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Interfacial properties, micellization, and synergism of surfactants in hydrocarbon/aqueous systems

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City University of New York, 1989

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INTERFACIAL PROPERTIES, MICELLIZATION, AND SYNERGISM OF SURFACTANTS IN HYDROCARBON/AQUEOUS SYSTEMS

by

DENNIS S. MURPHY

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

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4/28/89
Date

Chair of Examining Committee

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Date

Executive Officer

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Abstract

INTERFACIAL PROPERTIES, MICELLIZATION, AND SYNERGISM OF SURFACTANTS IN HYDROCARBON/AQUEOUS SYSTEMS

by

Dennis S. Murphy

Adviser: Professor Milton J. Rosen

Structure/property relationships, and fundamental parameters for well purified, well characterized individual surfactants and binary surfactant mixtures in hydrocarbon/aqueous systems have been elucidated. For the individual surfactants, fundamental parameters measured include: critical micelle concentration in the aqueous phase, maximum interfacial excess concentration and minimum area per molecule at hydrocarbon/aqueous solution interfaces, efficiency and effectiveness of interfacial tension reduction, and standard thermodynamic parameters of micellization and adsorption. Individual surfactants investigated are: $C_{12}H_{25}(OC_2H_4)_8OH$, $C_{12}H_{25}(OC_2H_4)_4OH$, $C_{12}H_{25}(OC_2H_4)_3OH$, $C_{12}H_{25}(OC_2H_4)_2OH$, $C_{16}H_{33}(OC_2H_4)_8OH$, N-decyl-2-pyrrolidine, N-octyl-2-pyrrolidine, $C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$, $C_{12}H_{25}SO_3^-Na^+$, two isomeric compounds, $C_{16}H_{33}(OC_2H_4)_5SO_4^-Na^+$, where in both compounds the hydrophobