ionic Strength of the Solution on Synergism in Surface Tension Reduction Efficiency at 25 ° C.

System	Medium	ln (C_1^{o}/C_2^{o})	β^{σ}	α_1^{*}	1- $C_{12,min}/C_1^{o}$
$C_{12}(EO)_8$ - 2° LAS	0.005 M T.I.S. (NaCl)	-2.07	-4.0	0.76	0.22
$C_{12}(EO)_8$ - 2° LAS	0.01 M T.I.S. (NaCl)	-1.70	-4.3	0.69	0.31
$C_{12}(EO)_8$ - 4° LAS	0.005 M T.I.S. (NaCl)	-2.12	-3.8	0.78	0.17
$C_{12}(EO)_8$ - 4° LAS	0.01 M T.I.S. (NaCl)	-2.05	-3.9	0.76	0.19
$C_{12}(EO)_8$ - 4° LAS	0.025 M T.I.S. (NaCl)	-0.98	-3.8	0.63	0.40
$C_{12}(EO)_8$ - 4° LAS	0.05 M T.I.S. (NaCl)	-0.39	-3.7	0.56	0.53
$C_{12}(EO)_8$ - 4°LAS	0.1 M T.I.S. (NaCl)	-0.14	-3.5	0.52	0.61

Table 16 (continued) Effect of Ionic Strength of the Solution on Synergism in Surface Tension Reduction Efficiency at 25 ^{o} C.

System	Medium	ln (C_1^o/C_2^o)	β^σ	α_1^*	1- $C_{12,min}/C_1^o$
$C_{12}(EO)_8$ - AOT	0.01 M T.I.S. (NaCl)	-1.24	-2.8	0.74	0.21
$C_{12}(EO)_8$ - AOT	0.025 M T.I.S. (NaCl)	-0.69	-2.4	0.63	0.29
$C_{12}(EO)_8$ - AOT	0.05 M T.I.S. (NaCl)	-0.05	-1.7	0.52	0.35

The quantity $1 - C_{12,min}/C_1^o = \dfrac{C_1^o - C_{12,min}}{C_1^o}$, where $C_1^o < C_2^o$, is a measure of the degree of synergism in surface tension reduction efficiency , the larger this quantity, the larger the synergistic effect. This quantity is related to Eq.[61],

$$C_{12,min} = C_1^o \exp\left[\beta^\sigma \left[\frac{\beta^\sigma - \ln (C_1^o/C_2^o)}{2\beta^\sigma}\right]^2\right],$$ which

determines the value of the $C_{12,min}/C_1^o$ ratio. As the difference between β^σ and ln (C_1^o/C_2^o) becomes larger, the $C_{12,min}/C_1^o$ ratio decreases and the degree of synergism increases.

As the ionic strength of the solution increases, there is a larger decrease in C_2^o of LAS or AOT than C_1^o of $C_{12}(EO)_8$, leading to a decrease in the absolute value of ln (C_1^o/C_2^o). This is because in adsorption of ionic surfactants at the aqueous solution/air interface, an increase in the ionic strength of the solution significantly lowers the electrical repulsion between ionic heads of surfactant ions already at the interface and the similarly charged oncoming surfactant ions, but in adsorption of nonionic surfactant, $C_{12}(EO)_8$, at the aqueous solution/air interface, the increase in

the ionic strength of the solution only slightly lowers the repulsion between $C_{12}(EO)_8$ already at the interface and the oncoming $C_{12}(EO)_8$.

From Eq.[61] and the data in table 16, it is apparent that as the ionic strength of the solution increases, the difference between β^σ and ln (C_1^o/C_2^o) becomes larger, the $C_{12,min}/C_1^o$ ratio decreases and the quantity 1 - $C_{12,min}/C_1^o$ increases, indicating an increase in the degree of synergism in surface tension reduction efficiency with increase in the ionic strength of the solution.

It is apparent from Eq.[61] and the data in table 16 that the system $C_{12}(EO)_8$ - 4° LAS in 0.1 M T.I.S.(NaCl) has the largest difference between β^σ and $\ln(C_1^o/C_2^o)$, and therefore, lowest value of the $C_{12,min}/C_1^o$ ratio, leading to the largest degree of synergism.

And the data in table 16 indicate that the value of α_1^*, the mole fraction of surfactant 1 in the total surfactant in the solution phase at the point of maximum synergism, decreases with increase in the ionic strength of the solution.

3.2.2 Effect of LAS Structure on Synergism in Surface Tension Reduction Efficiency

Systems $C_{12}(EO)_8$ - 2° LAS and $C_{12}(EO)_8$ - 4° LAS were investigated in NaCl solutions of 0.005 and 0.01 M T.I.S. at 25 ° C. Values of β^{σ}, ln (C_1^{o}/C_2^{o}), α_1^{*}, and 1 - $C_{12,min}/C_1^{o}$ are listed in table 17.

Table 17 Effect of LAS Structure on Synergism in Surface Tension Reduction Efficiency at 25 ° C.

System	Medium	ln (C_1^{o}/C_2^{o})	β^{σ}	α_1^{*}	1- $C_{12,min}/C_1^{o}$
$C_{12}(EO)_8$ - 4° LAS	0.005 M T.I.S. (NaCl)	-2.12	-3.8	0.78	0.17
$C_{12}(EO)_8$ - 2° LAS	0.005 M T.I.S. (NaCl)	-2.07	-4.0	0.76	0.22
$C_{12}(EO)_8$ - 4° LAS	0.01 M T.I.S. (NaCl)	-2.05	-3.9	0.76	0.19
$C_{12}(EO)_8$ - 2° LAS	0.01 M T.I.S. (NaCl)	-1.70	-4.3	0.69	0.31

Change in the chemical structure of surfactant affects the molecular interaction parameter β^{σ} which in turn affects the degree of synergism in surface tension reduction efficiency. Since 2 ^{o} LAS is more surface active than 4^{o} LAS (C_2^{o} of 2^{o} LAS < C_2^{o} of 4 ^{o} LAS, see tables 9 and 11),therefore, as LAS is change from 4 ^{o} LAS to 2^{o} LAS, there will be a decrease in the absolute value of ln (C_1^{o}/C_2^{o}). From table 17, when systems $C_{12}(EO)_8$ - 4^{o} LAS and $C_{12}(EO)_8$ - 2^{o} LAS in NaCl solutions of the same ionic strength, are compared, it appeares that as LAS is changed from 4^{o} LAS to 2^{o} LAS, the difference between β^{σ} and ln (C_1^{o}/C_2^{o}) becomes larger, the C_{12},min/C_1^{o} ratio decreases and the degree of synergism in surface tension reduction efficiency increases.

3.2.3 Effect of Temperature on Synergism in Surface Tension Reduction Efficiency

The system $C_{12}(EO)_8$ - 2° LAS was investigated in NaCl solution of 0.01 M T.I.S. at 25 °, 35 °, and 40 ° C, respectively. Values of β^{σ}, ln (C_1^{o}/C_2^{o}), α_1^{*}, and 1- $C_{12,min}/C_1^{o}$ are listed in table 18

Table 18 Effect of Temperature on Synergism in Surface Tension Reduction Efficiency. System : $C_{12}(EO)_8$ - 2° LAS, 0.01 M T.I.S.(NaCl)

Temp(° C)	β^{σ}	ln (C_1^{o}/C_2^{o})	α_1^{*}	1- $C_{12,min}/C_1^{o}$
25	-4.3	-1.70	0.69	0.31
35	-3.7	-1.82	0.75	0.22
40	-3.4	-1.91	0.78	0.15

Since change in microenvironmental factor (temperature in this case) affects the molecular interaction parameter β^{σ}, therefore it is to be expected that the change in the temperature will affect the degree of synergism in this respect.

In this investigation, C_1^{o} values of $C_{12}(EO)_8$ are 3.31×10^{-5}, 2.29×10^{-5}, and 2.0×10^{-5} M at 25°, 35°, and 40° C, respectively. C_2^{o} values of 2° LAS are 18.2×10^{-5}, 14.1×10^{-5}, and 13.5×10^{-5} M at 25°, 35°, and 40° C,respectively. From this data, it is apparent that there is a larger % decrease in C_1^{o} than in C_2^{o} with increase in temperature over the range investigated, leading to an increase in the absolute value of ln (C_1^{o}/C_2^{o})

From the data in table 18, it is apparent that as the temperature increases, the absolute value of β^{σ} decreases , but the absolute value of ln (C_1^{o}/C_2^{o}) increases, therefore, the difference between β^{σ} and ln (C_1^{o}/C_2^{o}) becomes smaller with increase in the temperature, leading to a decrease in the quantity 1 - $C_{12,min}/C_1^{o}$, indicating the decrease in the degree of synergism in surface tension reduction efficiency with increase in the temperature.

3.2.4 Effect of Oxyethylene Group on Synergism in Surface Tension Reduction Efficiency

Systems $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ and $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$ were investigated in 1.95×10^{-3} M Mg^{2+} solution at 25 ^{o} C. Values of β^{σ}, ln (C_1^{o}/C_2^{o}), α_1^{*}, and 1 - $C_{12,min}/C_1^{o}$ are listed in table 19

Table 19 Effect of Oxyethylene Group on Synergism in Surface Tension Reduction Efficiency at 25 ^{o} C. Medium : 1.95×10^{-3} M Mg^{2+} .

System	ln (C_1^{o}/C_2^{o})	β^{σ}	α_1^{*}	1 - $C_{12,min}/C_1^{o}$
$C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ ($C_1^{o} = 2.09\times10^{-4}$ M, $C_2^{o} = 12.2\times10^{-4}$ M)	-1.76	-2.1	0.95	0.12
$C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$ ($C_1^{o} = 2.37\times10^{-4}$ M, $C_2^{o} = 12.2\times10^{-4}$ M)	-1.64	-3.7	0.74	0.36

It is apparent from the data in table 19 that C_1^o of $C_{12}(EO)_4SO_4Na$ is greater than that of $C_{12}(EO)_3SO_4Na$, leading to the decrease in the absolute value of $\ln(C_1^o/C_2^o)$ with increase in the number of oxyethylene groups in polyoxyethylenated anionic.

From the data in table 19, it is also apparent that as the number of oxyethylene groups in the polyoxyethylenated nonionic increases from 3 to 4, the difference between β^σ and $\ln (C_1^o/C_2^o)$ becomes larger, the quantity $1 - C_{12,min}/C_1^o$ increases from 0.12 to 0.36, indicating an increase in the degree of synergism in surface tension reduction efficiency with this change.

3.3 Synergism in Mixed Micelle Formation

The system $C_{12}(EO)_8$ - 2^o LAS was investigated in distilled water and in NaCl solutions of 0.005 M T.I.S. at 25 ^{o} C, and 0.01 M T.I.S. at 25 ^{o}, 35 ^{o}, and 40 ^{o} C, respectively. The system $C_{12}(EO)_8$ - 4^o LAS was investigated in distilled water and in NaCl solutions of 0.01, 0.025, 0.05, and 0.1 M T.I.S. at 25 ^{o} C. The experimental data for these systems are listed in tables 20 - 24. From the data in these tables, it is apparent that the calculated values of C_{12}^M,min, the minimum CMC of the mixture at the point of maximum synergism in mixed micelle formation are very close to the experimental values.

Table 20 Synergism in Mixed Micelle Formation at 25 °C.

System : $C_{12}(EO)_8$ - 2° LAS in H_2O

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	87.5×10^{-5}	-
0.1075	0.497	15.1×10^{-5}	-5.2
0.2833	0.580	9.12×10^{-5}	-5.1
0.7111	0.693	6.31×10^{-5}	-5.6
1.0	1.0	11.5×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.702, C_{12}^M,min (calcd) = 6.30×10^{-5} mol dm^{-3}

$\ln (C_1^M/C_2^M) = -2.07$, $\beta^M_{av} = 5.3$

System : $C_{12}(EO)_8$ - 2° LAS in 0.005 M T.I.S.(NaCl)

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	43.2×10^{-5}	-
0.675	0.636	4.84×10^{-5}	-5.6
0.7640	0.659	4.70×10^{-5}	-5.8
1.0	1.0	11.0×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.620, C_{12}^M,min (calcd) = 4.80×10^{-5} mol dm^{-3}

$\ln (C_1^M/C_2^M) = -1.40$, $\beta^M_{av} = -5.7$

Table 21 Synergism in Mixed Micelle Formation at 25 ° and 35 ° C

System : $C_{12}(EO)_8$ - 2° LAS in 0.01 M T.I.S.(NaCl) at 25 ° C

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	33.5×10^{-5}	-
0.6002	0.60	4.68×10^{-5}	-5.4
0.7576	0.65	4.79×10^{-5}	-5.5
1.0	1.0	11.0×10^{-5}	-

α_1^*,M(calcd) = 0.60, C_{12}^M,min (calcd) = 4.67×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -1.1, β^M_{av} = -5.4

System : $C_{12}(EO)_8$ - 2° LAS in 0.01 M T.I.S.(NaCl) at 35 ° C

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	26.9×10^{-5}	-
0.6797	0.658	4.57×10^{-5}	-4.3
0.7608	0.688	4.62×10^{-5}	-4.3
1.0	1.0	7.76×10^{-5}	-

α_1^*,M(calcd) = 0.646, C12^M,min (calcd) = 4.56×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -1.24, β^M_{av} = -4.3

Table 22 Synergism in Mixed Micelle Formation at 40 ° and 25 ° C

System : $C_{12}(EO)_8$ - 2° LAS in 0.01 M T.I.S.(NaCl) at 40 ° C

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	26.3×10^{-5}	-
0.6797	0.675	4.57×10^{-5}	-3.9
0.7562	0.708	4.68×10^{-5}	-3.8
1.0	1.0	6.92×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.675, C_{12}^M,min (calcd) = 4.58×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -1.34, β^M_{av} = -3.8

System : $C_{12}(EO)_8$ - 4°LAS in H_2O at 25 ° C

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	16.8×10^{-4}	-
0.5158	0.699	9.55×10^{-5}	-4.8
0.8091	0.759	7.76×10^{-5}	-5.2
1.0	1.0	11.0×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.780 , C_{12}^M,min (calcd) = 7.90×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -2.73, β^M_{av} = -5.0

Table 23 Synergism in Mixed Micelle Formation at 25 °C

System : $C_{12}(EO)_8$ - 4° LAS in 0.01 M T.I.S.(NaCl)

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	70.8×10^{-5}	-
0.0282	0.362	27.5×10^{-5}	-4.0
0.1331	0.499	12.9×10^{-5}	-4.6
0.7566	0.698	6.16×10^{-5}	-5.4
1.0	1.0	11.0×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.732, C_{12}^M,min (calcd) = 6.12×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -1.86, β^M_{av} = -4.7

System : $C_{12}(EO)_8$ - 4° LAS in 0.025 M T.I.S.(NaCl)

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	31.3×10^{-5}	-
0.4571	0.577	5.62×10^{-5}	-4.4
0.6275	0.623	4.9×10^{-5}	-4.8
1.0	1.0	9.77×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.632, C_{12}^M,min (calcd) = 4.9×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -1.16, β^M_{av} = -4.6

Table 24 Synergism in Mixed Micelle Formation at 25 °C

System : $C_{12}(EO)_8$ - 4° LAS in 0.05 M T.I.S.(NaCl)

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	20.0×10^{-5}	-
0.4365	0.539	5.25×10^{-5}	-4.2
0.5534	0.576	4.84×10^{-5}	-4.1
1.0	1.0	9.77×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.591, C_{12}^M,min (calcd) = 4.81×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -0.71, β^M_{av} = -4.2

System : $C_{12}(EO)_8$ - 4° LAS in 0.1 M T.I.S.(NaCl)

α_1	X_1^M	C_{12}^M, mol dm^{-3}	β^M
0	0	12.9×10^{-5}	-
0.4365	0.514	4.17×10^{-5}	-3.7
0.5372	0.546	3.70×10^{-5}	-4.1
1.0	1.0	8.51×10^{-5}	-

$\alpha_1^{*,M}$(calcd) = 0.555 , C_{12}^M,min (calcd) = 3.72×10^{-5} mol dm^{-3}

ln (C_1^M/C_2^M) = -0.40, β^M_{av} = -3.9

3.3.1 Effect of Ionic Strength of The Solution on Synergism in Mixed Micelle Formation

The system $C_{12}(EO)_8$ - 2° LAS was investigated in distilled water and in NaCl solutions of 0.005 and 0.01 M T.I.S., the system $C_{12}(EO)_8$ - 4 ° LAS was investigated in distilled water and in NaCl solutions of 0.01, 0.025, 0.05, and 0.1 M T.I.S, all at 25 ° C. Values of β^M, ln (C_1M/C_2M), $\alpha_1^{*,M}$ and 1- $C_{12}M,min/C_1M$ are listed in table 25.

Table 25 Effect of Ionic Strength of the Solution on Synergism in Mixed Micelle Formation at 25 ° C

System	Medium	ln (C_1M/C_2M)	β^M	$\alpha_1^{*,M}$	1- $C_{12}M,min/C_1M$
$C_{12}(EO)_8$-2°LAS	H_2O	-2.07	-5.3	0.70	0.42
$C_{12}(EO)_8$-2°LAS	0.005 M T.I.S. (NaCl)	-1.40	-5.7	0.62	0.56
$C_{12}(EO)_8$-2°LAS	0.01 M T.I.S. (NaCl)	-1.10	-5.4	0.60	0.60
$C_{12}(EO)_8$-4°LAS	H_2O	-2.73	-5.0	0.78	0.28
$C_{12}(EO)_8$-4°LAS	0.01 M T.I.S. (NaCl)	-1.86	-4.7	0.73	0.44
$C_{12}(EO)_8$-4°LAS	0.025 M T.I.S (NaCl)	-1.16	-4.6	0.63	0.49
$C_{12}(EO)_8$-4°LAS	0.05 M T.I.S. (NaCl)	-0.71	-4.2	0.59	0.51
$C_{12}(EO)_8$-4°LAS	0.1M T.I.S (NaCl)	-0.41	-3.9	0.55	0.55

The quantity $1 - C_{12}^{M,min}/C_1^M = \dfrac{C_1^M - C_{12}^{M,min}}{C_1^M}$, where $C_1^M < C_2^M$, is a measure of the degree of synergism in mixed micelle formation , the larger this quantity, the larger the synergistic effect. This quantity is related to Eq.[67],

$$C_{12}^{M,min} = C_1^M \exp\left[\beta^M \left[\frac{\beta^M - \ln (C_1^M/C_2^M)}{2\beta^M} \right]^2 \right],$$

which determines the value of the $C_{12}^{M,min}/C_1^M$ ratio. It is apparent from Eq.[67]that as the difference between β^M and $\ln (C_1^M/C_2^M)$ becomes larger, the $C_{12}^{M,min}/C_1^M$ ratio decreases and the degree of synergism increases.

In aqueous solution, the presence of electrolyte causes a change in the CMC, the effect being more pronounced for anionics than for nonionics (81). As ionic strength of the solution increases, there is a larger decrease in C_2^M of 2° LAS or 4° LAS than C_1^M of $C_{12}(EO)_8$, leading to a decrease in the absolute value of $\ln (C_1^M/C_2^M)$. This is because in anionics, an increase in the ionic strength of the solution decreases the thickness of the ionic atmosphere surrounding the ionic head groups with the result of a significantly decrease in the electrical repulsion between them in the micelle, leading to a significantly decrease in the CMC, but in nonionic, the increase in the ionic strength of the solution only slightly increases the salting out of hydrophobic group, leading to a slightly decrease in the CMC .

From Eq.[67] and the data in table 25, it is apparent that as the ionic strength of the solution increases, the difference between β^M and $\ln (C_1^M/C_2^M)$ becomes larger, the $C_{12}^{M,min}/C_1^M$ ratio decreases and the quantity $1 - C_{12}^{M,min}/C_1^M$ increases, indicating an increase in the degree of synergism in mixed micelle formation with increase in the ionic strength of the solution.

It is apparent from Eq.[67] and the data in table 25 that the system $C_{12}(EO)_8$ - 2° LAS in 0.01 M T.I.S. (NaCl) has the largest difference between β^M and $\ln (C_1^M/C_2^M)$, and therefore, lowset value of the $C_{12}^{M,min}/C_1^M$ ratio, leading to

the largest degree of synergism. And the data in table 25 indicate that the value of $\alpha_1^{*,M}$, the mole fraction of surfactant 1 in the total surfactant in the solution phase at the point of maximum synergism in mixed micelle formation, decreases with increase in the ionic strength of the solution.

3.3.2 Effect of LAS Structure on Synergism in Mixed Micelle Formation.

Systems $C_{12}(EO)_8$ - 4 ^{o} LAS and $C_{12}(EO)_8$ - 2 ^{o} LAS were investigated in distilled water and in NaCl solution of 0.01 M T.I.S. at 25 ^{o} C. Values of $\ln (C_1^M/C_2^M)$, β^M, $\alpha_1^{*,M}$ and 1- $C_{12}^{M,min}/C_1^M$ are listed in table 26.

Table 26 Effect of LAS Structure on Synergism in Mixed Micelle Formation at 25 ^{o} C

System	Medium	$\ln (C_1^M/C_2^M)$	β^M	$\alpha_1^{*,M}$	1- $C_{12}^{M,min}/C_1^M$
$C_{12}(EO)_8$-4^{o}LAS	H_2O	-2.73	-5.0	0.78	0.28
$C_{12}(EO)_8$-2^{o}LAS	H_2O	-2.07	-5.3	0.70	0.42

$C_{12}(EO)_8$-4^{o}LAS	0.01 M T.I.S. (NaCl)	-1.86	-4.7	0.73	0.44
$C_{12}(EO)_8$-2^{o}LAS	0.01 M T.I.S.	-1.10	-5.4	0.60	0.60

Change in the chemical structure of surfactant affects the molecular interaction parameter β^M which in turn affects the degree of synergism in mixed micelle formation. This is consistent with the results shown in table 26.

In aqueous medium, the CMC of surfactants is affected by the position of the hydrophilic group in the molecule. As the hydrophilic group is moved from a terminal position to a more central position in the hydrophobic group, the hydrophobic group seems to act as if it had become branched at the position of the hydrophilic group. This causes a steric effect in micelle formation, leading to an increase in the CMC, therefore,4° LAS will have a higher CMC (C_2^M) value than 2°- LAS (see tables 20,21,22,and23), with the result of a decrease in the absolute value of ln (C_1^M/C_2^M) as LAS is changed from 4° LAS to 2° LAS.

On comparison of systems $C_{12}(EO)_8$ - 4° LAS and $C_{12}(EO)_8$ - 2° lAS in water and in NaCl solution of 0.01 M T.I.S., it is apparent from the data in table 26 that as LAS is changed from 4° LAS to 2° LAS , the absolute value of β^M increases, but the absolute value of ln (C_1^M/C_2^M) decreases, therefore, the difference between β^M and ln (C_1^M/C_2^M) becomes larger, and the degree of synergism in mixed micelle formation increases.

3.3.3 Effect of Temperature on Synergism in Mixed Micelle Formation.

The system $C_{12}(EO)_8$ - 2° LAS was investigated in NaCl solution of 0.01 M T.I.S. at 25 °, 35 ° and 40 ° C, respectively. Values of β^M, ln (C_1^M/C_2^M), $\alpha_1^{*,M}$ and 1- $C_{12}^M,min/C_1^M$ are listed in table 27.

Table 27 Effect of Temperature on Synergism in Mixed Micelle Formation.

System : $C_{12}(EO)_8$ - 2° LAS in 0.01 M T.I.S.(NaCl)				
Temp.(° C)	ln (C_1^M/C_2^M)	β^M	$\alpha_1^{*,M}$	1- $C_{12}^M,min/C_1^M$
25	-1.10	-5.4	0.60	0.60
35	-1.24	-4.3	0.64	0.41
40	-1.34	-3.8	0.66	0.34

Since synergism in mixed micelle formation involves molecular interaction parameter β^M, and change in temperature affects β^M, therefore, it is to be expected that the change in temperature will effect the degree of synergism in this respect.

The effect of temperature on the CMC of surfactants in aqueous medium is complex (81), the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature. Temperature increase causes decreased hydration of hydrophilic group, which favors micellization.

However, temperature increase also causes disruption of the structure water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. In this investigation, the CMC (C_1^M) values of $C_{12}(EO)_8$ are $11x10^{-5}$, $7.76x10^{-5}$, and $6.92x10^{-5}$ M at 25 °, 35 °, and 40 ° C, respectively. The CMC (C_2^M) of 2 ° LAS are $33.1x10^{-5}$, $26.9x10^{-5}$, and $26.3x10^{-5}$ M at 25 °, 35 °, and 40 ° C, respectively. From this data, it is apparent that there is a larger % decrease in C_1^M than in C_2^M with increase in temperature over the temperature range investigated, leading to an increase in the absolute value of ln (C_1^M/C_2^M).

From the the data in table 27, it is apparent that as temperature increases, the absolute value of β^M decreases, but the absolute value of ln (C_1^M/C_2^M) increases, therefore, the difference between β^M and ln (C_1^M/C_2^M) becomes smaller, and the quantity 1 - $C_{12}^M,min/C_1^M$, which is a measure of the degree of synergism in mixed micelle formation, decreases with increase in temperature in the range investigated.

3.4 Synergism in Surface Tension Reduction Effectiveness.

Systems $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ and $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$ were investigated in 1.95×10^{-3} M Mg^{2+} solution at 25 ^{o} C. Data for these systems are shown in table 28.

Table 28 Synergism in Surface Tension Reduction Effectiveness at 25 ^{o} C.
Medium : 1.95×10^{-3} M Mg^{2+}

System	$\beta^{\sigma} - \beta^{M}$	$\ln [\frac{C_1^{o,cm}}{C_2^{o,cmc}} . \frac{C_2^{M}}{C_1^{M}}]$	Synergism in γ reduction effectiveness	
			Theory	Experiment
$C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$	-0.9	0.12	Yes	Yes
$C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$	-1.9	0.23	Yes	Yes

Table 28 lists the values of $\beta^{\sigma} - \beta^{M}$ and $\ln [\frac{C_1^{o,cmc}}{C_2^{o,cmc}} . \frac{C_2^{M}}{C_1^{M}}]$ for the systems investigated. From a comparison of these values, the two systems investigated met the conditions for the existence of synergism in surface tension reduction effectiveness, i.e., (1) $\beta^{\sigma} - \beta^{M} < 0$

and

(2) $\beta^{\sigma} - \beta^{M} > \ln [(C_1^{o,cmc}/C_2^{o,cmc})(C_2^{M}/C_1^{M})]$

And the two systems investigated showed synergism in this respect experimentally which is consistent with the theoretical prediction.

Table 29 Values of calculated and experimental γ_{cmc}, and $1 - \gamma^*_{cmc}/\gamma^o_{cmc,lower}$
Medium : 1.95×10^{-3} M Mg^{2+}

System	$\gamma^*_{cmc}(\alpha_1^*)$ calcd (mNm^{-1})	$\gamma_{cmc}(\alpha_1)$ expt'l (mNm^{-1})	$1 - \gamma^*_{cmc}/\gamma^o_{cmc,lower}$
$C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$	33.5 (0.03)	32.5 (0.14)	0.03
($\gamma^o_{cmc1} = 35.4$ mNm^{-1}, $\gamma^o_{cmc2} = 34.6$ mNm^{-1})			
$C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$	32.9 (0.10)	31.7 (0.13)	0.05
($\gamma^o_{cmc1} = 37.1$ mNm^{-1}, $\gamma^o_{cmc2} = 34.6$ mNm^{-1})			

Table 29 lists value of the quantity $1 - \gamma^*_{cmc}/\gamma^o_{cmc,lower}$, which is a measure of the degree of synergism in surface tension reduction effectiveness, $\gamma^o_{cmc,lower}$ is the lower surface tension value of either individual surfactant at its CMC (i.e., γ^o_{cmc1} or γ^o_{cmc2}).

Table 29 also lists calculated values of γ^*_{cmc} (the lowest surface tension attainable at the CMC of any mixture of the two components) at the point of maximum synergism and of α_1^* at that point. For comparison, experimental values of γ_{cmc}, not necessary at the point of maximum synergism, and the α_1 values at which they were taken, are listed. The good agreement between calculated γ^*_{cmc} and experimental γ_{cmc} values, in spite of the fact that the latter values were not taken at α_1^* for maximum synergism, is due to the existence in mixtures showing considerable synergism in this respect of a large range of α_1 (4) over which the value of γ_{cmc} does not deviate too much from γ^*_{cmc}.

From the data in table 29, it is apparent that the degree of synergism in surface tension reduction effectiveness increases with increase in the number of oxyethylene groups in polyoxyethylenated anionic surfactant.

3.5 Negative Synergism in Surface Tension Reduction Effectiveness

The system $C_{12}(EO)_8$ - 4^o LAS was investigated in distilled water and in NaCl solutions of 0.005 and 0.01 M T.I.S. at 25 ^{o} C. Data for the systems investigated are shown in table 30.

Table 30 Negative Synergism in Surface Tension Reduction Effectiveness at 25 ^{o} C
System : $C_{12}(EO)_8$ - 4^o LAS

Medium	$\beta^\sigma - \beta^M$	$\ln[(C_1^{o,cmc}/C_2^{o,cmc})(C_2^M/C_1^M)]$	Negative synergism in γ reduction effectiveness	
			Theory	Experiment
H_2O	2.6	-0.44	Yes	Yes
0.005M T.I.S. (NaCl)	1.6	-0.05	Yes	Yes
0.01 M T.I.S. (NaCl)	0.8	0.07	Yes	Yes

Table 30 lists the values of $\ln[(C_1^{o,cmc}/C_2^{o.cmc})(C_2^M/C_1^M)]$ and $\beta^\sigma - \beta^M$ for the system investigated. From a comparison of these values, the system investigated met the conditions for the existence of negative synergism in surface tension reduction effectiveness, i.e., (1) $\beta^\sigma - \beta^M > 0$ and

(2) $\beta^\sigma - \beta^M > |\ln[(C_1^{o,cmc}/C_2^{o,cmc})(C_2^M/C_1^M)]|$ The system investigated showed negative synergism in this respect experimentally which is consistent with the theoretical prediction.

Table 31 Values of calculated and experimental γ_{cmc} and $|1 - \gamma^*_{cmc}/\gamma^o_{cmc,higher}|$

System : $C_{12}(EO)_8$ - 4^o LAS

Medium	$\gamma^*_{cmc}(\alpha_1^*)$ calcd(mNm^{-1})	$\gamma_{cmc}(\alpha_1)$ expt(mNm^{-1})	$\lvert 1 - \gamma^*_{cmc}/\gamma^o_{cmc,higher} \rvert$
H_2O	40.5 (0.02)	38.5 (0.52)	0.10
(γ^o_{cmc1} = 34.6 mNm^{-1} , γ^o_{cmc2} = 36.9 mNm^{-1})			
0.005 M T.I.S.	37.5 (0.11)	36.8 (0.77)	0.08
(NaCl)	(γ^o_{cmc1} = 34.6 mNm^{-1} , γ^o_{cmc2} = 34.2mNm^{-1})		
0.01 M T.I.S.	35.7 (0.21)	35.1 (0.13)	0.03
(NaCl)	(γ^o_{cmc1} = 34.6 mNm^{-1}, γ^o_{cmc2} = 33.7 mNm^{-1})		

Table 31 lists value of the quantity $|1 - \gamma^*_{cmc}/\gamma^o_{cmc,higher}|$, which is a measure of the degree of negative synergism in surface tension reduction effectiveness, $\gamma^o_{cmc,higher}$ is the higher surface tension value of either individual

surfactant at its CMC (i.e., γ^{o}_{cmc1} or γ^{o}_{cmc2}). Table 31 also lists calculated values of γ^{*}_{cmc}(the highest surface tension attainable at the CMC of any mixture of the two components) at the point of maximum negative synergism and of α_1^{*}(the mole fraction of surfactant 1 in the total surfactant in the solution phase at the point of maximum negative synergism) . For comparison, experimental values of γ_{cmc}, not necessary at the point of maximum negative synergism, and the α_1 values at which they were taken are listed. There is the good agreement between calculated γ^{*}_{cmc} and experimental γ_{cmc} values, in spite of the fact that the latter values were not taken at α_1^{*} for maximum negative synergism. This may be due to the existence in mixtures showing considerable negative synergism in this respect of a large range of α_1 over which the value of γ_{cmc} does not deviate much from γ^{*}_{cmc}. From table 31, it is apparent that there is a decrease in the degree of negative synergism in surface tension reduction effectiveness with increase in ionic strength of the solution.

3.6 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain.

3.6.1 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in NaCl Solution of Polyoxyethylenated nonionic Surfactants.

We investigated complexation of Na^+ with ether oxygens in polyoxyethylene chain of $C_{12}(EO)_8$ and $C_{12}(EO)_4$ in 0.004 M T.I.S.(NaCl). In this investigation, we made 1:1(v/v) mixture of $C_{12}(EO)_X$ (X = 4,8) and 0.008 M NaCl , and then measured [Na^+] of the solution by a sodium ion selective electrode at 25° C, pH 5.2 before and after mixing the two solutions. From the data obtained, we determined $\Delta[Na^+]$ which is the concentration of Na^+ that complexed with ether oxygens in the polyoxyethylene chain of $C_{12}(EO)_X$. Values of $\Delta[Na^+]$, the complexation constant K, and the ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_X$ are listed in tables 32 and 33.

The complexation constant K for the reaction

$$C_{12}(EO)_X + Na^+ \rightleftharpoons C_{12}\overset{Na^+}{(EO)}_X$$

was calculated from the equation

$$K = \gamma_{C_{12}\overset{Na^+}{(EO)}_X} .[C_{12}\overset{Na^+}{(EO)}_X]/[C_{12}(EO)_X] \gamma_{Na^+}[Na^+]$$

Where [ ] refer to molar concentration.

Ionic activity coefficients, γ_i, were calculated at 25° C by using Debye - Hückel equation,

$$\log \gamma_i = - 0.509 Z_i^2 [I]^{1/2} / 1 + 0.33 \alpha [I]^{1/2}$$

Where α is mean distance approach of the ions (in A°), α = 1.2 and 0.3 for $C_{12}\overset{Na^+}{(EO)}_X$ and Na^+, respectively, I is the ionic strength of the solution.

Table 32 Complexation of Na^+ with Ether Oxygens in Polyoxyethylene Chain of $C_{12}(EO)_8$ in 0.004 M T.I.S.(NaCl) at 25° C, pH 5.2.

$[C_{12}(EO)_8]$,M x10^4 initial	$\Delta[Na^+]$,M x10^4	% error in $\Delta[Na^+]$	K $[dm^3/mol]$	% error in K	moles of Na^+ complexed / moles of initial $C_{12}(EO)_8$
30.7	4.99 ± 0.51	10	53 ± 6.5	12	0.16
23.6	3.99 ± 0.51	13	54 ± 8.5	16	0.17
21.4	3.59 ± 0.51	14	53 ± 8.5	16	0.17
19.5	3.29 ± 0.51	16	53 ± 9.5	18	0.17
16.9	2.79 ± 0.51	18	51 ± 11	22	0.16

Table 33 Complexation of Na^+ with Ether Oxygens in Polyoxyethylene Chain of $C_{12}(EO)_4$ in 0.004 M T.I.S.(NaCl) at 25° C, pH 5.2.

$C_{12}(EO)_4$,M x10^4 initial	$\Delta[Na^+]$,M x10^4	% error in $\Delta[Na^+]$	K (dm^3/mol)	% error in K	moles of Na^+ complexed / moles of initial $C_{12}(EO)_4$
16.9	1.57 ± 0.51	32	26 ± 9	34	0.09
14.7	1.37 ± 0.51	37	26 ± 10	38	0.09
12.8	1.17 ± 0.51	44	25 ± 11.5	46	0.09
11.0	1.07 ± 0.51	48	27 ± 14	52	0.10

From the data in tables 32 and 33, it is apparent that complexation of Na^+ with ether oxygens of the polyoxyethylene chain increases with increase in concentrations of $C_{12}(EO)_8$ or $C_{12}(EO)_4$, as would be expected from the above reaction. The complexation constant is essentially constant over the range of concentrations investigated. And from the data in tables 32 and 33, it is also apparent that there is a greater complexation of Na^+ with ether oxygens of the polyoxyethylene chain in $C_{12}(EO)_8$ than in $C_{12}(EO)_4$. This may be due to the greater ability of a chain with more oxyethylene units to complex Na^+(93). Tables 34 shows calculations of % error in $\Delta[Na^+]$ and in K for $C_{12}(EO)_8$ in 0.004 M T.I.S.(NaCl).

Table 34 Calculations of % error in $\Delta[Na^+]$ and in K for $C_{12}(EO)_8$ in 0.004 M T.I.S.(NaCl)

% error in $\Delta[Na^+]$		
$[C_{12}(EO)_8]$ before mix, $Mx10^4$	mV	$[Na^+]$, $Mx10^4$
61.4	-23.5, -23.5, -23.5, -23.5, -23.5, -24, -24, -24, -24.	0.98 ± 0.17
[NaCl] before mix, $Mx10^4$		
80.0	48.5, 48.5, 48.5, 48.5, 49. 49, 49, 49, 49.	81.8 ± 0.17
1:1 (V/V) mixture, theoret.	-	41.39 ± 0.34
1:1 (V/V) mixture, exptl.	8.5, 8.5, 8.5, 8.5, 9, 9, 9, 9, 9.	36.4 ± 0.17

$\Delta[Na^+] = 4.99x10^{-4} \pm 0.51x10^{-4}$ M

% error in $\Delta[Na^+] = 51/4.99 = 10$

Uncertainty in reading mV= 0.5 mV = $0.5x10^{-4}$ M Na^+

In these measurements, the number of reading = 9, therefore,

uncertainty = $0.5x10^{-4}/(9)^{1/2} = 0.17x10^{-4}$ M Na^+ .

Table 34 (continued)

Calculation of K

$\Delta[Na^+] = 4.99 \times 10^{-4} \pm 0.51 \times 10^{-4}$ M

$\gamma_{C_{12}(\overset{Na^+}{EO})_8} = 0.93$

$[C_{12}(\overset{Na^+}{EO})_8] = 4.99 \times 10^{-4} \pm 0.51 \times 10^{-4}$ M

$\gamma_{Na^+} = 0.928$

$[Na^+] = 36.4 \times 10^{-4} \pm 0.17 \times 10^{-4}$ M

$[C_{12}(EO)_8] = 30.7 \times 10^{-4} - (4.99 \times 10^{-4} \pm 0.51 \times 10^{-4})$ M

$K = \gamma_{C_{12}(\overset{Na^+}{EO})_8} \cdot [C_{12}(\overset{Na^+}{EO})_8] / [C_{12}(EO)_8] \cdot \gamma_{Na^+} \cdot [Na^+]$

Substituting the above values in the above equation, we obtained

$K = 53 + 6.5$ dm^3/mol

% error in K = 12.

3.6.2 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in Polyoxyethylenated nonionic - anionic Mixtures.

The system $C_{12}(EO)_8$ - AOT was investigated in NaCl solutions of 0.008, 0.006, 0.004, 0.003, and 0.002 M T.I.S. at 25° C, pH 5.2. Systems $C_{12}(EO)_4$ -AOT and $C_{12}(EO)_8$ - AAY were investigated in NaCl solution of 0.004 M T.I.S. at 25° C, pH 5.2.

In these investigations, $[Na^+]$ of NaCl solution of a given total ionic strength of $C_{12}(EO)_X$ (X= 4,8) and that of NaCl solution of anionic surfactant (AOT or AAY) of equal ionic strength were first measured by a sodium ion selective electrode at 25° C, pH 5.2, and then the $[Na^+]$ of the 1:1(V/V) mixture of NaCl solutions of $C_{12}(EO)_X$ and AOT (or AAY) were measured by the sodium ion selective electrode at the same conditions. From the data obtained, we determined $\Delta[Na^+]$, which is the concentration of Na^+ that complexed with ether oxygens of the polyoxyethylene chain . The complexation constant , K, for the reaction :

$$C_{12}(EO)_X + RSO_3^- + Na^+ \rightleftharpoons C_{12}(\overset{Na^+}{EO})_X.RSO_3^-$$

was calculated from the equation:

$$K = [C_{12}(\overset{Na^+}{EO})_X.RSO_3^-]/[C_{12}(EO)_X].\gamma_{RSO_3^-}.[RSO_3^-].\gamma_{Na^+}.[Na^+]$$

Ionic activity coefficients, γ_i, were calculated at 25° C by using the Debye - Hückel equation,

$$\log \gamma_i = -0.509\, Z_i^2\, (I)^{1/2}/1 + 0.33\, \alpha\, (I)^{1/2}$$

Where α = 0.3 and 0.6 for Na^+ and RSO_3^-, respectively. Values of $\Delta[Na^+]$ and K are listed in tables 35 - 41.

Table 35 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AOT Mixtures in 0.008 M T.I.S.(NaCl) (25° C, pH 5.2, $^{\alpha}C_{12}(EO)_8$ = 0.56).

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-5} $(dm^3/mol)^2$	% error in K
19.5	15.6	9.7 ± 0.51	5.2	2.9 ± 0.55	19
16.9	13.6	8.0 ± 0.51	6.4	2.7 ± 0.55	20
15.3	12.3	7.35 ± 0.51	6.9	3.1 ± 0.80	26
12.8	10.3	5.8 ± 0.51	8.8	3.0 ± 0.85	28
10.6	8.6	4.5 ± 0.51	11	2.9 ± 0.95	33

Average value of ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_8$ = 0.46

Table 36 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AOT Mixtures in 0.006 M T.I.S.(NaCl)(25° C, pH 5.2, $^{\alpha}C_{12}(EO)_8$ = 0.56)

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-5} $(dm^3/mol)^2$	% error in K
19.5	15.6	8.9 ± 0.51	5.7	2.7 ± 0.50	18
16.9	13.6	7.4 ± 0.51	6.9	2.8 ± 0.50	18
15.3	12.3	6.3 ± 0.51	8.0	2.6 ± 0.50	19
12.8	10.3	5.0 ± 0.51	10	2.6 ± 0.70	27
10.6	8.6	3.8 ± 0.51	13	2.4 ± 0.75	31

Average value of ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_8$ = 0.41

Table 37 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AOT Mixtures in 0.004 M T.I.S.(NaCl) (25° C, pH 5.2, $^{\alpha}C_{12}(EO)_8$ = 0.56)

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-5} $(dm^3/mol)^2$	% error in K	K' (dm^3/mol)
23.6	18.9	10.3 ± 0.51	5.0	2.8 ± 0.40	14	209 ± 18
21.4	17.2	9.3 ± 0.51	5.5	3.0 ± 0.50	17	202 ± 18
19.5	15.6	8.1 ± 0.51	6.3	2.9 ± 0.50	17	189 ± 20
16.9	13.6	6.3 ± 0.51	8.1	2.6 ± 0.50	19	161 ± 20
15.3	12.3	5.7 ± 0.51	9.0	2.6 ± 0.60	23	151 ± 21
12.8	10.3	4.5 ± 0.51	11	2.7 ± 0.70	27	136 ± 24

K' is K without RSO_3^-

Average value of ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_8$ = 0.40

On comparison of K in table 32 with K' in table 37, it is apparent that K for $C_{12}(EO)_8 + Na^+ \rightleftharpoons C_{12}(EO)_8.Na^+$, is greater in presence of anionic, AOT (RSO_3Na), than in absence of it. Therefore, RSO_3^- enhances complexation of Na^+ with ether oxygens of the polyoxyethylene chain.

Table 38 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AOT Mixtures in 0.003 M T.I.S.(NaCl)(25° C, pH 5.2, $^{\alpha}C_{12}(EO)_8$ = 0.56)

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-5} $(dm^3/mol)^2$	% error in K
19.5	15.6	6.85 ± 0.51	7.4	2.9 ± 0.50	17
16.9	13.6	5.80 ± 0.51	8.8	2.7 ± 0.50	18
15.3	12.3	5.20 ± 0.51	9.8	2.9 ± 0.60	21
12.8	10.3	3.95 ± 0.51	13	2.7 ± 0.70	26
10.6	8.6	3.0 ± 0.51	17	2.6 ± 0.85	33

Average value of ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_8$ = 0.32

Table 39 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AOT Mixtures in 0.002 M T.I.S.(NaCl) (25° C, pH 5.2, $^{\alpha}C_{12}(EO)_8$ = 0.56)

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-5} $(dm^3/mol)^2$	% error in K
19.5	15.6	6.0 ± 0.51	8.5	2.7 ± 0.45	17
16.9	13.6	4.5 ± 0.51	11	2.5 ± 0.50	20
15.3	13.6	4.2 ± 0.51	12	2.8 ± 0.70	25
12.8	10.3	3.2 ± 0.51	16	2.6 ± 0.75	29
10.6	8.6	2.4 ± 0.51	21	2.8 ± 0.95	34

Average value of ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_8$ = 0.27.

From the data in tables 35 -41, it is apparent that $\Delta[Na^+]$ increases with increase in concentrations of $C_{12}(EO)_X$ (X= 4,8) and $RSO_3^-Na^+$(AOT or AAY) in the mixture, as expected. When concentrations of $C_{12}(EO)_X$ and AOT(or AAY) increase, the equilibrium of the reaction

$$C_{12}(EO)_X + RSO_3^- + Na^+ \rightleftharpoons C_{12}(EO)_X.RSO_3^-$$

(with Na^+ associated with the complex)

will shift to the right hand side, leading to the greater complexation of Na^+ with ether oxygens of the polyoxyethylene chain.

Table 40 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_4$ - AOT Mixtures in 0.004 M T.I.S.(NaCl) (25° C, pH 5.2, $^{\alpha}C_{12}(EO)_4$ = 0.48).

$[C_{12}(EO)_4]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-4} $(dm^3/mol)^2$	% error in K	$K'(dm^3/mol)$
16.9	18.2	3.5 ± 0.51	15	4.5 ± 0.95	21	56 ± 10
14.7	15.8	2.9 ± 0.51	18	4.8 ± 1.2	25	54 ± 12
12.8	13.7	2.3 ± 0.51	22	4.8 ± 1.6	33	48 ± 13
11	11.8	1.8 ± 0.51	28	4.8 ± 1.8	38	41 ± 14

K' is K without RSO_3^-

Average value of ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_4$ = 0.15

On comparison of K in table 33 with K' in table 40, it is apparent that value of K for $C_{12}(EO)_4 + Na^+ \rightleftharpoons C_{12}(EO)_4.Na^+$, is greater in presence of AOT(RSO_3^-) than in absence of it. Therefore, RSO_3^- enhances complexation of Na^+ with ether oxygens of the polyoxyethylene chain.

Table 41 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AAY Mixtures in 0.004 M T.I.S.(NaCl) (25° C, pH 5.2, $\alpha_{C_{12}(EO)_8} = 0.62$

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AAY],Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-5} $(dm^3/mol)^2$	% error in K	K' (dm^3/mol)
29.9	18.5	8.6 ± 0.51	6	1.2 ± 0.10	8	106 ± 9
26.4	16.1	7.3 ± 0.51	7	1.2 ± 0.15	12	95 ± 8
23	14.1	6.2 ± 0.51	8	1.3 ± 0.25	19	92 ± 10
20	12.3	5.1 ± 0.51	10	1.3 ± 0.30	23	80 ± 11
17.4	10.7	4.3 ± 0.51	12	1.3 ± 0.35	27	74 ± 12

K' is K without RSO_3^-

Average value of moles of Na^+ complexed/moles of initial $C_{12}(EO)_8$ = 0.27

From the data in tables 37 and 40, it is apparent that the system $C_{12}(EO)_8$ - AOT has greater complexation of Na^+ with ether oxygens of the polyoxyethylene chain than the system $C_{12}(EO)_4$ - AOT , $^{K}C_{12}(EO)_8$ - AOT = 6 $^{K}C_{12}(EO)_4$ - AOT. This may be due to the greater ability of a chain with more oxyethylene units to complex the Na^+(93). And from the data in tables 37 and 41, it is also apparent that the system $C_{12}(EO)_8$ - AOT has greater complexation of Na^+ with ether oxygens of the polyoxyethylene chain than the system $C_{12}(EO)_8$ - AAY, $^{K}C_{12}(EO)_8$ - AOT = 2.4 ^{K} $C_{12}(EO)_8$ - AAY. This is because AOT has a longer hydrocarbon chain than AAY,therefore, the complexation is more enhanced by the hydrophobic interaction between the hydrophobic parts of the two surfactants in the system $C_{12}(EO)_8$ - AOT than in the system $C_{12}(EO)_8$ -AAY. On comparison of K in table 32 with K' in table 41,it is apparent that, K for $C_{12}(EO)_8 + Na^+ \rightleftharpoons C_{12}(EO)_8.Na^+$ is greater in presence of anionic, AAY(RSO_3Na), than in absence of it. Therefore, RSO_3^- enhances complexation of Na^+ with ether oxygens of the polyoxyethylene chain.

3.6.3 Effect of Ionic Strength of the Solution on Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in Polyoxyethylenated nonionic - anionic Mixture.

The system $C_{12}(EO)_8$ - AOT was investigated in NaCl solutions of 0.008, 0.006, 0.004, 0.003, and 0.002 M T.I.S. at 25° C, ph 5.2. Values of $\Delta[Na^+]$ and the complexation costant K are listed in table 42.

Table 42 Effect of Ionic Strength of the Solution on Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AOT Mixture at 25 °C, pH 5.2.

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	Medium	$\Delta[Na^+]$,Mx10^4	Kx10^{-5} $(dm^3/mol)^2$
19.5	15.6	0.008 M T.I.S.(NaCl)	9.7 ± 0.51	2.9 ± 0.55
19.5	15.6	0.006 M T.I.S.(NaCl)	8.9 ± 0.51	2.7 ± 0.50
19.5	15.6	0.004 M T.I.S.(NaCl)	8.1 ± 0.51	2.9 ± 0.50
19.5	15.6	0.003 M T.I.S.(NaCl)	6.85 ± 0.51	2.9 ± 0.50
19.5	15.6	0.002 M T.I.S.(NaCl)	6.0 ± 0.51	2.7 ± 0.45
16.9	13.6	0.008 M T.I.S.(NaCl)	8.0 ± 0.51	2.7 ± 0.55
16.9	13.6	0.006 M T.I.S.(NaCl)	7.4 ± 0.51	2.8 ± 0.50
16.9	13.6	0.004 M T.I.S.(NaCl)	6.3 ± 0.51	2.6 ± 0.50
16.9	13.6	0.003 M T.I.S.(NaCl)	5.8 ± 0.51	2.7 ± 0.50
16.9	13.6	0.002 M T.I.S.(NaCl)	4.5 ± 0.51	2.5 ± 0.50
15.3	12.3	0.008 M T.I.S.(NaCl)	7.35 ± 0.51	3.1 ± 0.80
15.3	12.3	0.006 M T.I.S.(NaCl)	6.3 ± 0.51	2.6 ± 0.50
15.3	12.3	0.004 M T.I.S.(NaCl)	5.7 ± 0.51	2.6 ± 0.60
15.3	12.3	0.003 M T.I.S.(NaCl)	5.2 ± 0.51	2.9 ± 0.60
15.3	12.3	0.002 M T.I.S.(NaCl)	4.2 ± 0.51	2.8 ± 0.70
12.8	10.3	0.008 M T.I.S.(NaCl)	5.8 ± 0.51	3.0 ± 0.85
12.8	10.3	0.006 M T.I.S.(NaCl)	5.0 ± 0.51	2.6 ± 0.7
12.8	10.3	0.004 M T.I.S.(NaCl)	4.5 ± 0.51	2.7 ± 0.70
12.8	10.3	0.003 M T.I.S.(NaCl)	3.95 ± 0.51	2.7 ± 0.70
12.8	10.3	0.002 M T.I.S.(NaCl)	3.2 ± 0.51	2.6 ± 0.75

From the data in table 42, it is apparent that there is an increase in $\Delta[Na^+]$ with increase in ionic strength of the solution, but values of the complexation constant K are essentially constant with this change.

Table 43 shows the data of complexation of Na^+ with ether oxygens of the polyoxyethylene chain in $C_{12}(EO)_8$ - AOT mixtures at 25° C, pH 5.2, at various $\alpha_{C_{12}(EO)_8}$ values.

Table 43 Effect of Molar Ratio in the Mixed Micelle on Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - AOT mixtures in 0.004 M T.I.S.(NaCl) at 25° C, pH 5.2

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	[AOT],Mx10^4 mixed initial	$\alpha_{C_{12}(EO)_8}$	$\Delta[Na^+]$,Mx10^4	$\frac{a_{Na^+(mix)}}{a_{Na^+(AOT)}}$	Kx10^{-5} $(dm^3/mol)^2$	X_1M
40	17.2	0.70	8.5 ± 0.51	0.75	1.1 ± 0.15	0.80
32	17.2	0.65	8.8 ± 0.51	0.73	1.7 ± 0.30	0.80
25	17.2	0.60	9.0 ± 0.51	0.70	2.6 ± 0.40	0.78
21.4	17.2	0.56	9.3 ± 0.51	0.66	3.0 ± 0.50	0.77
15	17.2	0.46	7.0 ± 0.51	0.74	3.2 ± 0.40	0.74
10	17.2	0.36	5.0 ± 0.51	0.78	2.9 ± 0.70	0.71
5.5	17.2	0.24	3.0 ± 0.51	0.81	2.9 ± 1.2	0.66

$a_{Na^+(mix)}$ and $a_{Na^+(AOT)}$ refer to the activities of Na^+ in mixed surfactant solution and in the blank AOT solution, respectively. Plot of $a_{Na^+(mix)}/a_{Na^+(AOT)}$ versus $[C_{12}(EO)_8]$ is shown in figure 2.

Table43 (continued)

α_1	C_{12}^M, mol dm^{-3}	β^M	X_1^M	moles of AOT / moles of $C_{12}(EO)_8$ in mixed micelle	moles of Na^+ complexed / moles of initial $C_{12}(EO)_8$ in mixed micelle
0.70	1.07×10^{-4}	-4.0	0.80	0.25	0.21
0.65	1.15×10^{-4}	-4.1	0.80	0.25	0.27
0.60	1.20×10^{-4}	-3.9	0.78	0.28	0.36
0.56	1.26×10^{-4}	-3.7	0.77	0.30	0.43
0.46	1.41×10^{-4}	-3.6	0.74	0.35	0.46
0.36	1.58×10^{-4}	-3.7	0.71	0.41	0.50
0.24	1.90×10^{-4}	-3.8	0.66	0.52	0.54

$C_1^M = 1.1\times10^{-4}$ mol dm^{-3}, $C_2^M = 22.4\times10^{-4}$ mol dm^{-3}

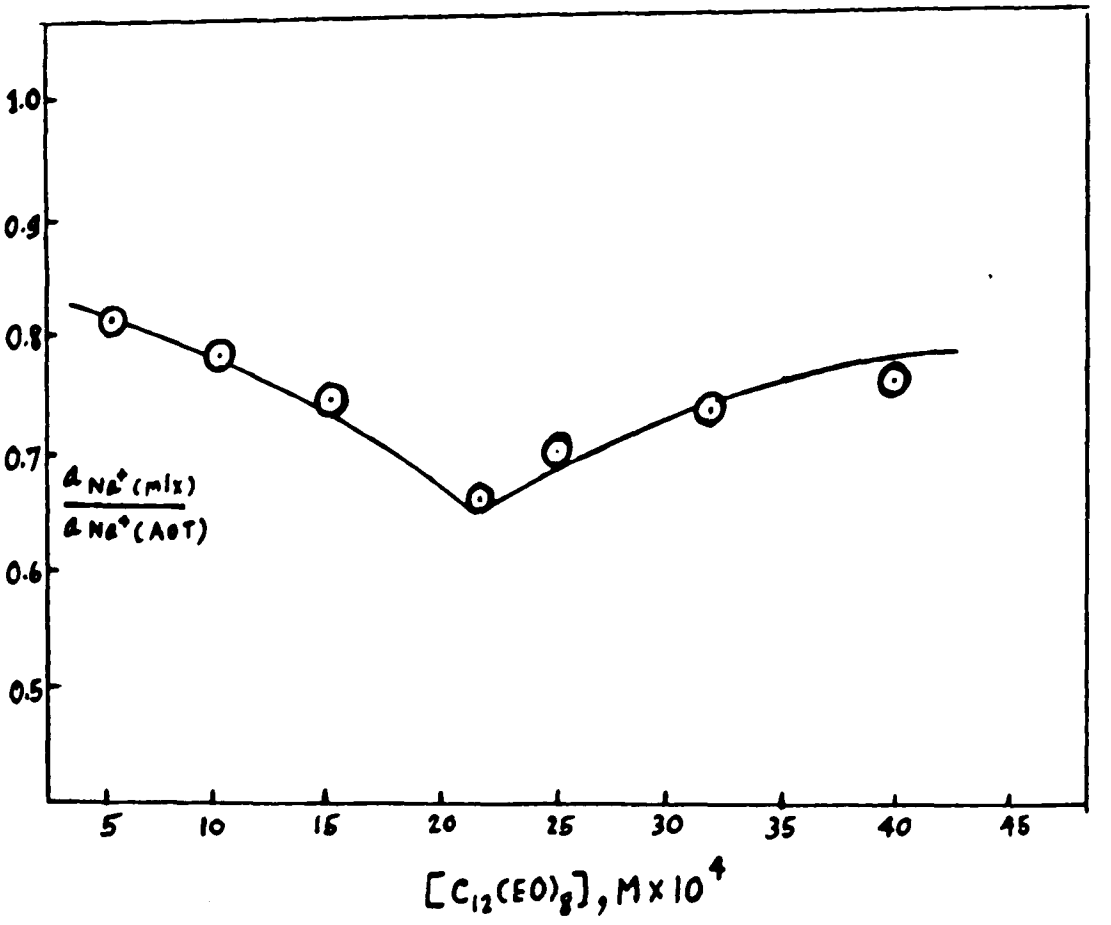


Figure 2. Plot of $^{a}Na^{+}(mix)/^{a}Na^{+}(AOT)$ versus $[C_{12}(EO)_8]$ in 0.004 M T.I.S.(NaCl)

It is seen from figure 2 that the activity ratio $^{a}Na^{+}(mix)/\ ^{a}Na^{+}(AOT)$ decreases gradually above a certain $C_{12}(EO)_8$ concentration and reached its minimum value in the concentration region of 21×10^{-4} M. Above this $C_{12}(EO)_8$ concentration , the ratio increases gradually, this means that Na^+ ions began to be released from the mixed micelle. The decrease of the activity ratio of Na^+ ion in the low $C_{12}(EO)_8$ concentration region suggests that the ionic head, SO_3^-, of AOT ($RSO_3^-Na^+$) are

opened to Na^+ ions in the bulk solution. This result is compatible with the loose polyoxyethylene chain packing in the mixed micelle. Perhaps the degree of counterion binding on the surface of the mixed micelle will depend on the number of RSO_3^- ions incorporated into the mixed micelle. On the contrary, the increase of the activity ratio in the region of high $C_{12}(EO)_8$ concentration is due to the close packing of the polyoxyethylene chains in the mixed micelle. The hydrophilic group of the RSO_3^- ion seem to be covered by the compact shell of polyoxyethylene chains.

3.6.4 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in Polyoxyethylenated nonionic - cationic Mixture.

The system $C_{12}(EO)_8$ - $C_{14}N(CH_3)_3Br$ was investigated in NaCl solution of 0.004 M T.I.S. at 25° C, pH 5.2. In this investigation, $[Na^+]$ of NaCl solution of $C_{12}(EO)_8$ and that of $C_{14}N(CH_3)_3Br$ were first measured by a sodium ion selective electrode at 25° C, pH 5.2 and then, $[Na^+]$ of 1:1(V/V) mixture of NaCl solutions of $C_{12}(EO)_8$ and $C_{14}N(CH_3)_3Br$ were measured by the sodium ion selective electrode at the same conditions. From the data obtained, we determined $\Delta[Na^+]$ and the complexation constant K for the reaction:

$$C_{12}(EO)_8 + Na^+ + Br^- \rightleftharpoons C_{12}(EO)_8.Br^-$$

was calculated from the equation

$$K = [C_{12}(\overset{Na^+}{EO})_8.Br^-]/[C_{12}(EO)_8].\gamma_{Br^-}.[Br^-].\gamma_{Na^+}.[Na^+]$$

Ionic activity coefficients, γ_i, were calculated at 25° C by using Debye - Hückel equation,

$$\log \gamma_i = - 0.509 Z_i^2 (I)^{1/2}/1 + 0.33 \alpha (I)^{1/2}$$

Where $\alpha = 0.3$ for Na^+ and Br^-. Values of $\Delta[Na^+]$ and K are listed in table 44.

Table 44 Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in $C_{12}(EO)_8$ - $C_{14}N(CH_3)_3Br$ Mixtures in 0.004 M NaCl (25° C, pH 5.2 , $\alpha_{C_{12}(EO)_8} = 0.56$).

$[C_{12}(EO)_8]$,Mx10^4 mixed initial	$[C_{14}NBr]$,Mx10^4 mixed initial	$\Delta[Na^+]$,Mx10^4	% error in $\Delta[Na^+]$	Kx10^{-4} $(dm^3/mol)^2$	% error in K	K′ (dm^3/mol)
26.8	21.5	2.6 ± 0.51	20	1.8 ± 0.40	22	29 ± 7
23.6	18.9	2.0 ± 0.51	26	1.7 ± 0.55	32	25 ± 7
21.4	17.2	1.8 ± 0.51	28	1.8 ± 0.60	33	23 ± 8
19.5	15.6	1.6 ± 0.51	32	1.8 ± 0.70	39	22 ± 8
16.9	13.6	1.2 ± 0.51	42	1.7 ± 0.85	50	18 ± 8

K′ is K without $C_{14}NBr$

Average value of ratio moles of Na^+ complexed/moles of initial $C_{12}(EO)_8 = 0.08$.

From the data in table 44, it is apparent that there is a little complexation of Na^+ with ether oxygens of the polyoxyethylene chain in $C_{12}(EO)_8$ - $C_{14}N(CH_3)_3Br$ mixture. From calculation of K for $C_{12}(EO)_8 + Na^+ \rightleftharpoons C_{12}(EO)_8.Na^+$, value is less in presence of cationic than in absence of any surfactant. Therefore, $C_{14}N^+(CH_3)_3$ competes with Na^+ for ether oxygens of the polyoxyethylene chain .

3.6.5 Effect of Structure of Cationic and Anionic Surfactants on Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain.

The systems $C_{12}(EO)_8$ - AOT and $C_{12}(EO)_8$ - $C_{14}N^+(CH_3)_3Br$ were investigated in NaCl solution of 0.004 M T.I.S. at 25° C, pH 5.2. Values of K are listed in table 45.

Table 45 Effect of Structure of Cationic and Anionic Surfactants on Complexation of Na^+ with Ether Oxygens of the Polyoxyethylene Chain in 0.004 M T.I.S.(NaCl) (25° C, pH 5.2, $\alpha_{C_{12}(EO)_8} = 0.56$).

$[C_{12}(EO)_8]$, $Mx10^4$, Mixed initial	[AOT], $Mx10^4$ Mixed initial	$Kx10^{-4}$ $(dm^3/mol)^2$	$[C_{12}(EO)_8]$, $Mx10^4$, Mixed initial	$[C_{14}N(CH_3)_3Br]$, $Mx10^4$, Mixed initial	$Kx10^{-4}$, $(dm^3/mol)^2$
23.6	18.9	28 ± 4.0	23.6	18.9	1.7 ± 0.55
21.4	17.2	30 ± 5.0	21.4	17.2	1.8 ± 0.60
19.5	15.6	29 ± 5.0	19.5	15.6	1.8 ± 0.70
16.9	13.6	26 ± 5.0	16.9	13.6	1.7 ± 0.50

From the data in table 45, it is apparent that K of the system $C_{12}(EO)_8$ - AOT is significantly greater than that of the system $C_{12}(EO)_8$ - $C_{14}N(CH_3)_3Br$, i.e., the system $C_{12}(EO)_8$ - AOT has significantly greater complexation of Na^+ with ether oxygens of the polyoxyethylene chain than the system $C_{12}(EO)_8$ - $C_{14}N(CH_3)_3Br$. This is due to the fact that the positively charged ether oxygens of the polyoxyethylene chain in the complex are stabilized by the negatively charged anionic surfactant ion (RSO_3^-).
On the other hand, $C_{14}N^+(CH_3)_3$ competes with Na^+ in forming complex with ether oxygens of the polyoxyethylene chain.

Appendix

Table A 1 Surface tension data for $C_{12}(EO)_8$ in water at 25 ^{o} C

C, mol dm $^{-3}$ x 10 ^{4}	γ, mNm^{-1}	- log C
1.949	34.60	3.720
1.230	34.67	3.910
0.9354	35.17	4.029
0.7568	37.06	4.121
0.7079	37.45	4.150
0.3020	42.60	4.520
0.2089	45.20	4.680
0.1514	46.20	4.820
0.0813	50.80	5.090

Table A 2 Surface tension data for 2 ^{o} LAS in water at 25 ^{o} C

C, mol dm^{-3} x10^{3}	γ, mNm^{-1}	- log C
3.540	39.60	2.451
2.171	39.80	2.663
1.057	39.60	2.976
0.7646	41.18	3.116
0.4169	48.80	3.380
0.3236	52.00	3.490

Table A 3 Surface tension data for $C_{12}(EO)_8$ - 2 ^{o} LAS mixture in water at 25 ^{o} C, $\alpha_1 = 0.2833$

C_{12}, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
3.087	39.90	3.510
2.573	39.80	3.590
1.544	39.85	3.811
1.029	39.78	3.988
0.6174	42.14	4.209
0.3860	45.20	4.413
0.1544	50.79	4.812

Table A 4 Surface tension data for $C_{12}(EO)_8$ - 2 ^{o} LAS mixture in water at 25 ^{o} C, $\alpha_1 = 0.1075$

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
6.304	39.80	3.200
3.152	39.85	3.501
2.101	39.90	3.678
1.261	41.30	3.899
0.7003	44.60	4.155
0.4202	48.47	4.376
0.2626	51.70	4.581

Table A 5 Surface tension data for $C_{12}(EO)_8$ - 2 ° LAS in water at 25 ° C,

$\alpha_1 = 0.7111$

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
1.221	39.33	3.913
0.8140	39.31	4.089
0.4884	40.52	4 .312
0.2930	43.20	4.533
0.2442	44.20	4.613
0.1628	46.65	4.788

Table A 6 Surface tension data for $C_{12}(EO)_8$ in 0.005 M T.I.S. (NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{4}	γ, mNm^{-1}	- log C
0.6480	37.12	4.188
0.5184	39.00	4.286
0.3240	42.10	4.489
0.1944	45.44	4.712
0.1296	48.06	4.886

Table A 7 Surface tension data for 2 ^{o} LAS in 0.005 M T.I.S. (NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{3}	γ, mNm^{-1}	- log C
5.849	38.45	3.233
4.679	38.45	3.330
3.509	40.10	3.455
2.340	42.20	3.631
1.671	45.70	3.777
1.170	47.60	3.932

Table A 8 Surface tension data for $C_{12}(EO)_8$ - 2 ^{o} LAS mixture in 0.005 M T.I.S.(NaCl) at 25 ^{o} C, $\alpha_1 = 0.6750$

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
9.114	37.60	4.040
7.291	37.60	4.137
4.375	38.41	4.358
3.646	39.70	4.438
2.917	41.64	4.535
1.823	44.81	4.740

Table A 9 Surface tension data for $C_{12}(EO)_8$ - 2 ° LAS mixture in 0.005 M T.I.S.(NaCl) at 25 ° C, α_1 = 0.7640

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
8.196	37.40	4.086
4.918	37.50	4.308
4.098	38.58	4.387
2.951	41.12	4.530
2.049	43.85	4.688
1.639	45.45	4.785

Table A 10 Surface tension data for $C_{12}(EO)_8$ in 0.01 M T.I.S.(NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{5}	γ, mNm^{-1}	- log C
10.01	35.16	4.000
4.712	39.72	4.327
3.927	41.10	4.406
2.356	45.50	4.627
1.178	48.70	4.928

Table A 11 Surface tension data for 2 ^{o} LAS in 0.01 M T.I.S. (NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{4}	γ, mNm^{-1}	- log C
4.632	36.80	3.334
3.860	36.70	3.413
2.316	39.89	3.635
1.544	43.30	3.811
0.9264	47.75	4.033

Table A 12 Surface tension data for $C_{12}(EO)_8$ - 2 ° LAS mixture in 0.01 M T.I.S.(NaCl) at 25 ° C, α_1 = 0.7576

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
9.676	36.50	4.014
8.063	36.50	4.094
4.147	37.54	4.382
2.419	41..39	4.616
1.489	44.80	4.827

Table A 13 Surface tension data for $C_{12}(EO)_8$ - 2 ° LAS mixture in 0.01 M T.I.S.(NaCl) at 25 ° C, α_1= 0.6002

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
11.58	36.71	3.936
5.790	36.90	4.237
3.308	39.44	4.480
2.316	42.05	4.634
1.448	45.46	4.389

Table A 14 Surface tension data for 4 ^{o} LAS in water at 25 ^{o} C

C, Mol dm^{-3} x10^{3}	γ, mNm^{-1}	- log C
2.185	36.87	2.660
1.820	36.87	2.740
1.311	39.36	2.882
1.092	41.63	2.962
0.7283	44.85	3.138
0.5200	49.50	3.284
0.3642	53.40	3.439

Table A 15 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in water at 25 ^{o} C, $\alpha_1 = 0.5158$

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
1.456	38.64	3.837
1.213	38.52	3.916
0.8736	38.97	4.058
0.5824	41.47	4.235
0.2912	45.48	4.536
0.1456	49.71	4.836

Table A 16 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS in water at 25 ^{o} C,

$\alpha_1 = 0.8091$

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
9.085	38.07	4.042
7.571	38.04	4.121
5.451	39.87	4.264
3.028	43.65	4.518
1.817	46.95	4.740
1.514	47.93	4.821

Table A 17 Surface tension data for 4 ^{o} LAS in 0.005 M T.I.S.(NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{3}	γ, mNm^{-1}	- log C
1.528	34.15	2.816
1.222	34.18	2.913
0.9168	34.30	3.038
0.6112	35.87	3.214
0.4366	38.85	3.360
0.2547	43.28	3.594

Table A 18 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS in 0.005 M T.I.S.(NaCl) at 25 ^{o} C, α_1 = 0.3992

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
12.11	36.37	3.917
9.688	36.41	4.014
7.266	36.83	4.138
4.844	39.60	4.315
3.633	41.76	4.440
2.422	44.56	4.616

Table A19 Surface tension data for $C_{12}(EO)_8$ - 4° LAS mixture in 0.005 M T.I.S.(NaCl) at 25 °C , α_1 = 0.7686

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
6.539	36.73	4.184
5.950	36.77	4.225
3.923	39.56	4.407
3.139	41.40	4.503
2.616	42.40	4.582
1.959	44.6	4.700

Table A 20 Surface tension data for 4 ^{o} LAS in 0.01 M T.I.S.(NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{3}	γ, mNm^{-1}	- log C
2.297	33.66	2.639
0.9844	33.68	3.007
0.6563	34.17	3.183
0.4594	37.20	3.338
0.2552	42.10	3.593
0.1312	47.54	3.882

Table A21 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in 0.01 M T.I.S.(NaCl) at 25 ^{o} C, α_1 = 0.02824

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
14.18	33.21	2.848
8.726	33.23	3.059
4.727	33.53	3.325
2.836	34.22	3.547
1.418	38.83	3.848
0.5672	45.74	4.246
0.2836	51.00	4.548

Table A22 Surface tension data for $C_{12}(EO)_8$ - 4° LAS mixture in 0.01 M T.I.S.(NaCl) at 25 °C, α_1 = 0.1331

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
3.966	34.50	3.402
3.173	34.54	3.498
2.380	34.85	3.623
1.586	35.47	3.800
0.7932	38.66	4.100
0.4407	42.90	4.356
0.1762	50.06	4.754

Table A 23 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in 0.01 M T.I.S.(NaCl) at 25 ^{o} C, $\alpha_1 = 0.7566$

C_{12}, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
8.134	36.39	4.090
6.507	36.52	4.186
4.067	39.20	4.390
2.711	41.91	4.567
1.627	45.71	4.788
1.162	47.76	4.936

Table A 24 Surface tension data for $C_{12}(EO)_8$ in 0.025 M T.I.S. (NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^5	γ, mNm^{-1}	- log C
28.18	34.60	3.550
17.78	34.60	3.750
7.002	36.50	4.155
5.602	38.15	4.252
3.981	40.50	4.400
3.360	41.70	4.474
2.334	43.93	4.633

Table A 25 Surface tension data for 4 ^{o} LAS in 0.025 M T.I.S.(NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{4}	γ, mNm^{-1}	- log C
6.238	31.94	3.205
4.990	31.90	3.302
2.994	32.21	3.524
2.495	33.87	3.603
1.497	37.83	3.825
0.998	40.83	4.000

Table A 26 Surface tension data for $C_{12}(EO)_8$ - 4° LAS mixture in 0.025 M T.I.S.(NaCl) at 25 °C, α_1 = 0.4571

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
1.352	34.00	3.869
1.082	34.07	3.966
0.5408	34.80	4.267
0.4328	36.31	4.364
0.3380	38.06	4.471
0.2705	39.86	4.567

Table A 27 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in 0.025 M T.I.S.(NaCl) at 25 ^{o} C, $\alpha_1 = 0.6275$

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
1.046	34.60	3.980
0.6276	34.84	4.202
0.4184	36.20	4.379
0.3487	37.57	4.457
0.2510	40.28	4.600
0.2092	41.53	4.680

Table A 28 Surface tension data for $C_{12}(EO)_8$ in 0.05 M T.I.S. (NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{5}	γ, mNm^{-1}	- log C
7.728	35.45	4.112
6.182	37.50	4.209
4.637	39.50	4.333
3.091	42.20	4.510
1.855	45.60	4.730
1.546	46.80	4.810

Table A 29 Surface tension data for 4 ^{o} LAS in 0.05 M T.I.S.(NaCl) at 25 ^{o} C

C, Mol dm^{-3} x10^{4}	γ, mNm^{-1}	- log C
12.48	30.60	2.904
6.240	30.40	3.206
3.566	30.40	3.448
2.080	30.60	3.682
1.560	32.43	3.807
1.040	35.91	3.983
0.780	38.11	4.108
0.567	40.90	4.246

Table A 30 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in 0.05 M T.I.S.(NaCl) at 25 ^{o} C, α_1 =0.4365

C_{12}, Mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
2.888	32.78	3.539
1.733	32.78	3.761
1.155	32.76	3.937
0.5776	33.25	4.238
0.4950	33.50	4.305
0.2888	37.51	4.539
0.2166	39.68	4.664

Table A 31 Surface tensiondata for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in 0.05 M T.I.S.(NaCl) at 25 ^{o} C,α_1 = 0.5534

C_{12}, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
1.33	33.14	3.876
0.798	33.25	4.098
0.570	33.44	4.244
0.380	35.20	4.420
0.266	37.90	4.575
0.190	40.56	4.721

Table A 32 Surface tension data for $C_{12}(EO)_8$ in 0.1 M T.I.S. (NaCl) at 25 ^{o} C

C_{12}, mol dm^{-3} x10^{4}	γ, mNm^{-1}	- log C_{12}
2.899	34.70	3.538
1.450	34.59	3.839
1.160	34.60	3.936
0.8128	34.60	4.090
0.6711	35.80	4.170
0.4832	38.44	4.316
0.2899	42.50	4.538
0.2319	44.00	4.634
0.1611	46.02	4.793
0.0966	49.50	5.01

Table A 33 Surface tension data for 4 ^{o} LAS in 0.1 M T.I.S. (NaCl) at 25 ^{o} C

C, mol dm^{-3} x10^{3}	γ, mNm^{-1}	- log C
1.248	28.64	2.904
0.9980	28.80	3.000
0.6238	28.62	3.205
0.3564	28.80	3.448
0.2079	28.65	3.682
0.1248	29.22	3.904
0.0959	31.11	4.018
0.0446	37.55	4.351
0.0250	42.70	4.602
0.0192	44.90	4.717

Table A 34 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in 0.1M T.I.S.(NaCl) at 25 ^{o} C, α_1= 0.4365

C_{12}, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
5.757	31.47	3.238
2.888	31.30	3.539
1.650	31.34	3.780
0.9627	31.38	4.016
0.7219	31.50	4.141
0.5250	31.54	4.279
0.3610	32.63	4.442
0.2220	36.62	4.654
0.1640	39.73	4.785
0.1203	41.80	4.921

Table A 35 Surface tension data for $C_{12}(EO)_8$ - 4 ^{o} LAS mixture in 0.1 M T.I.S.(NaCl) at 25 ^{o} C, $\alpha_1 = 0.5372$

C_{12}, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
1.058	31.88	3.976
0.6348	31.92	4.197
0.4069	32.30	4.390
0.3023	34.07	4.520
0.2885	34.63	4.541
0.1814	38.65	4.742
0.1374	41.20	4.863
0.1008	43.51	5.000

Table A 36 Surface tension data for $C_{12}(EO)_8$ in 0.01 M T.I.S. (NaCl) at 35 ° C

C, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C
1.518	33.60	3.819
1.214	33.65	3.916
0.7590	33.92	4.120
0.5060	36.20	4.296
0.2530	41.57	4.597
0.1898	43.43	4.721
0.1265	45.94	4.900

Table A 37 Surface tension data for 2 ^{o} LAS in 0.01 M T.I.S. (NaCl) at 35 ^{o} C

C, mol dm^{-3} x10^{4}	γ, mNm^{-1}	- log C
3.576	36.34	3.447
2.861	36.36	3.543
1.788	39.93	3.748
1.192	43.59	3.924
0.8940	46.01	4.040
0.5960	49.66	4.225

Table A 38 Surface tension data for $C_{12}(EO)_8$ - 2 ^{o} LAS mixture in 0.01 M T.I.S.(NaCl) at 35 ^{o} C, α_1 = 0.6797

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
9.305	35.63	4.030
6.203	35.62	4.208
3.722	37.15	4.429
2.658	39.37	4.575
2.068	41.17	4.684
1.550	43.15	4.810
1.240	45.04	4.906

Table A 39 Surface tension data for $C_{12}(EO)_8$ - 2 ^{o} LAS mixture in 0.01 M T.I.S.(NaCl) at 35 ^{o} C, α_1 = 0.7608

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
8.800	35.38	4.056
5.867	35.40	4.231
3.520	37.16	4.453
2.514	39.58	4.600
1.676	42.50	4.770
1.006	46.35	4.996

Table A 40 Surface tension data for $C_{12}(EO)_8$ in 0.01M T.I.S. (NaCl) at 40 °C

C, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C
8.912	33.35	4.050
7.396	33.40	4.130
4.390	35.57	4.307
3.698	37.75	4.432
2.645	40.52	4.509
1.849	42.42	4.733

Table A 41 Surface tension data for 2 ^{o} LAS in 0.01 M T.I.S. (NaCl) at 40 ^{o} C

C, mol dm^{-3} x10^{4}	γ, mNm^{-1}	- log C
3.311	35.90	3.480
2.861	35.90	3.543
2.384	37.00	3.623
1.907	39.20	3.720
1.192	43.30	3.924
0.9536	45.32	4.020
0.6357	48.81	4.196

Table A 42 Surface tension data for $C_{12}(EO)_8$ - 2 ^{o} LAS mixture in 0.01 M T.I.S.(NaCl) at 40 ^{o} C, α_1 = 0.7562

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
9.169	34.71	4.038
6.113	34.73	4.210
4.075	35.68	4.389
3.056	37.76	4.514
2.037	40.73	4.690
1.528	42.88	4.815

Table A 43 Surface tension data for $C_{12}(EO)_8$ - 2 ^{o} LAS mixture in 0.01 M T.I.S.(NaCl) at 40 ^{o} C, α_1 = 0.6797

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
7.079	34.96	4.150
6.203	34.94	4.208
3.802	36.30	4.420
3.102	37.95	4.509
2.585	39.15	4.558
2.068	40.70	4.684
1.379	43.77	4.860

Table A 44 Surface tension data for AOT in H_2O at 25 ^{o} C.

C, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C
30.90	29.90	2.510
28.18	30.10	2.550
25.75	30.30	2.589
21.46	31.88	2.668
15.45	35.10	2.811
10.30	37.85	2.987
7.725	40.60	3.112
6.310	42.50	3.200

Table A 45 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in H_2O at 25° C, $\alpha_1 = 0.0186$

C_{12}, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
16.63	32.08	2.779
13.86	32.16	2.858
8.315	34.40	3.080
5.543	37.11	3.256
4.158	39.18	3.381
2.772	41.90	3.557

Table A 46 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in H_2O at 25° C, $\alpha_1 = 0.0292$

C_{12}, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C_{12}
15.22	32.60	2.818
12.68	32.65	2.890
7.610	34.40	3.119
4.348	37.90	3.362
3.261	39.76	3.487
2.170	42.85	3.663

Table A 47 Surface tension data for AOT in 0.01 M T.I.S. (NaCl) at 25° C.

C, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C
27.54	26.70	2.560
22.39	26.90	2.650
15.25	27.75	2.817
7.625	31.38	3.118
5.083	33.56	3.294
2.542	37.61	3.595
1.694	39.75	3.771
1.017	42.73	3.993

Table A 48 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in 0.01 MT.I.S.(NaCl) at 25° C, $\alpha_1 = 0.7346$

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
9.332	35.00	4.030
8.180	35.03	4.087
6.818	35.64	4.166
4.096	38.94	4.388
3.409	40.38	4.467
2.273	42.80	4.644

Table A 49 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in 0.01 MT.I.S.(NaCl) at 25° C, $\alpha_1 = 0.4443$.

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
15.85	34.25	3.800
13.70	34.29	3.884
10.89	34.52	3.963
6.535	37.28	4.184
4.357	39.85	4.360
3.268	41.81	4.485

Table A 50 Surface tension data for AOT in 0.025 M T.I.S.(NaCl) at 25° C.

C, mol dm^{-3} x10^4	γ, mNm^{-1}	-log C
11.22	26.50	2.950
8.860	26.51	3.053
7.383	27.03	3.132
4.430	30.33	3.354
2.953	32.60	3.530
1.477	36.68	3.831
0.9843	39.01	4.007
0.5495	42.50	4.26

Table A 51 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in 0.025 MT.I.S.(NaCl) at 25° C, $\alpha_1 = 0.6322$.

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	-log C_{12}
11.48	33.65	3.940
9.567	33.65	4.019
5.740	35.84	4.241
3.827	38.51	4.417
2.399	41.50	4.620
1.640	44.00	4.785

Table A 52 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in 0.025 MT.I.S.(NaCl) at 25° C, α_1 = 0.4363.

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
15.72	32.95	3.804
13.10	32.95	3.883
7.860	34.40	4.104
6.550	35.50	4.184
4.367	38.31	4.360
2.620	41.60	4.582
1.950	43.50	4.710

Table A 53 Surface tension data for AOT in 0.05 M T.I.S. (NaCl) at 25° C.

C, mol dm^{-3} x10^4	γ, mNm^{-1}	- log C
7.025	25.33	3.153
5.854	25.37	3.232
3.512	28.43	3.454
2.342	30.74	3.630
1.171	34.48	3.931
0.7807	36.88	4.107
0.3802	41.10	4.420

Table A 54 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in 0.05 MT.I.S.(NaCl) at 25° C, $\alpha_1 = 0.3974$.

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
12.88	31.90	3.890
10.60	31.94	3.975
8.833	32.44	4.054
5.300	36.02	4.276
3.533	38.78	4.452
2.650	40.70	4.577

Table A 55 Surface tension data for $C_{12}(EO)_8$ - AOT mixture in 0.05 MT.I.S.(NaCl) at 25° C, $\alpha_1 = 0.5190$.

C_{12}, mol dm^{-3} x10^5	γ, mNm^{-1}	- log C_{12}
11.48	32.40	3.940
8.412	32.72	4.070
7.010	33.55	4.150
4.206	37.10	4.376
3.505	38.33	4.455
2.103	41.70	4.678

Table A 56 Surface tension data for $C_{12}(EO)_2SO_4Na$ in 1.95×10^{-3} M Mg^{2+} at 25° C.

C, mol dm^{-3} $\times 10^5$	γ, mNm^{-1}	- log C
56.33	34.29	3.249
42.25	34.26	3.374
35.21	35.09	3.453
21.12	40.11	3.675
14.08	43.16	3.851

Table A 57 Surface tension data for $C_{12}SO_3Na$ in 1.95×10^{-3} M Mg^{2+} at 25° C.

C, mol dm^{-3} $\times 10^4$	γ, mNm^{-1}	- log C
12.68	36.31	2.897
8.454	39.86	3.073
4.227	45.76	3.374
2.818	50.47	3.550
1.409	57.11	3.851

Table A 58 Surface tension data for $C_{12}(EO)_2SO_4Na$ - $C_{12}SO_3Na$ mixture in 1.95×10^{-3} M Mg^{2+} at 25° C, $\alpha_1 = 0.199$.

C_{12}, mol dm^{-3} $\times 10^5$	γ, mNm^{-1}	- log C_{12}
52.83	39.72	3.277
35.22	42.87	3.453
24.55	46.00	3.610
17.61	49.62	3.754

Table A 59 Surface tension data for $C_{12}(EO)_3SO_4Na$ in 1.95×10^{-3} M Mg^{2+} at 25°C

C, mol dm^{-3} $\times 10^4$	γ, mNm^{-1}	- log C
9.228	35.39	3.035
7.382	35.43	3.130
4.614	35.47	3.335
2.768	37.10	3.558
1.845	40.04	3.734
0.9228	44.73	4.034

Table A 60 Surface tension data for $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_3Na$ mixture in 1.95×10^{-3} M Mg^{2+} at 25° C, $\alpha_1 = 0.1407$

C_{12}, mol dm^{-3} $\times 10^4$	γ, mNm^{-1}	- log C_{12}
15.85	31.80	2.800
13.18	31.80	2.880
9.772	33.80	3.010
6.559	37.10	3.183
3.279	43.90	3.484
1.639	49.70	3.785

Table A 61 Surface tension data for $C_{12}(EO)_4SO_4Na$ in 1.95×10^{-3} M Mg^{2+} at 25° C

C, mol dm^{-3} $\times 10^5$	γ, mNm^{-1}	- log C
54.00	37.09	3.268
40.50	37.10	3.393
27.00	37.92	3.569
20.25	40.19	3.694
12.02	44.00	3.920
0.6750	47.44	4.171

Table A 62 Surface tension data for $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_3Na$ mixture in $1.95x10^{-3}$ M Mg^{2+} at 25° C, $\alpha_1 = 0.1003$.

C_{12}, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C_{12}
13.18	33.00	2.880
6.761	38.50	3.170
4.677	41.40	3.330
3.388	44.20	3.470

Table A 63 Surface tension data for $C_{12}SO_4Na$ in $1.95x10^{-3}$ M Mg^{2+} at 25° C

C, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C
20.51	34.68	2.688
19.77	34.63	2.704
18.31	34.79	2.737
14.65	37.52	2.834
10.98	39.75	2.959

Table A 64 Surface tension data for $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ mixture in $1.95x10^{-3}$ M Mg^{2+} at 25° C, $\alpha_1 = 0.1407$.

C_{12}, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C_{12}
11.09	32.47	2.955
8.879	32.48	3.052
7.397	34.35	3.131
5.188	37.50	3.285
3.698	40.94	3.432
2.957	42.84	3.529

Table A 65 Surface tension data for $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ mixture in $1.95x10^{-3}$ M Mg^{2+} at 25° C, $\alpha_1 = 0.6202$.

C_{12}, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C_{12}
16.77	33.72	2.775
13.42	33.76	2.872
6.710	33.95	3.173
3.355	36.86	3.474
2.239	40.00	3.650
1.677	42.68	3.775
1.345	44.16	3.875

Table A 66 Surface tension data for $C_{12}(EO)_3SO_4Na$ - $C_{12}SO_4Na$ mixture in $1.95x10^{-3}$ M Mg^{2+} at 25° C, $\alpha_1 = 0.952$.

C_{12}, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C_{12}
6.554	34.50	3.183
4.369	34.40	3.360
3.277	34.87	3.485
2.184	38.09	3.661
1.092	44.00	3.962

Table A 67 Surface tension data for $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$ mixture in $1.95x10^{-3}$ M Mg^{2+} at 25° C, $\alpha_1 = 0.1373$.

C_{12}, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C_{12}
14.75	31.70	2.831
9.834	31.61	3.007
4.917	35.33	3.308
2.458	41.96	3.609
1.475	47.20	3.831

Table A 68 Surface tension data for $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$ mixture in $1.95x10^{-3}$ M Mg^{2+} at 25° C, $\alpha_1 = 2408$.

C_{12}, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C_{12}
8.411	32.00	3.075
5.608	32.10	3.251
4.467	33.50	3.350
2.129	38.45	3.552
1.402	45.22	3.853
1.122	47.40	3.950

Table A 69 Surface tension data for $C_{12}(EO)_4SO_4Na$ - $C_{12}SO_4Na$ mixture in $1.95x10^{-3}$ M Mg^{2+} at 25° C, $\alpha_1 = 7216$.

C_{12}, mol dm^{-3} $x10^4$	γ, mNm^{-1}	- log C_{12}
4.467	32.70	3.350
3.742	32.72	3.420
3.388	32.70	3.470
2.806	33.50	3.552
1.871	36.71	3.728
1.175	41.00	3.930
0.9354	43.35	4.029

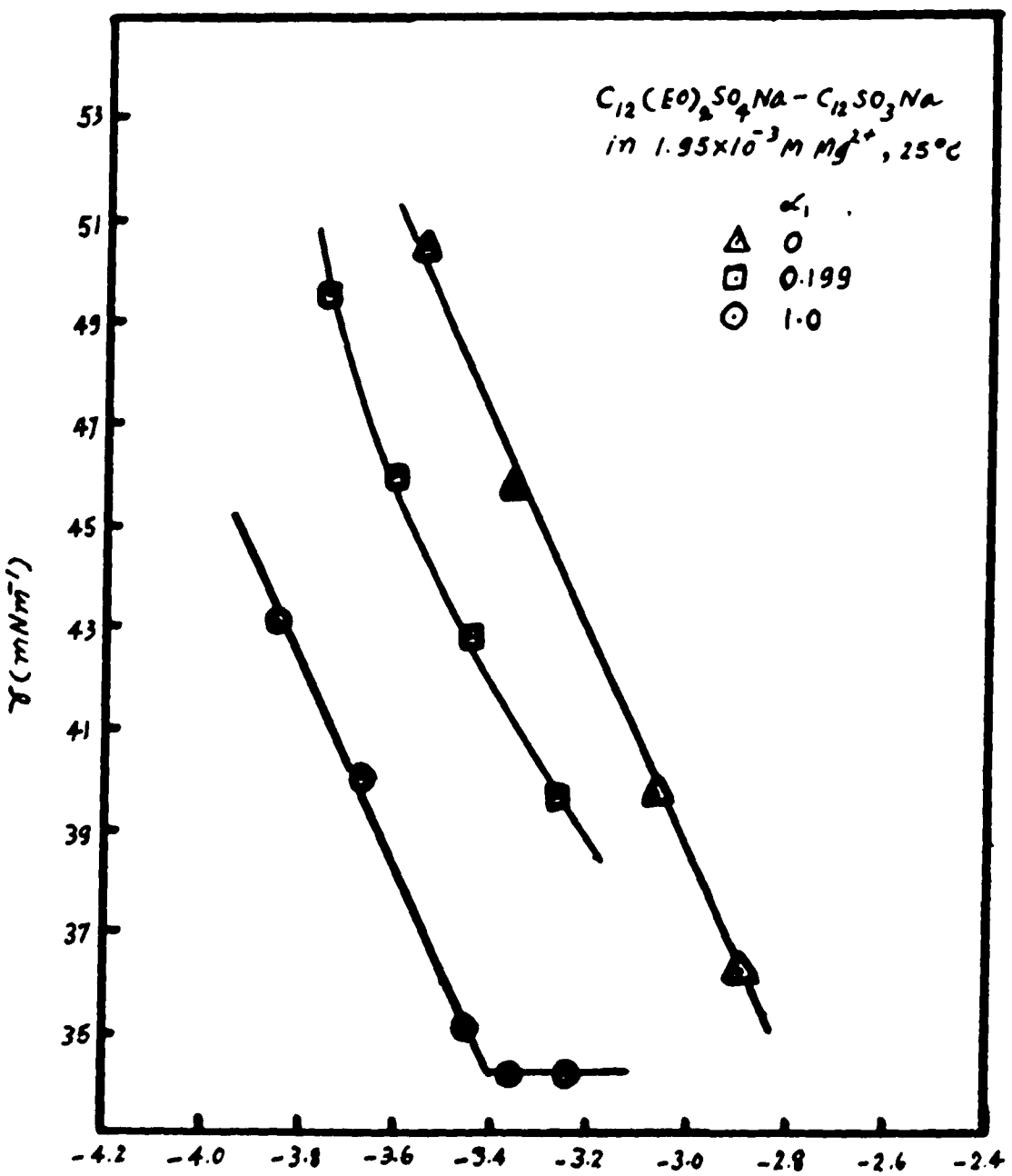

$C_{12}(EO)_2SO_4Na - C_{12}SO_3Na$
in 1.95×10^{-3} M Mg^{2+}, 25°C
α_1
0
0.199
1.0
53
51
49
47
45
43
41
39
37
35
γ (mN/m)
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
-2.4
log C_{12}

Figure 3

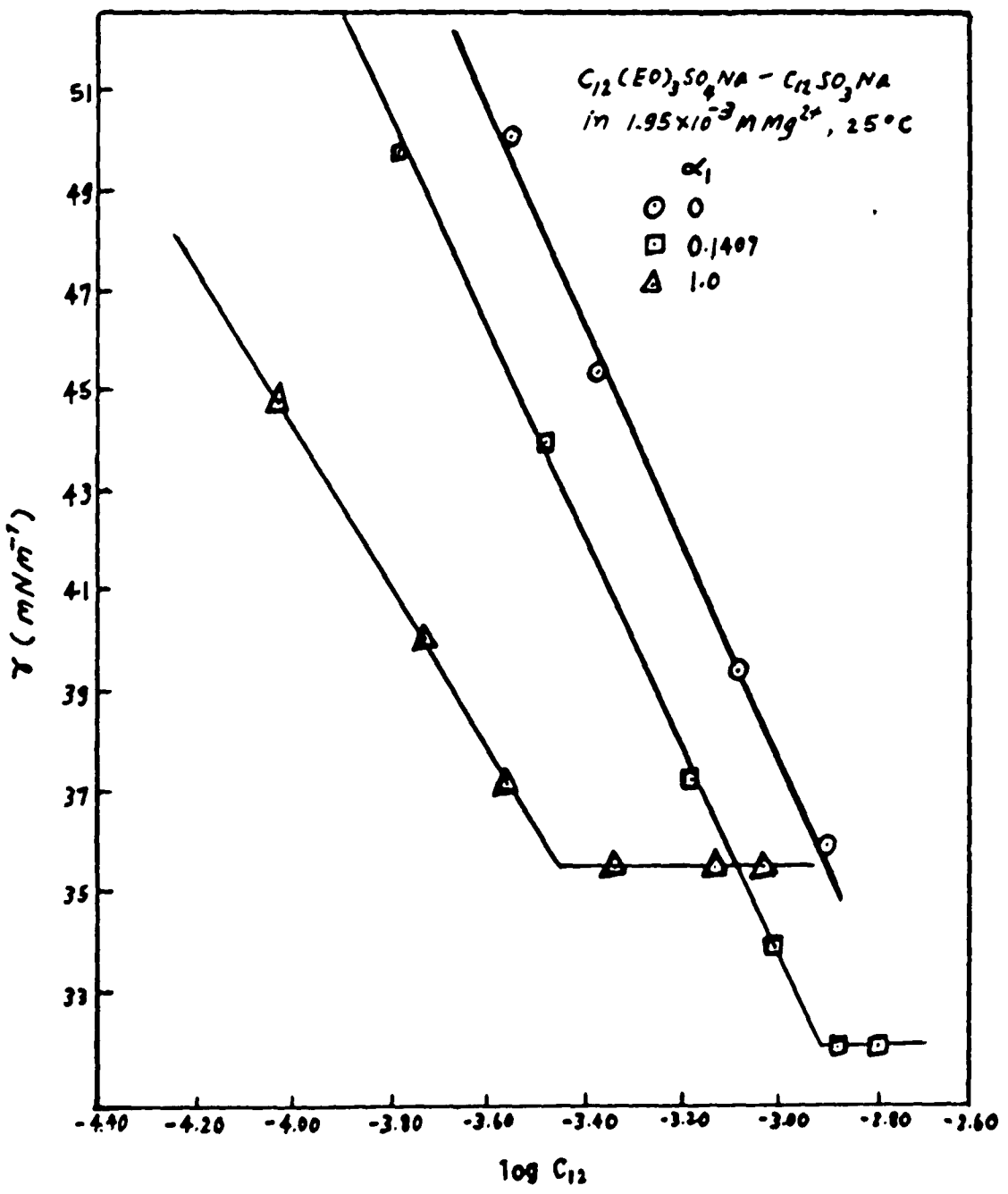

$C_{12}(EO)_3SO_4Na - C_{12}SO_3Na$
in 1.95×10^{-3} M Mg^{2+}, 25°C
α_1
0
0.1407
1.0
γ (mNm⁻¹)
51
49
47
45
43
41
39
37
35
33
-4.40
-4.20
-4.00
-3.80
-3.60
-3.40
-3.20
-3.00
-2.80
-2.60
log C_{12}

Figure 4

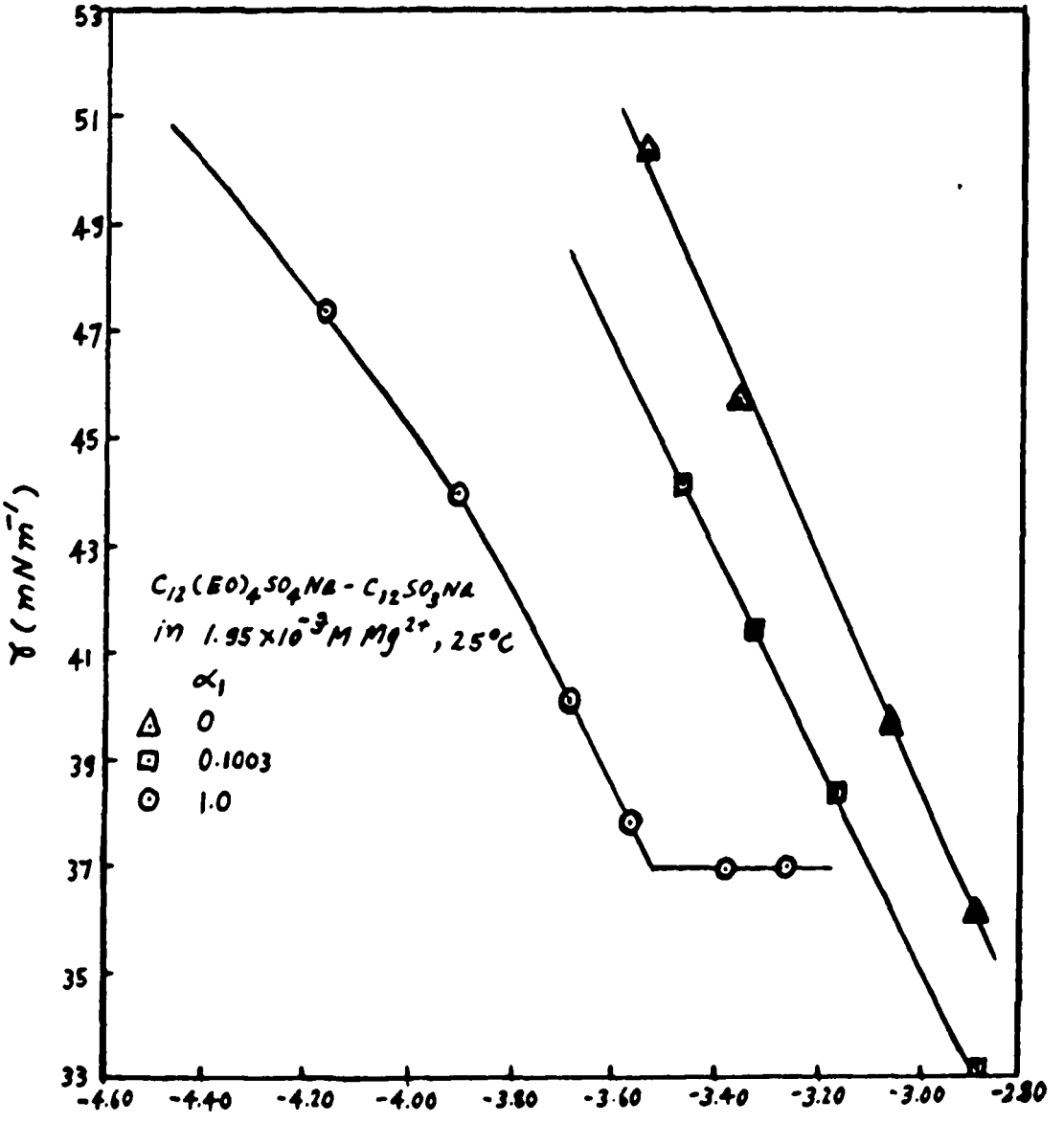

γ (mNm⁻¹)
53
51
49
47
45
43
41
39
37
35
33
-4.60
-4.40
-4.20
-4.00
-3.80
-3.60
-3.40
-3.20
-3.00
-2.80
log C12
C12(EO)4SO4Na - C12SO3Na
in 1.95×10⁻³M Mg2+, 25°C
α1
Δ 0
□ 0.1003
⊙ 1.0

Figure 5

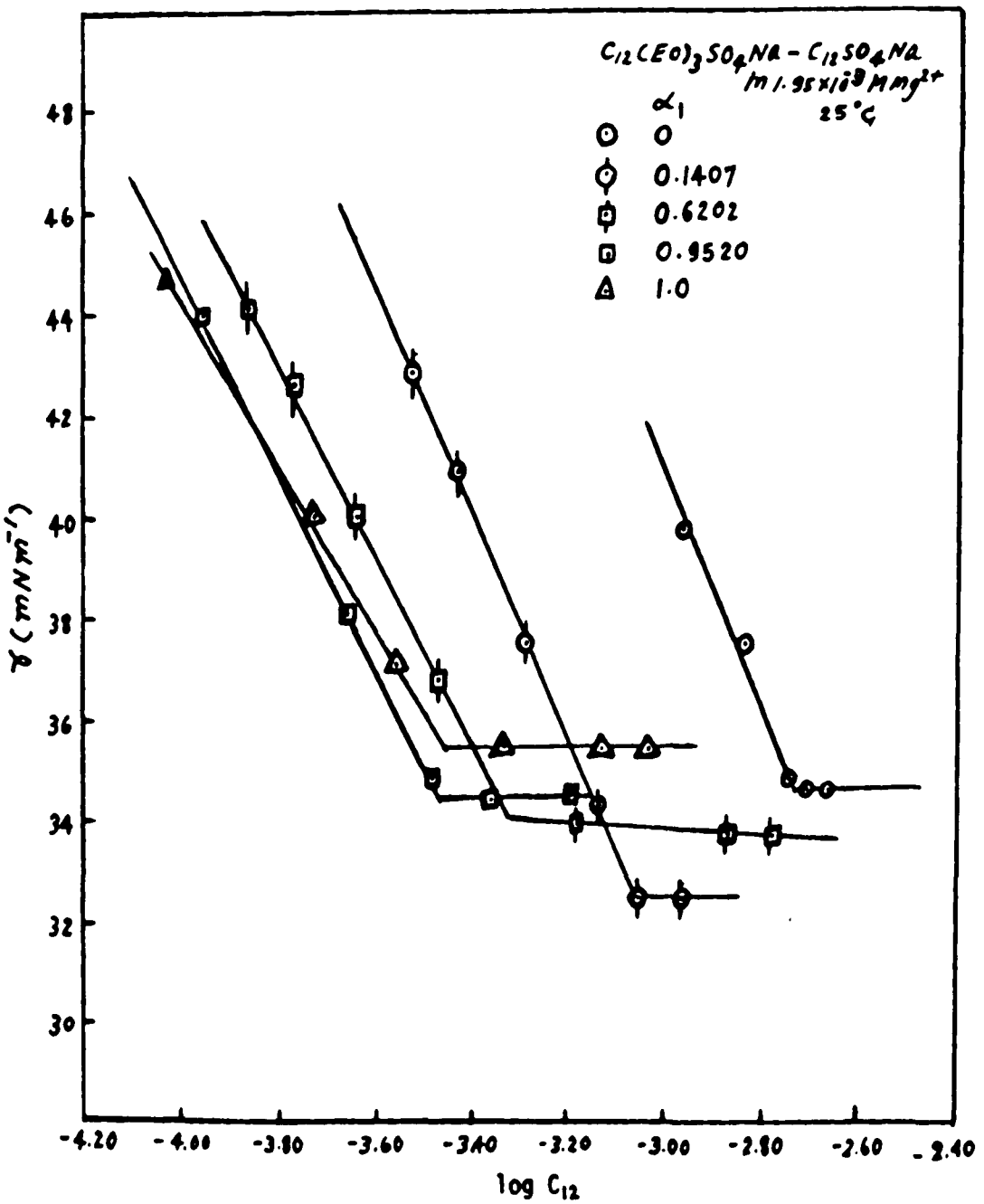

$C_{12}(EO)_3SO_4Na - C_{12}SO_4Na$
in 1.95×10^{-3} M Mg^{2+}
25°C
α_1
0
0.1407
0.6202
0.9520
1.0
γ (mN/m)
48
46
44
42
40
38
36
34
32
30
-4.20
-4.00
-3.80
-3.60
-3.40
-3.20
-3.00
-2.80
-2.60
-2.40
log C_{12}

Figure 6

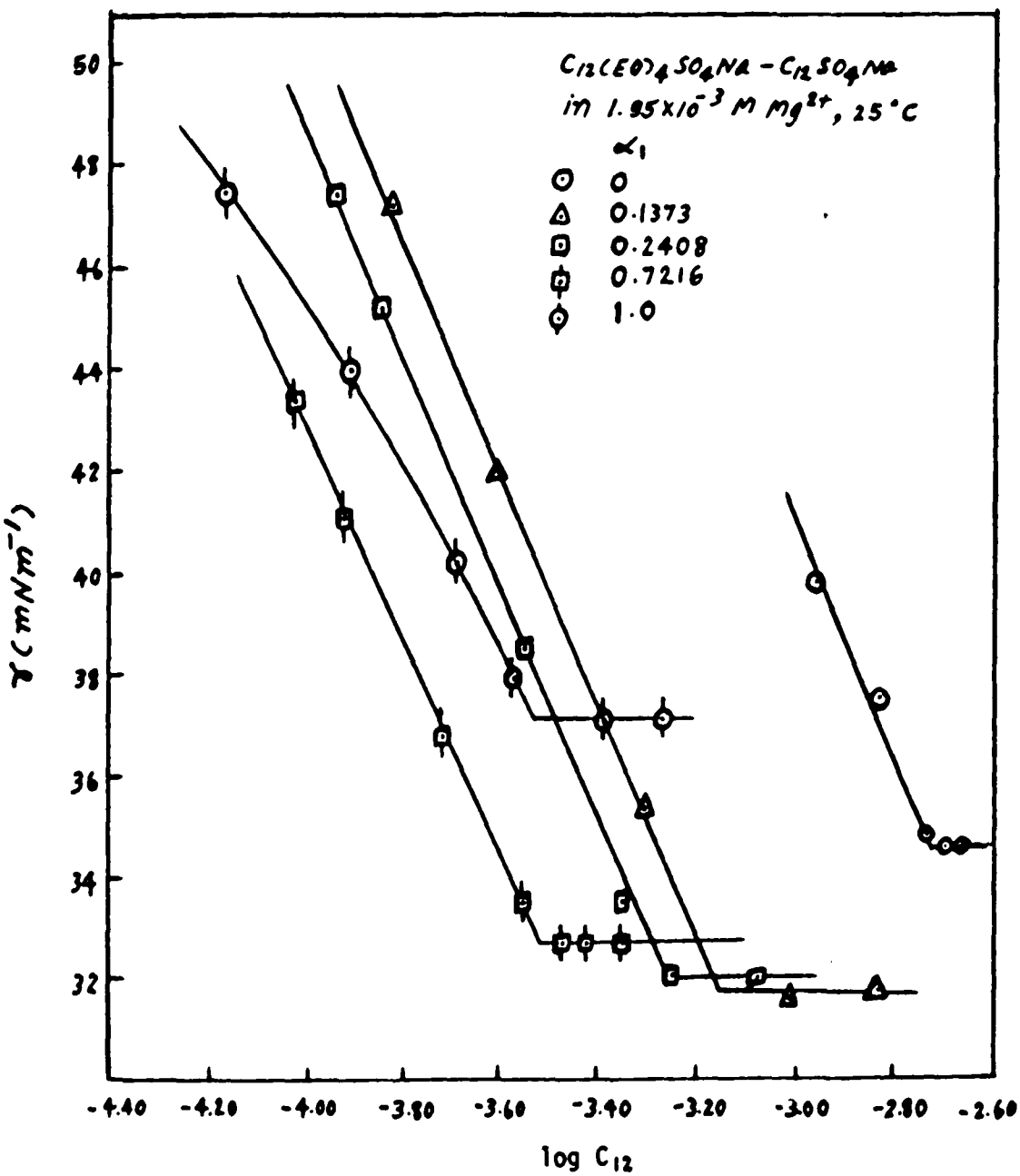

$C_{12}(EO)_4SO_4Na - C_{12}SO_4Na$
in 1.95×10^{-3} M Mg^{2+}, 25°C
α_1
0
0.1373
0.2408
0.7216
1.0
γ (mN m⁻¹)
50
48
46
44
42
40
38
36
34
32
-4.40
-4.20
-4.00
-3.80
-3.60
-3.40
-3.20
-3.00
-2.80
-2.60
log C_{12}

Figure 7

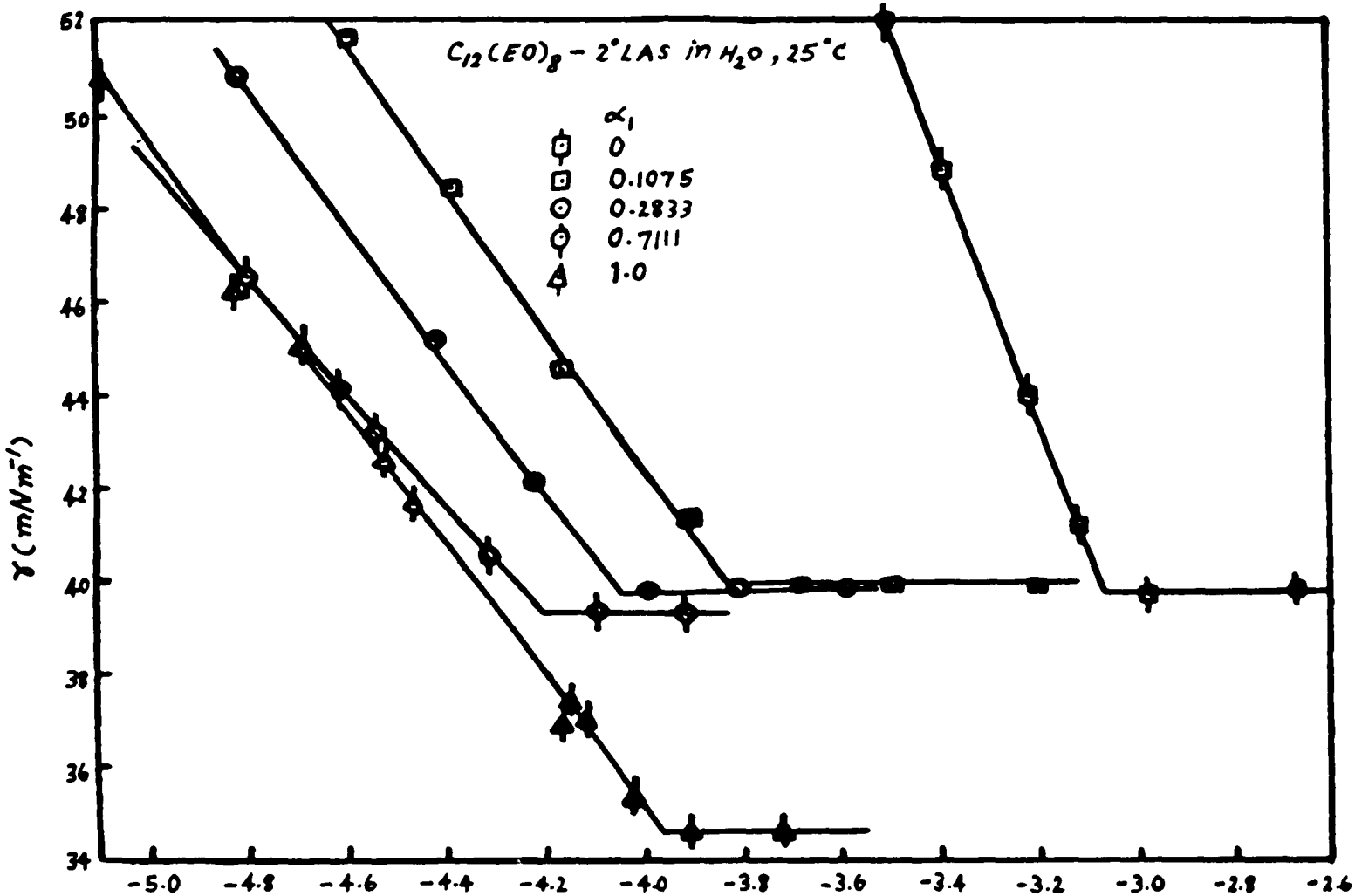

$C_{12}(EO)_8$ – 2°LAS in H_2O, 25°C
α_1
0
0.1075
0.2833
0.7111
1.0
γ (mN/m⁻¹)
52
50
48
46
44
42
40
38
36
34
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
log C_{12}

Figure 8

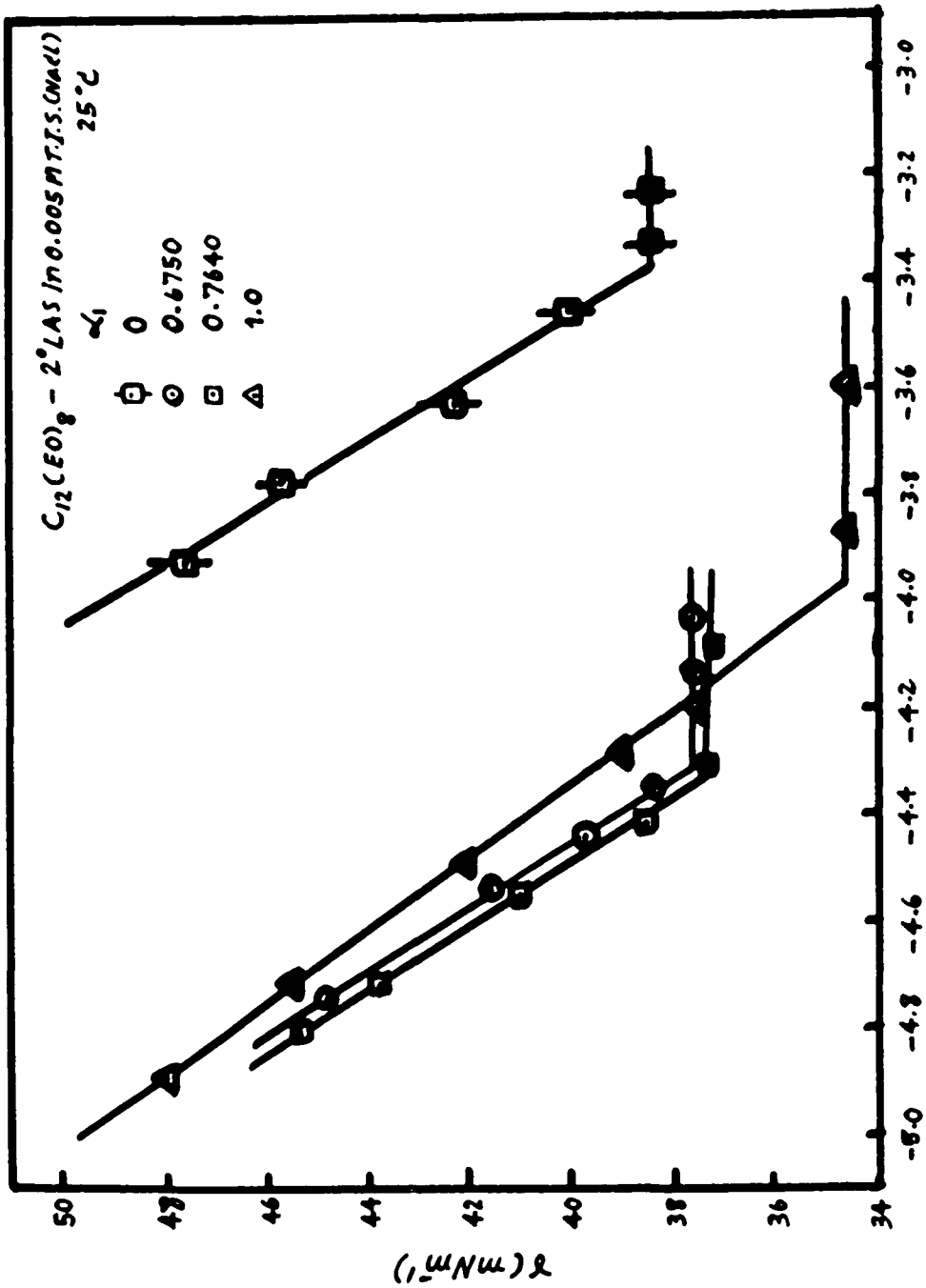

$C_{12}(EO)_8$ - 2°LAS in 0.005 M T.F.S. (NaCl) 25°C
α_1
0
0.6750
0.7640
1.0
γ (mNm⁻¹)
50
48
46
44
42
40
38
36
34
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
log C_{12}

Figure 9

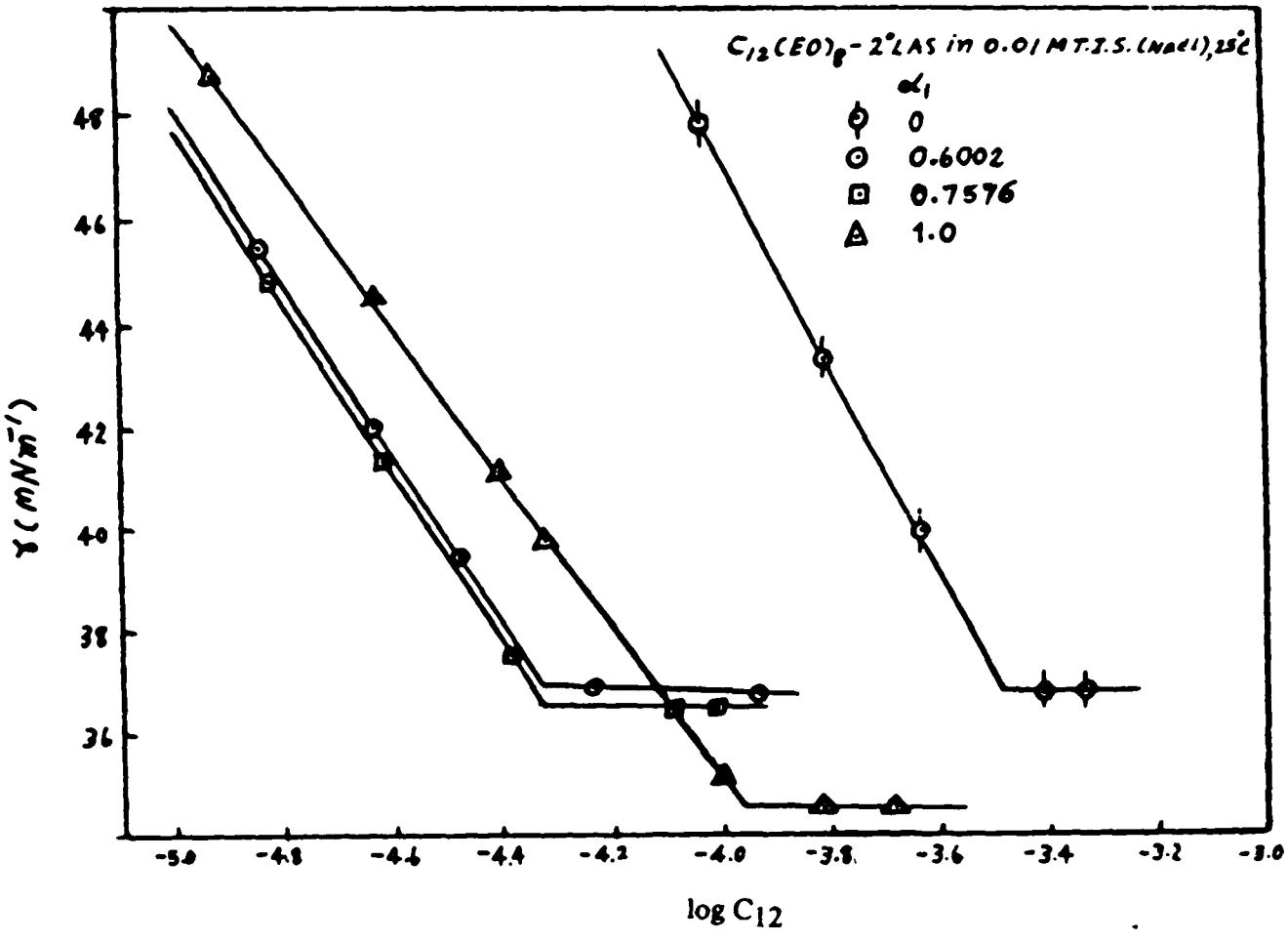

$C_{12}(EO)_8$ - 2°LAS in 0.01 M T.I.S. (NaCl), 25°C
α_1
0
0.6002
0.7576
1.0
γ (mNm⁻¹)
48
46
44
42
40
38
36
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
log C_{12}

Figure 10

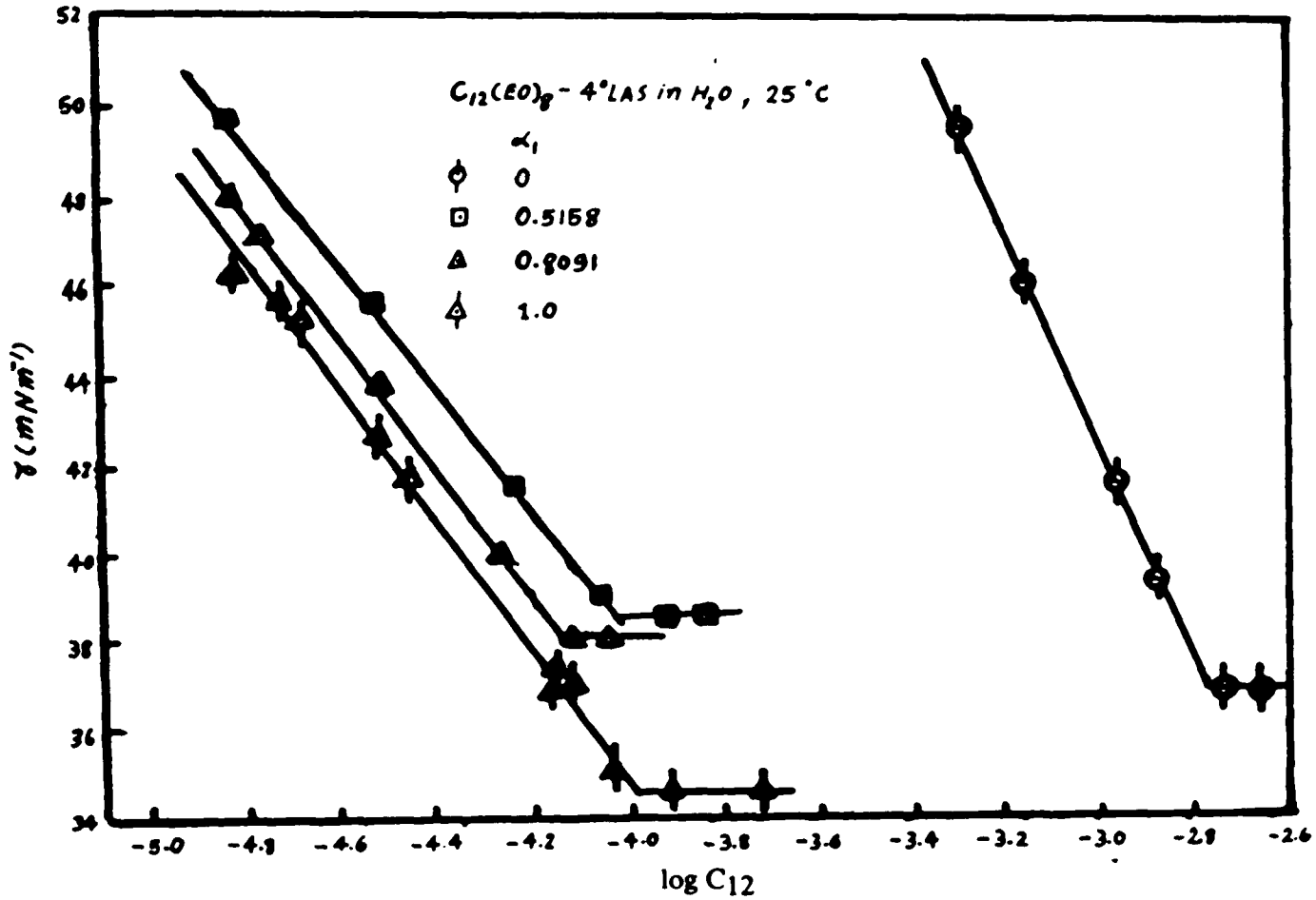
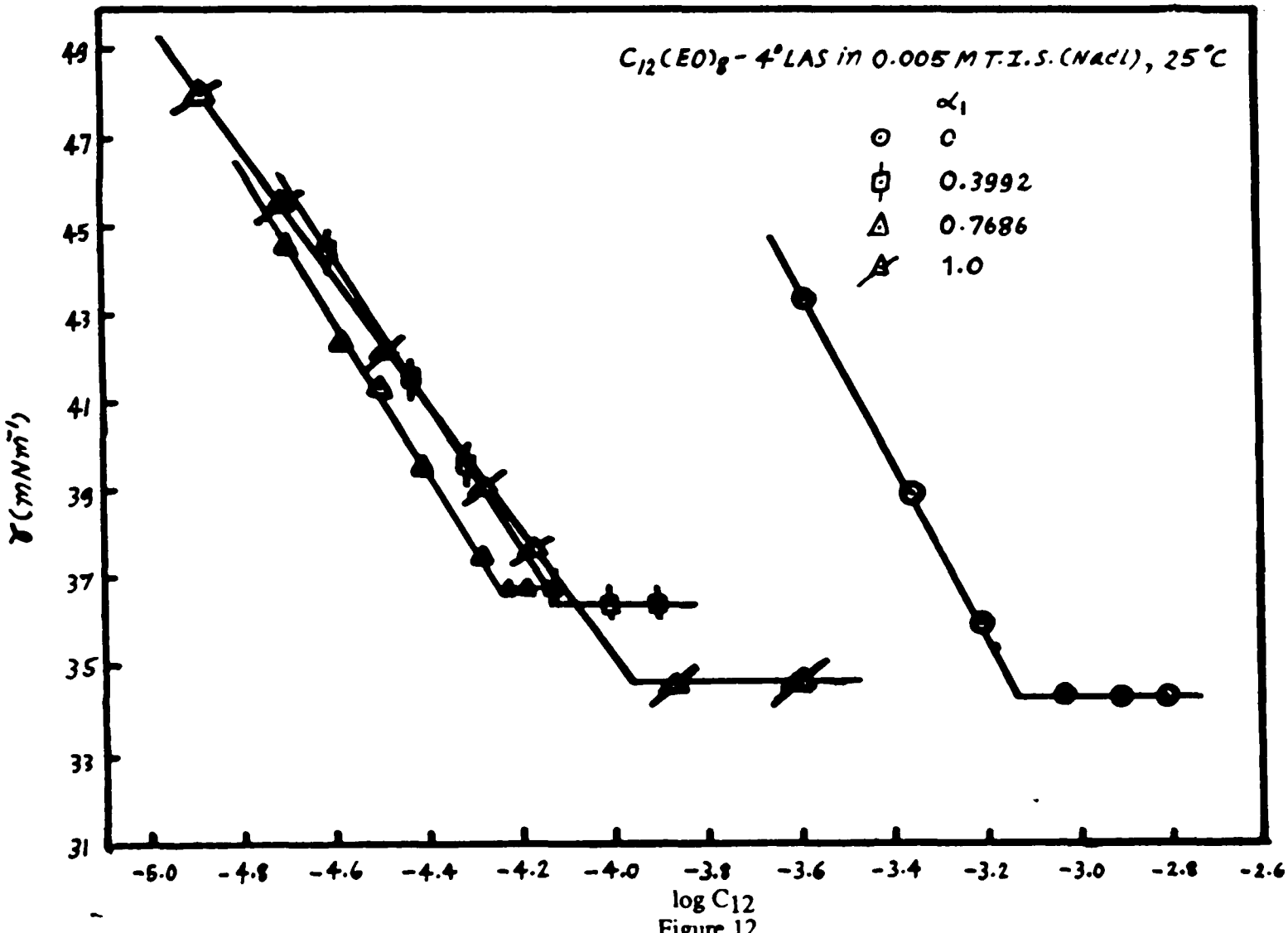

$C_{12}(EO)_8$ - 4°LAS in H_2O, 25 °C
α_1
0
0.5158
0.8091
1.0
γ (mNm⁻¹)
52
50
48
46
44
42
40
38
36
34
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
log C_{12}

Figure 11


$C_{12}(EO)_8$ - 4°LAS in 0.005 M T.I.S. (NaCl), 25°C
α_1
0
0.3992
0.7686
1.0
γ (mN m⁻¹)
49
47
45
43
41
39
37
35
33
31
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
log C_{12}
Figure 12

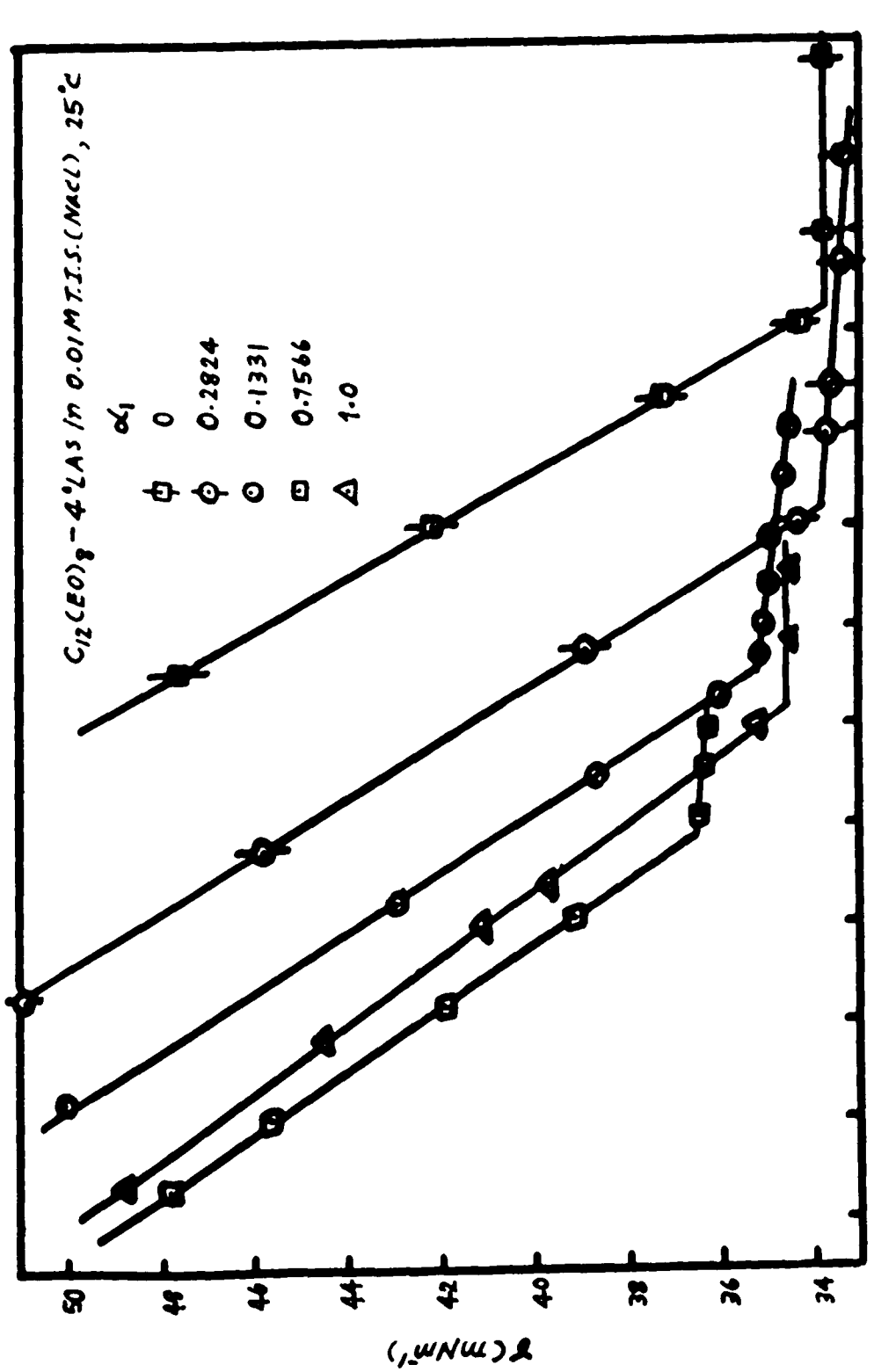

$C_{12}(EO)_8 - 4'LAS$ in 0.01M I.S.(NaCl), 25°C
α_1
0
0.2824
0.1331
0.7566
1.0
γ(mNm⁻¹)
50
48
46
44
42
40
38
36
34
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
log C_{12}

Figure 13

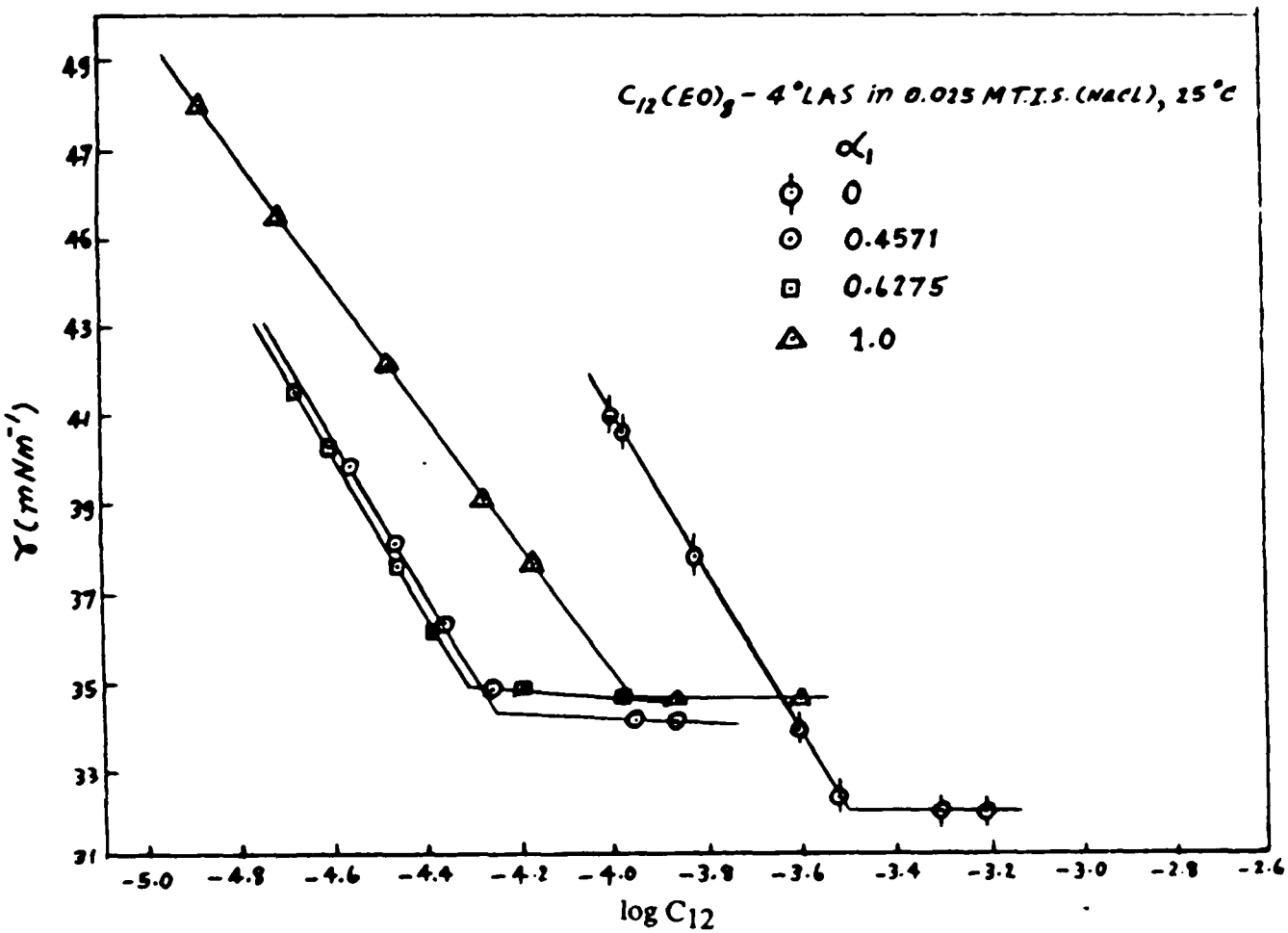

$C_{12}(EO)_3$ - 4°LAS in 0.025 M T.I.S. (NaCl), 25°C
α_1
0
0.4571
0.6275
1.0
γ (mNm⁻¹)
49
47
46
43
41
39
37
35
33
31
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
log C_{12}

Figure 14

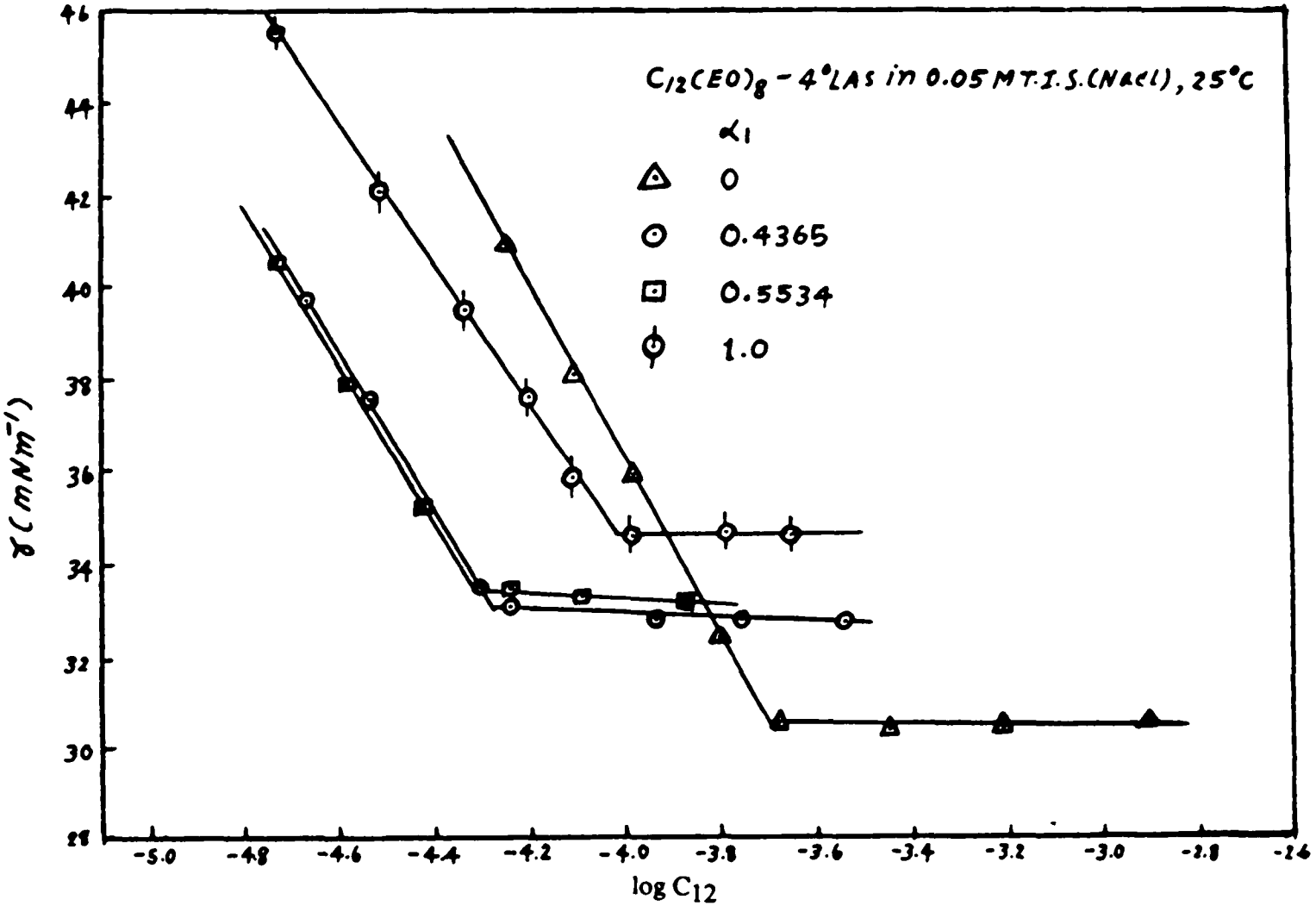

$C_{12}(EO)_8$ - 4°LAS in 0.05 M T.I.S.(NaCl), 25°C
α_1
0
0.4365
0.5534
1.0
γ (mNm⁻¹)
log C_{12}
46
44
42
40
38
36
34
32
30
28
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6

Figure 15

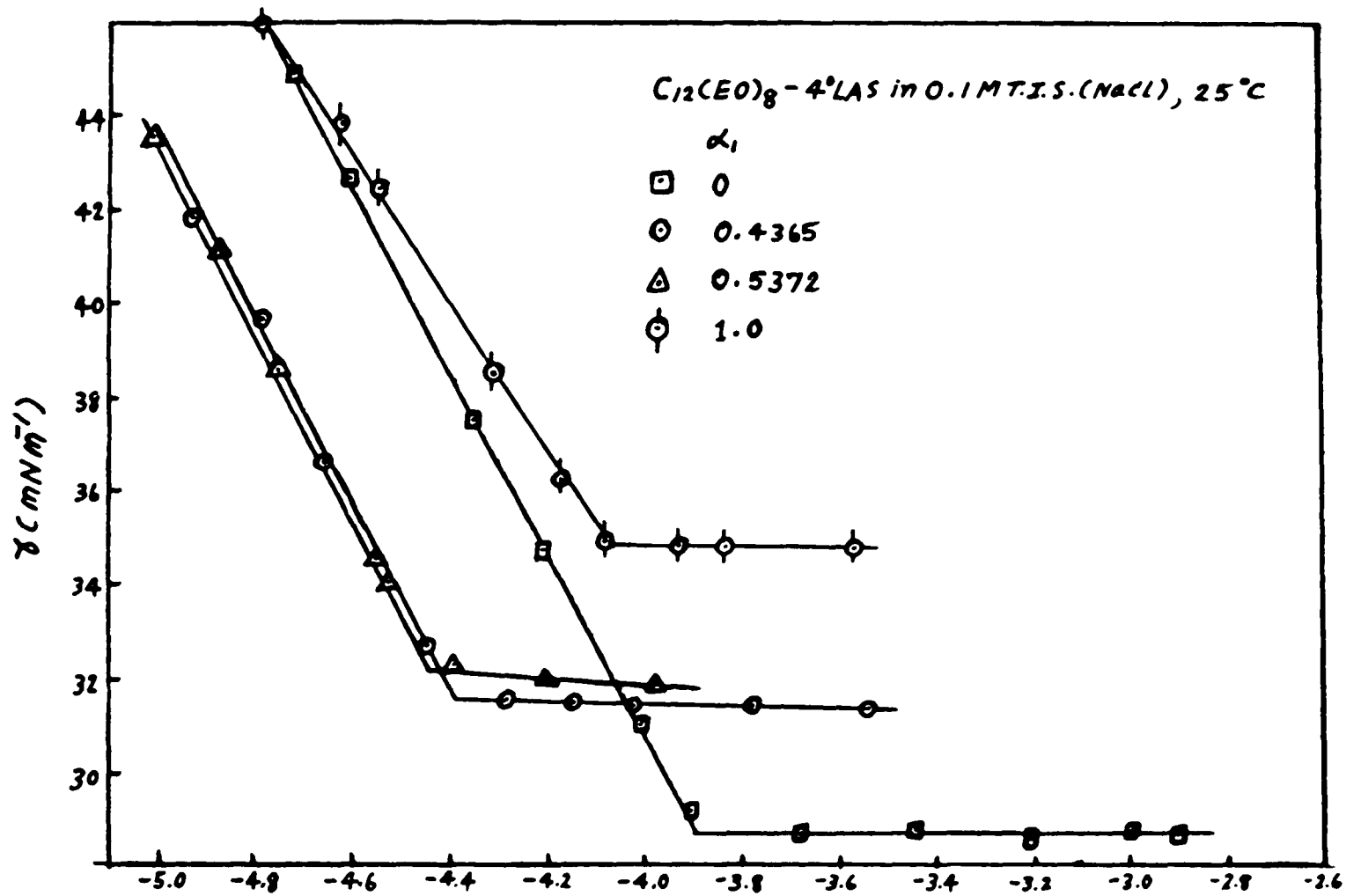

C12(EO)8 - 4°LAS in 0.1M T.I.S.(NaCl), 25°C
α1
0
0.4365
0.5372
1.0
γ (mNm⁻¹)
44
42
40
38
36
34
32
30
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6
log C12

Figure 16

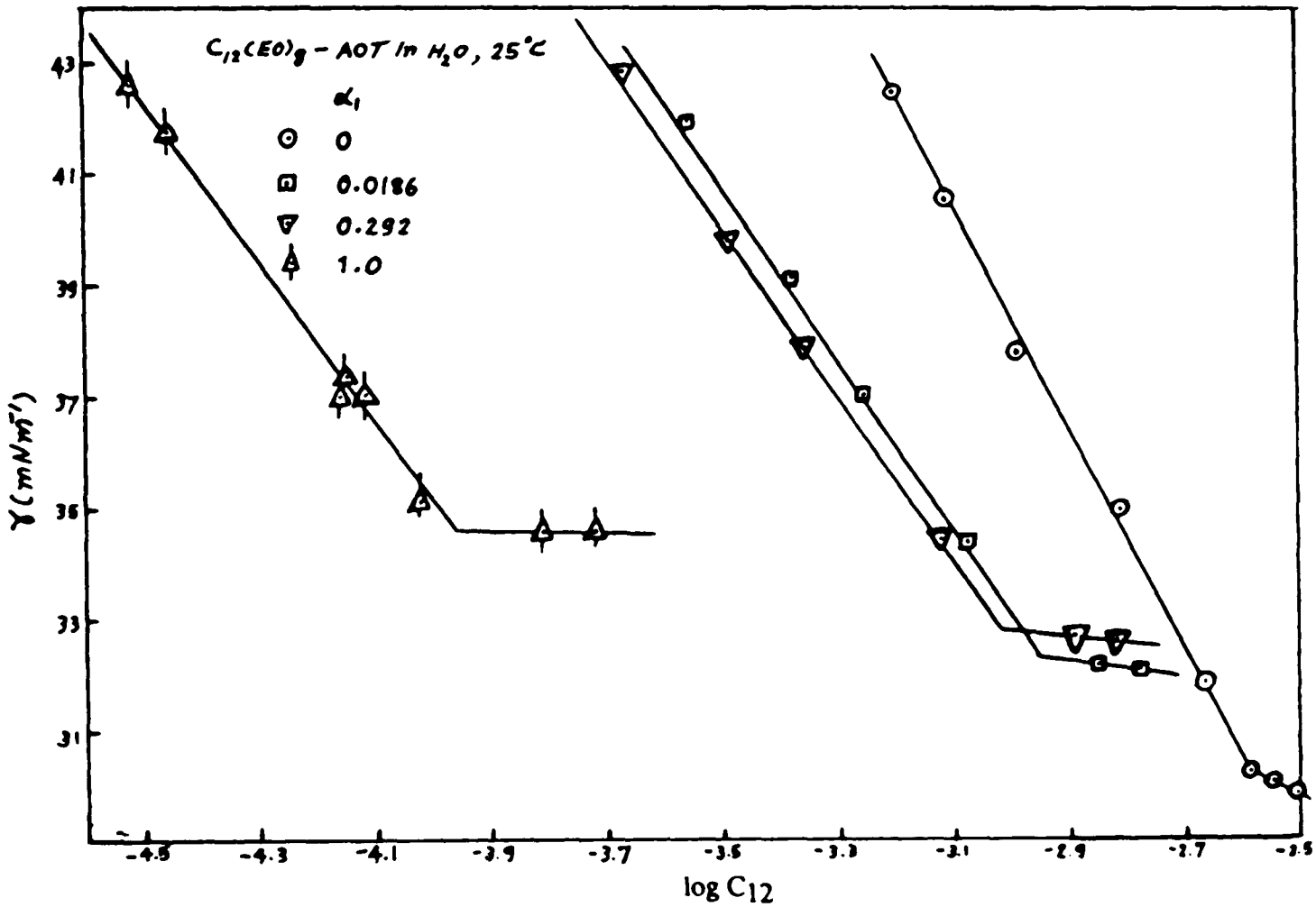

$C_{12}(EO)_8$ – AOT in H_2O, 25°C
α_1
0
0.0186
0.292
1.0
γ (mNm⁻¹)
43
41
39
37
35
33
31
-4.5
-4.3
-4.1
-3.9
-3.7
-3.5
-3.3
-3.1
-2.9
-2.7
-2.5
log C_{12}

Figure 17

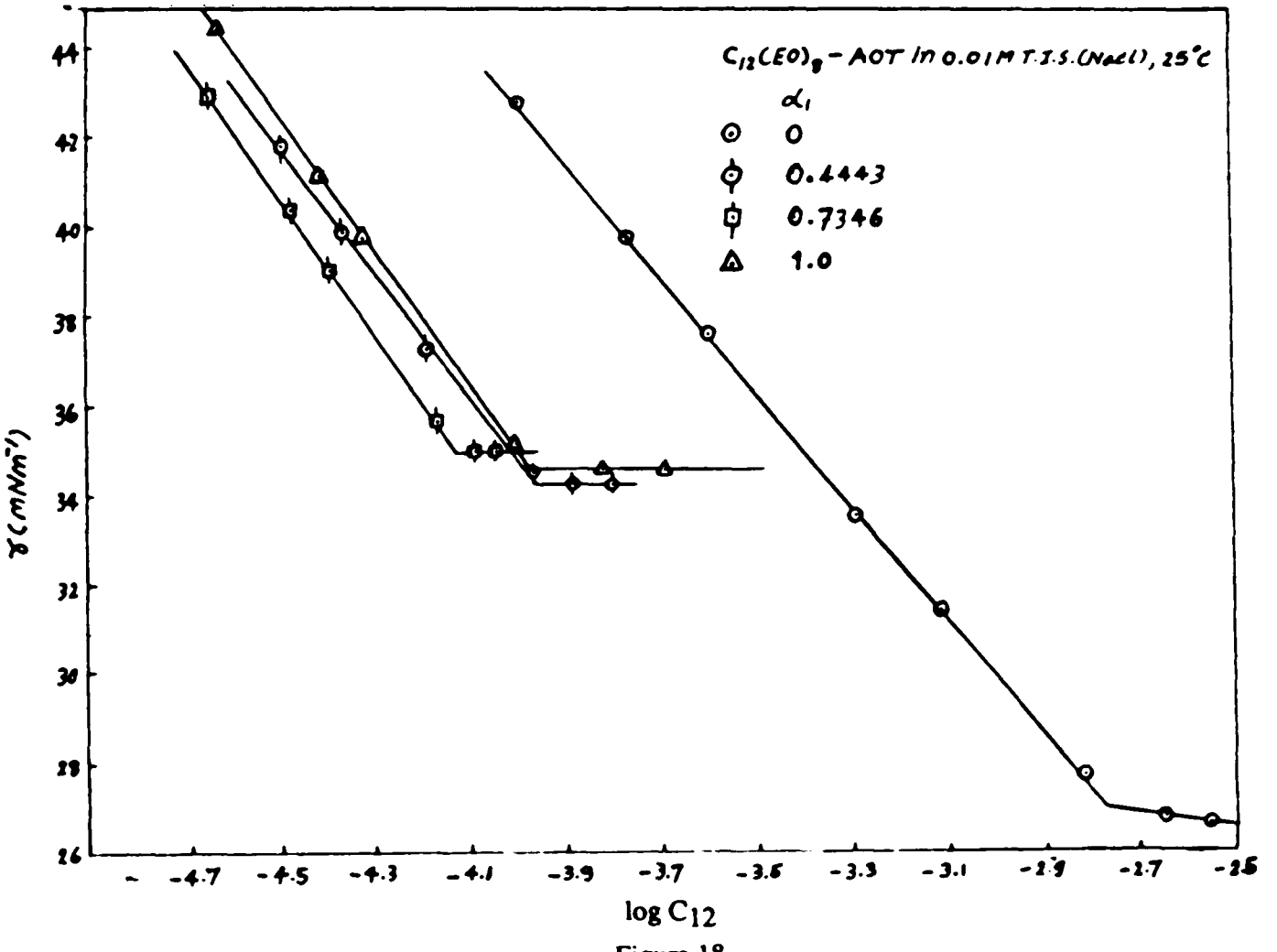

$C_{12}(EO)_8$ – AOT in 0.01M T.I.S.(NaCl), 25°C
α_1
0
0.4443
0.7346
1.0
γ (mNm⁻¹)
44
42
40
38
36
34
32
30
28
26
-4.7
-4.5
-4.3
-4.1
-3.9
-3.7
-3.5
-3.3
-3.1
-2.9
-2.7
-2.5
log C_{12}

Figure 18

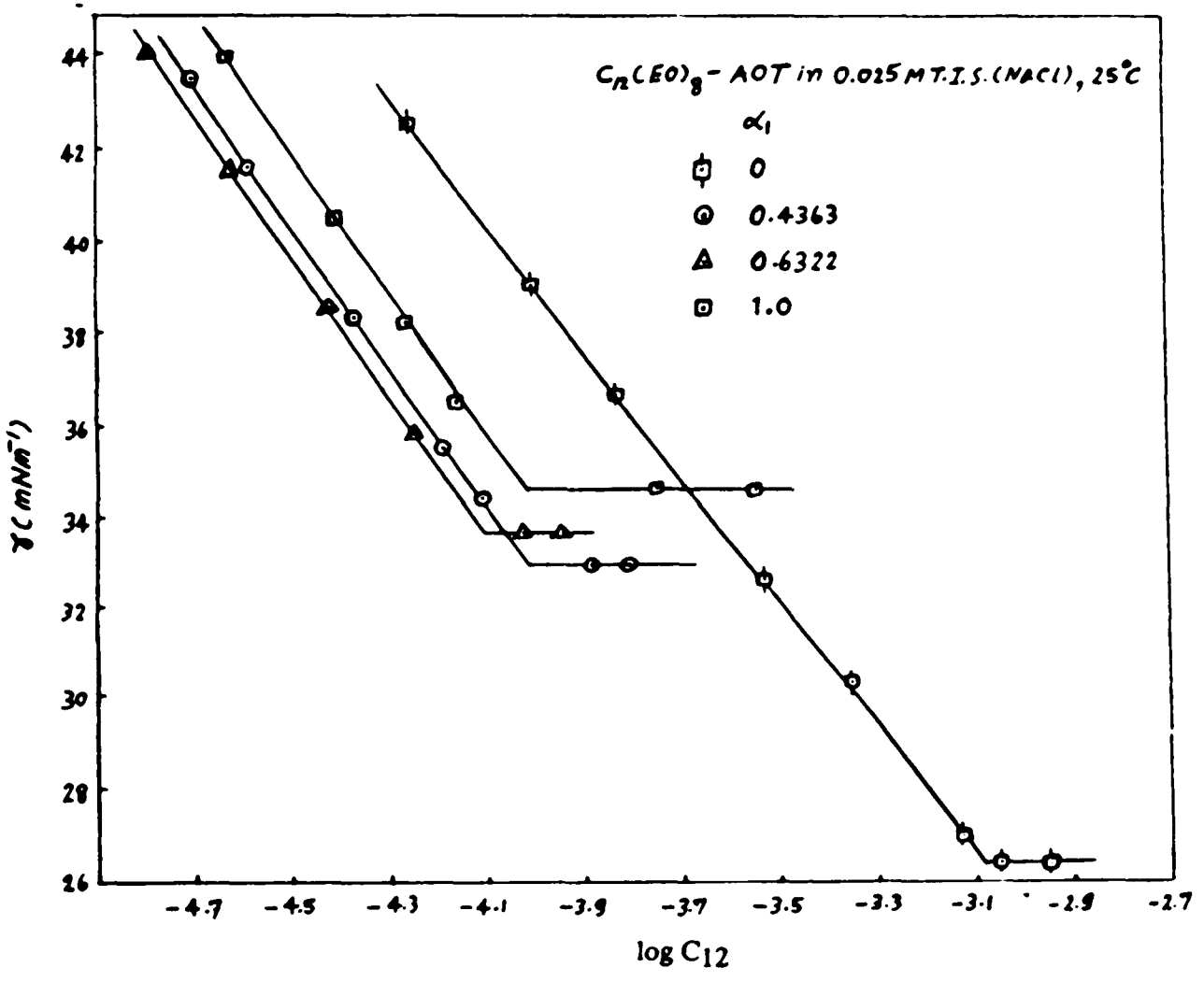

$C_n(EO)_8$ - AOT in 0.025 M T.I.S. (NaCl), 25°C
α_1
0
0.4363
0.6322
1.0
γ (mNm⁻¹)
44
42
40
38
36
34
32
30
28
26
-4.7
-4.5
-4.3
-4.1
-3.9
-3.7
-3.5
-3.3
-3.1
-2.9
-2.7
log C_{12}

Figure 19

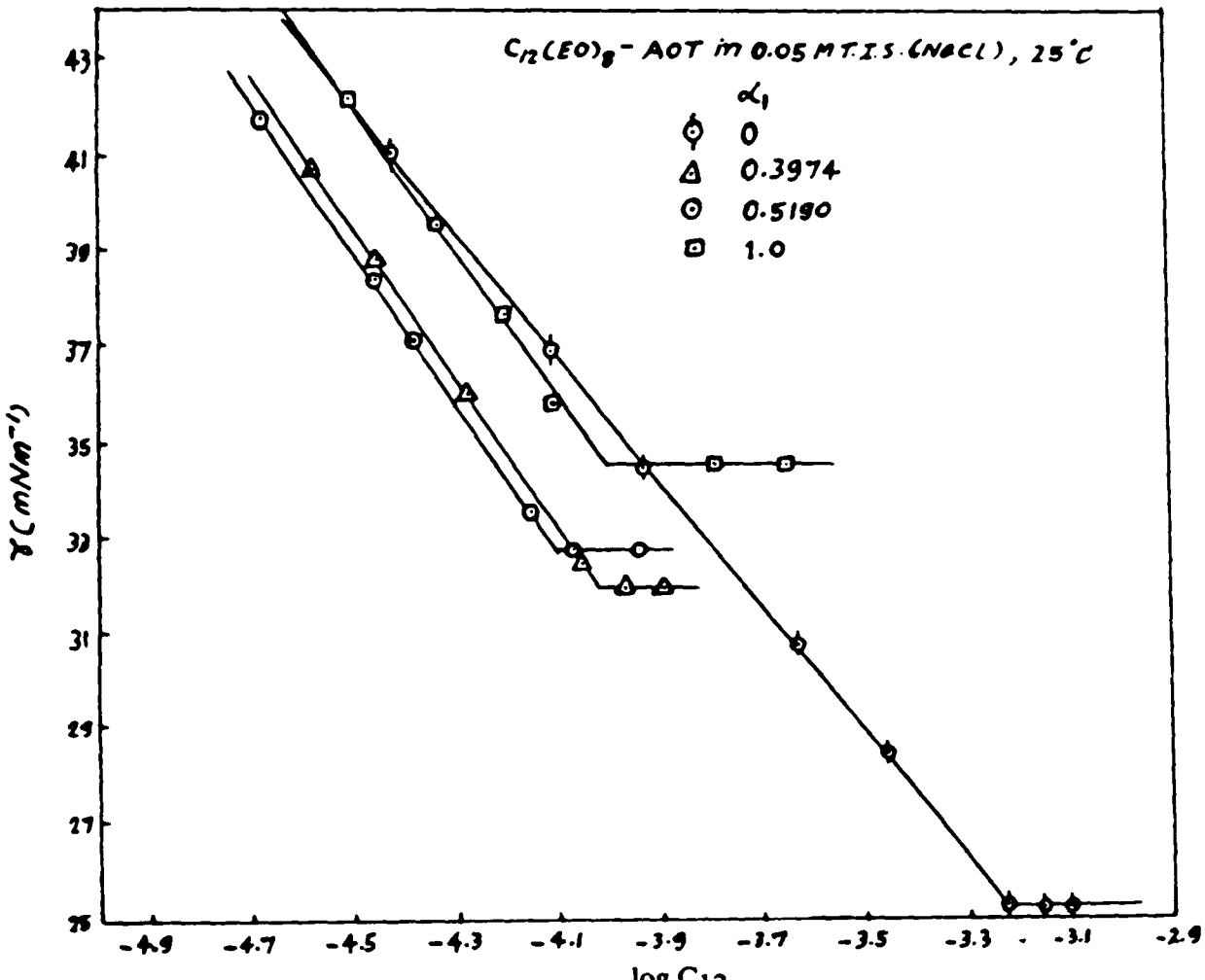

$C_{12}(EO)_8$ - AOT in 0.05 M T.I.S. (NaCl), 25°C
α_1
0
0.3974
0.5190
1.0
43
41
39
37
35
33
31
29
27
25
γ (mNm⁻¹)
-4.9
-4.7
-4.5
-4.3
-4.1
-3.9
-3.7
-3.5
-3.3
-3.1
-2.9
log C_{12}

Figure 20

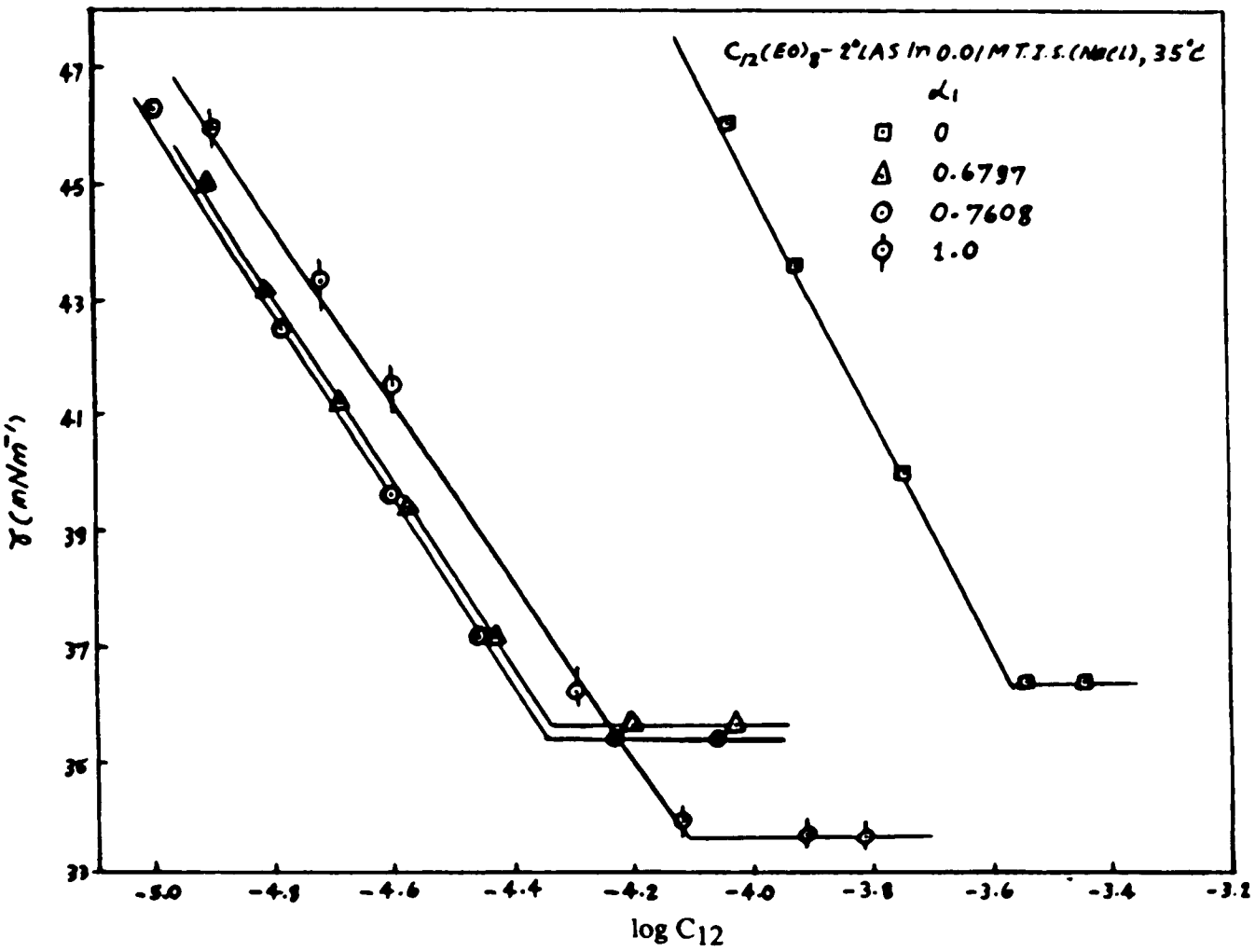

$C_{12}(EO)_8$ + 2°LAS in 0.01M T.I.S.(NaCl), 35°C
α_1
0
0.6797
0.7608
1.0
γ (mNm⁻¹)
47
45
43
41
39
37
35
33
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
log C_{12}

Figure 21

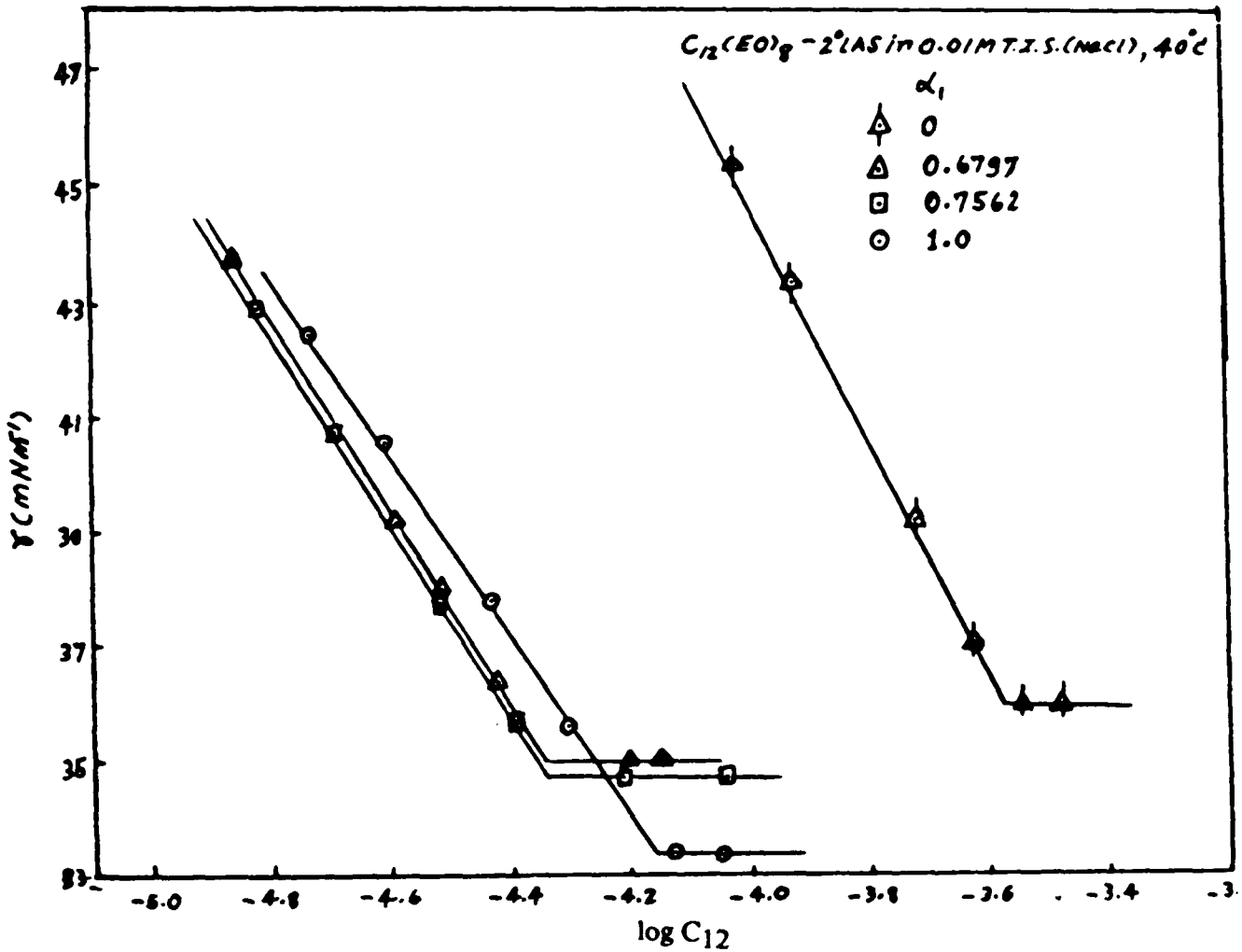

$C_{12}(EO)_8$ - 2°LAS in 0.01M T.I.S.(NaCl), 40°C
α_1
0
0.6797
0.7562
1.0
γ (mN/m)
47
45
43
41
39
37
35
33
-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
log C_{12}

Figure 22

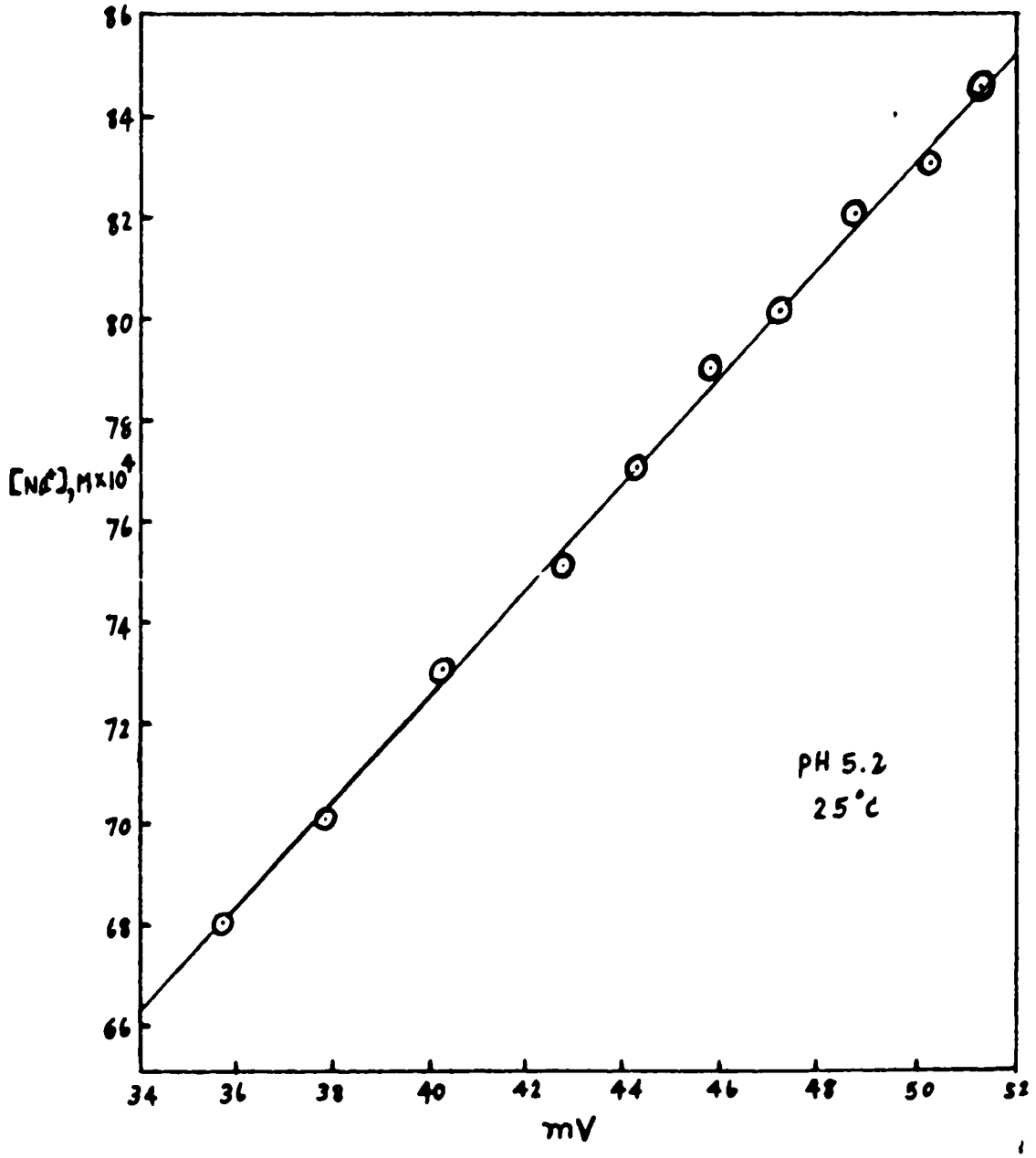

86
84
82
80
78
76
74
72
70
68
66
[NaCl], M x 10^4
34
36
38
40
42
44
46
48
50
52
mV
pH 5.2
25°C

Figure 23

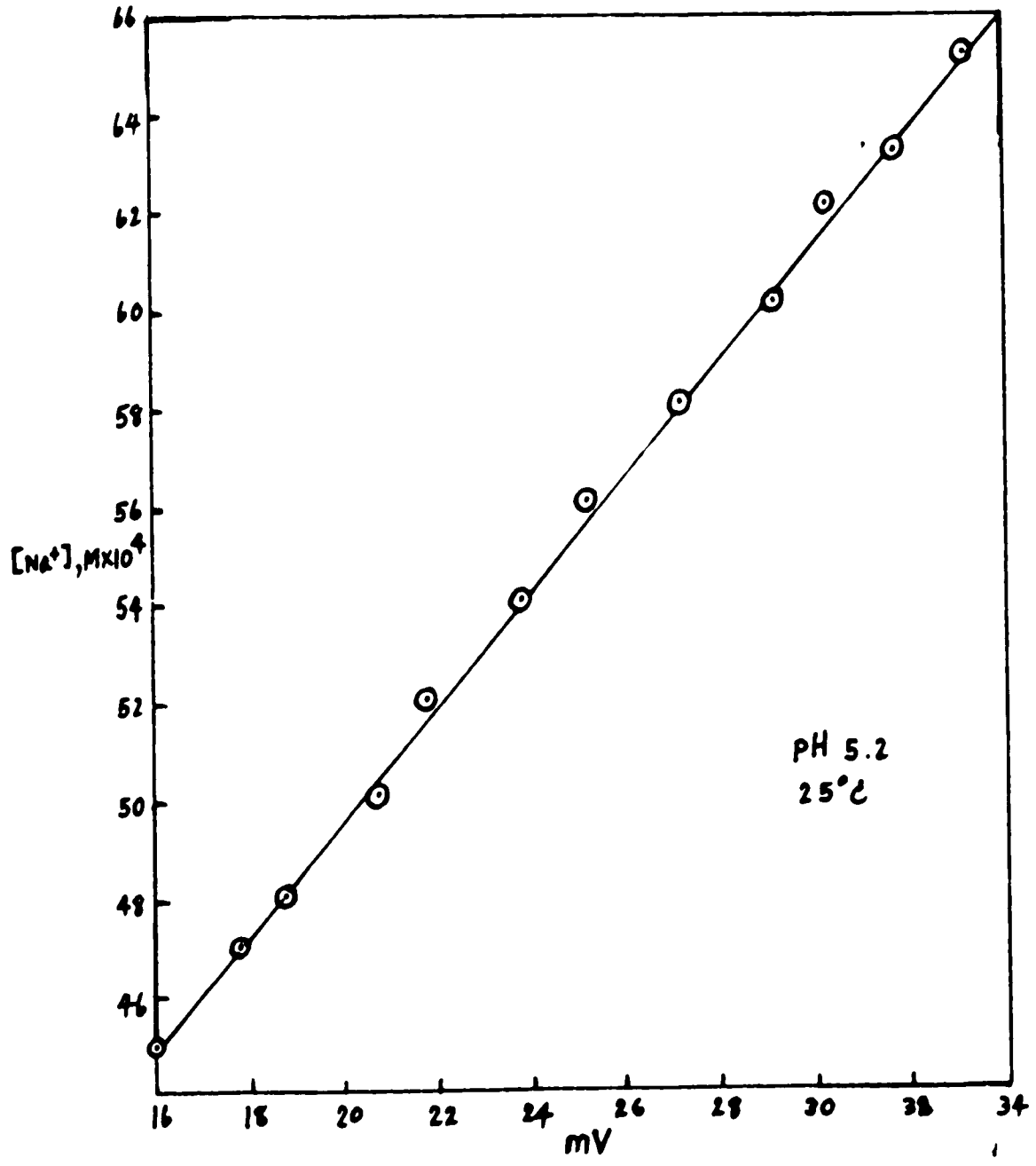

66
64
62
60
58
56
54
52
50
48
46
[Na+], M x 10^4
16
18
20
22
24
26
28
30
32
34
mV
pH 5.2
25°C

Figure 24

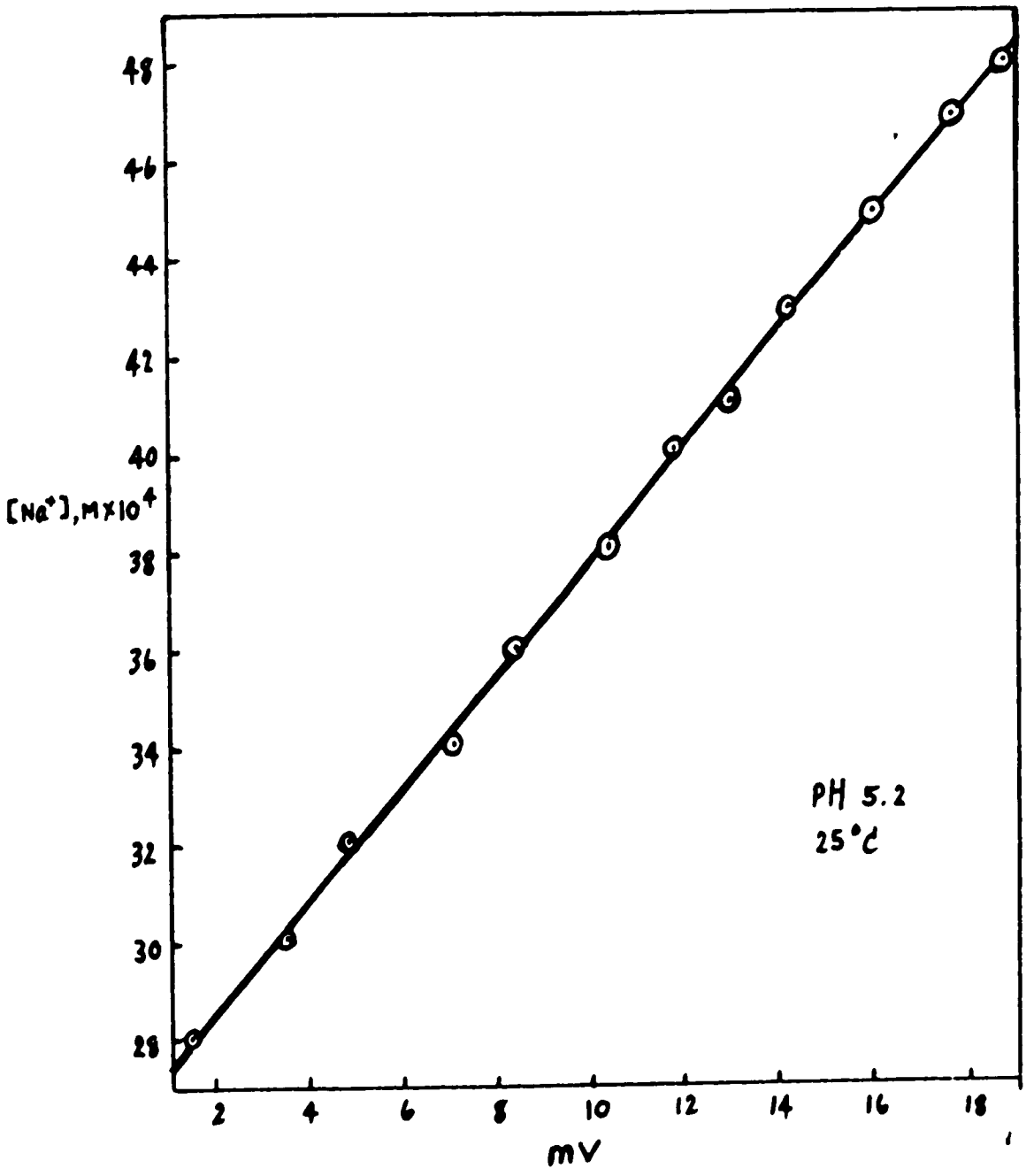

48
46
44
42
40
[Na⁺], M×10⁴
38
36
34
32
30
28
2
4
6
8
10
12
14
16
18
mV
PH 5.2
25°C

Figure 25

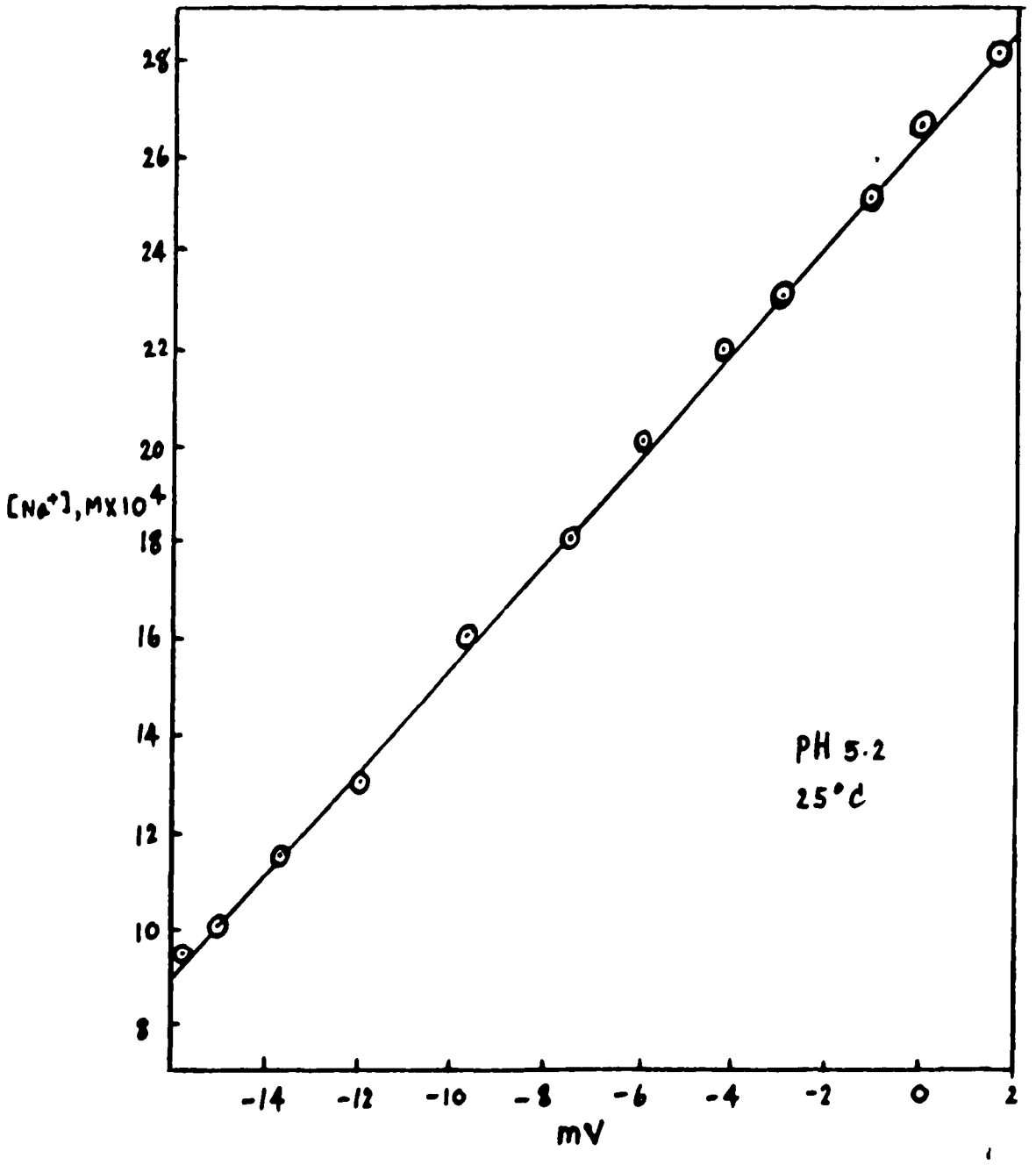


Figure 26

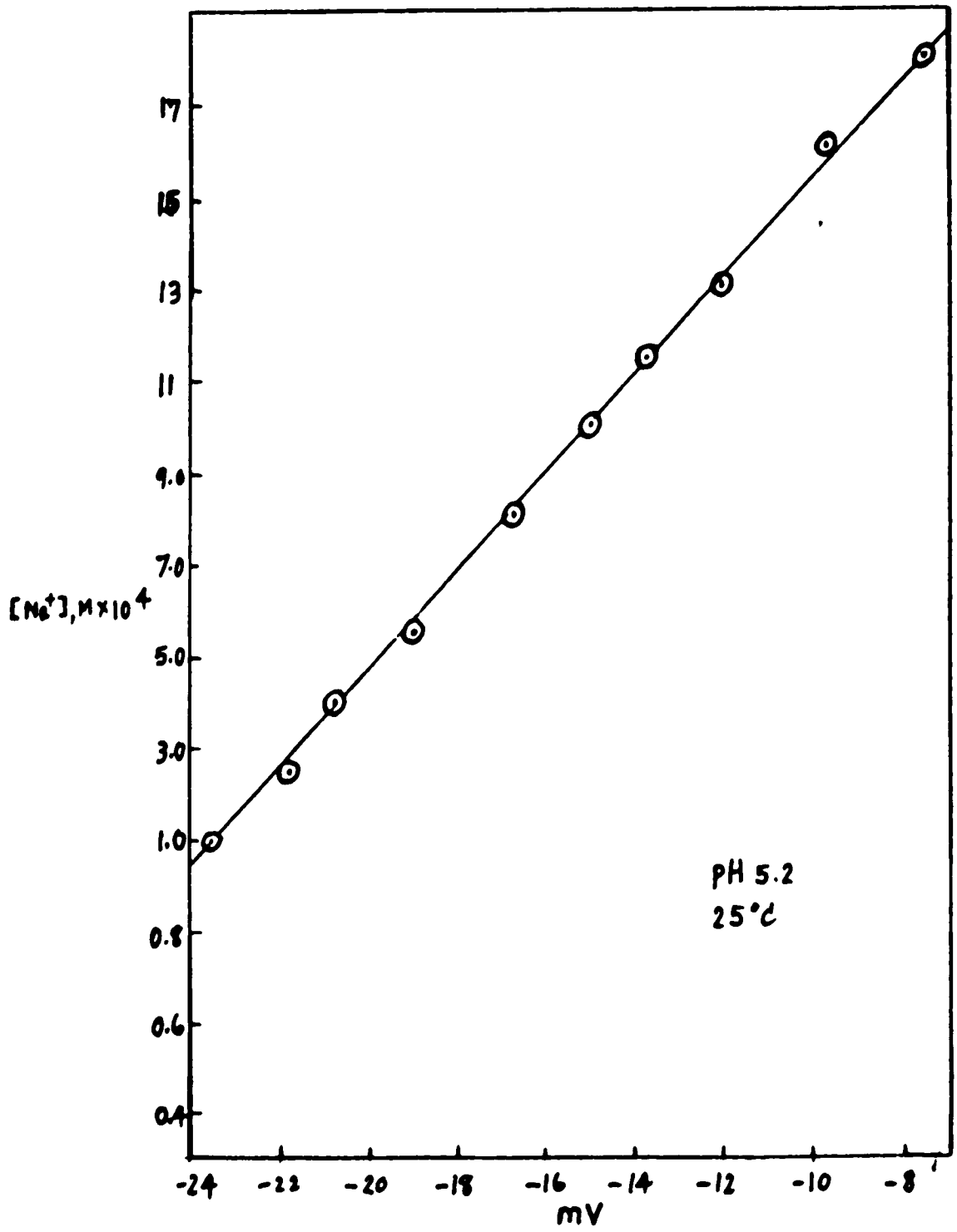

17
15
13
11
9.0
7.0
5.0
3.0
1.0
0.8
0.6
0.4
[Na+], M x 10^4
-24
-22
-20
-18
-16
-14
-12
-10
-8
mV
pH 5.2
25°C

Figure 27

Bibliography

1. Lucassen - Reynders, E.H. ; Lucassen, J. ; Giles, D. , J. Colloid Interface Sci. 1981, 81, 150.
2. Rosen, M.J. ; Hua, X.Y., J. Colloid Interface Sci . 1982, 90 , 176.
3. Rosen, M.J. ; Hua, X.Y., J. Amer. Oil Chem.Soc . 1982, 59, 582.
4. Rosen, M.J. ; Zhu, B.Y., J. Colloid Interface Sci. 1984, 99, 427.
5. Rosen, M.J. ; Zhu, B.Y., J. Colloid Interface Sci. 1984, 99, 435.
6. Rubingh, D.N. ; Jones, T., " Ind. Eng. Chem. Prod. Res. Dev. ".1982, 21, 176.
7. Clint, J.H., J. Chem. Soc. Faraday Trans I. 1975, 71, 1327.
8. Garrett, P.R., J. Chem. Soc. Faraday Trans I. 1976, 72, 2174.
9. Ingram, B.T. ; Lukhurst, A.H.W., in " Surface active agents ". S.C.I. London, 1979, p 89.
10. Lucassen - Reynders, E.H., J. Colloid Interface Sci. 1973, 42, 563.
11. Ingram, B.T., Colloid Polymer Sci. 1980, 258, 191.
12. Lucassen - Reynders, E.H., Koll. Zuz. Polym. 1972, 250, 356.
13. Rosen, M.J. ; Hua, X.Y., J. Colloid Interface Sci. 1982, 90, 212.
14. Rosen, M.J. ; Hua, X.Y., J. Colloid Interface Sci. 1988, 125, 730.
15. Hutchinson, E., J. Colloid Interface Sci. 1948, 3, 413.
16. Goodrich, F.C., 2nd Int. Congr. Surface Activity. 1957, 1, 85.
17. Goddard, E.D. ; Schulman, J.H., J. Colloid Interface Sci. 1953, 8, 329.
18. Lange, H., Koll. Zuz. Polym. 1953, 131, 96.
19. Shinoda, K., J. Phys. Chem. 1954, 58, 541.
20. Lange, H. ; Beck, K.H., Koll. Zuz. Polym. 1973, 251, 424.

21. Rubingh, D.N., in " Solution Chemistry of Surfactants " , Mittal, K.L., Ed., Plenum Press, New York, 1979, vol 1, p 337.

22. Holland, P.M., in " Phenomena in Mixed Surfactant Systems ", Scamehorn, J.F., Ed., American Chemical Society, Washington, DC, 1986, ACS Symposium Series 311, p 102.

23. Kronberg, B. ; Lindstrom, M. ; Stenius, P., in " Phenomena in Mixed Surfactant Systems ", Scamehorn, J.H., Ed., American Chemical Society, Washington, DC, 1986, ACS Symposium Series 311, p 225.

24. Fried, V. ; Blukis, U. ; Hameka, H.F., " Physical Chemistry ", Macmillan, New York, 1977, pp 224, 252.

25. Rosen, M.J. ; Gu, B., J. Colloid Interface Sci. 1989, 129, 537.

26. Kolp, D.G., J. Phys. Chem. 1963, 67, 51.

27. Rosen, M.J. ; Davis, F. ; Michael, G., J. Phys. Chem. 1964, 68, 3219.

28. Erikson, J.C., Acta. Chem. Scand. 1963, 17, 1478.

29. Clifford, J. ; Pethica, B.A., Trans. Farad. Soc. 1964, 60, 1483.

30. Clifford, J. ; Pethica, B.A., Trans. Farad. Soc. 1965, 61, 182.

31. Clifford, J., Trans. Farad. Soc. 1965, 61, 1276.

32. Yan, J.F. ; Palmer, M.B., J. Colloid Interface Sci. 1969, 30, 177.

33. Haque, R., J. Phys. Chem. 1968, 72, 3056.

34. Bailey, R.E. ; Cady, G.H., J. Phys. Chem. 1969, 73, 1612.

35. Inoue, H. ; Nakagawa, T., " 4th International Congress on Surface Active - Substance ", Brussel, 1969, BIV, 11.

36. Odberg, L. ; Bengt, S. ; Ingvar, D., J. Colloid Interface Sci. 1972, 41, 298.

37. Atkinson, R.E. ; Clint, G.E., ; Walker, T., J. Colloid Interface Sci. 1974, 46,32.

38. Muller, N. ; Johnson, T.W., J. Phys. Chem. 1969, 73, 2042.

39. Muller, N. ; Birkhaln, R.H., J. Phys. Chem. 1967, 71, 957.

40. Muller, N. ; Birkhaln, R.H., J. Phys. Chem. 1968, 72, 583.

41. Muller, B. ; Platko, F.E., J. Phys. Chem. 1971, 75, 547.

42. Muller, N. ; Simsohn, H., J. Phys. Chem. 1971, 75, 942.

43. Florence, A.T. ; Parfit, R.T., J. Phys. Chem. 1971, 75, 3555.

44. Tokiwa, F. ; Tsujii, K., J. Phys. Chem. 1971, 75, 3560.

45. Tokiwa, F. ; Tsujii, K., J. Colloid Interface Sci. 1972, 41, 343.

46. Inoue, H. ; Nakagawa, T., J. Phys. Chem. 1966, 70, 1108.

47. Bansal, V.K. ; Biswas, A., Trans. I.M.M., London, (Section C), 1975, 84, C - 131.

48. Kalibabchuk, N., Kolloidn Zh. 1975, 37, 166.

49. Corkill, J.M., Trans. Farad. Soc. 1967, 63, 247.

50. Hendrikx, Y., J. Colloid Interface Sci. 1978, 69, 493.

51. Yoshio, A., Yukagaku, 1974, 23, 737.

52. Mukhayer, G.I. ; Davis, S.S., J. Colloid Interface Sci. 1975, 53, 224.

53. Mukhayer, G.I. ; Davis, S.S., ; Tomlison, E., J. Pharm. Sci. 1975, 64, 147.

54. Job, P., Ann. Chim. 1828, 9, 113.

55. Daviss, S.S. ; Mukhayer, G.I., J. Colloid Interface Sci. 1976, 56, 350.

56. Mukhayer, G.I. ; Davis, S.S., J. Colloid Interface Sci. 1977, 59, 350.

57. Mukhayer, G.I. ; Davis, S.S., J. Colloid Interface Sci. 1977, 61, 582.

58. Yoda, O. ; Megro, K. ; Kondo, T. ; Ino, T., Nippon Kagaku. 1956, 77, 905.

59. Nakagawa, T. ; Inoue, H., Ibid. 1956, 78, 104.

60. Corkill, J.M. ; Goodman, J.F. ; Tate, J.R., Trans. Farad. Soc. 1964, 60, 986.

61. Shick, M.J. ; Manning, D.J., J. Am. Oil Chem. Soc.1966, 43, 133.

62. Tokiwa, F. ; Moriyama, N., J. Colloid Interface Sci. 1969, 30, 338.

63. Tokiwa, F. ; Aigami, K., Koll. Zuz. Polym. 1970, 239, 687.

64. Akasu, H. ; Ueno, M. ; Meguro, K., J. Am. Oil Chem. Soc. 1874, 51, 519.

65. Meguro, K. ; Akasu, H. ; Ueno, M., Ibid. 1976, 53, 145.

66. Akasu, H. ; Nishii, M. ; Ueno, M. ; Meguro, K., J. Colloid Interface Sci. 1976, 54, 278.

67. Funasaki, N. ; Hada, S., J. Phys. Chem. 1979, 83, 2471.

68. Takasawa, Y. ; Ueno, M. ; Meguro, K., J. Colloid Interface Sci. 1980, 78, 207.

69. Meguro, K. ; Kanbe, T. ; Esumi, K., J. Am. Oli Chem. Soc. 1983, 60, 1050.

70. William, E.F. ; Dixon, J.K., J. Colloid Interface Sci. 1958, 12, 452.

71. Miller, M.L. ; Dixon, J.K., Ibid. 1958, 13, 411.

72. Sato, Y. ; Ueno, M. ; Kishimoto, H., Yukagaku. 1975, 95, 1286.

73. Ueno, M. ; Kishimoto, H., Nippon Kagaku Kaishi. 1980, 53, 375.

74. Chang, J.H. ; Muto, Y. ; Esumi, K., J. Am Oil Chem. Soc. 1985, 62, 1709.

75. Rosen, M.J. ; Hua, X.Y., J. Colloid Interface Sci. 1982, 86, 164.

76. Wurtzchmitt, B.Z., Anal. Chem. 1950, 130, 105.

77. Rosen, M.J. ; Zhao, F., J. Colloid Interface Sci. 1983, 95, 443.

78. Rosen, M.J. ; Kwan, C.C., J. Phys. Chem. 1980, 81, 547.

79. Rosen, M.J. ; Cohen, A.W. ; Dahanayake, M. ; Hua, X.Y., J. Phys. Chem. 1982, 86, 541.

80. Zhao, G.X. ; Zhu, B.Y., in " Phenomena in Mixed Surfactant Systems ", Scamehorn, J.F., Ed, ACS Symposium Series 311, American Chemical Society, Washington, DC. 1986, p 184.

81. Rosen, M.J., " Surfactant and Interfacial Phenomena ", Wiley - Interscience, New York, 1989, pp 137, 142, 393.

82. Rosen, M.J., J. Am. Oil Chem. Soc. 1974, 51, 461.

83. Rosen, M.J., J. Colloid Interface Sci. 1976, 56, 320.

84. Rosen, M.J., J. Colloid Interface Sci. 1981, 79, 587.

85. Dahanayake, M. , Ph.D. Thesis. The City University of New York, 1985.

86. Rosen, M.J. ; Goldsmith, H.A., " Systematic Analysis of Surface - Active Agents ", 2nd ed, Wiley - Interscience, New York, 1972, p 427.

87. Dahanayake, M. ; Rosen, M.J., in " Structure/Performance Relationships in Surfactants ", Rosen , M.J., Ed, ACS Symposium Series 253, American Chemical Society, Washington, DC. 1984.

88. Reid, V.M. ; Alston, T. ; Heinerth, E., Tenside. 1967, 4, 292.

89. Wilhelmy, L., Ann. Phys. 1863, 119, 177.

90. Okahara, M. ; Kuo, P.L. ; Yamamura, S. ; Ikeda, I., J. Chem. Soc. Chem. - Commun, 1980, 586.

91. Toei, K. ; Motomizu, S. ; Umano, T., Talanta. 1982, 29, 103.

92. Anderson, N.H. ; Girling, J., Analyst (London). 1982, 107, 836.

93. Tsubouchi, M. ; Yamasaki, N. ; Yanigasawa, K., Anal. Chem. 1985, 57, 783.

94. Turro, N.J. ; Kuo, P.L., J. Phys. Chem. 1986, 90, 837.
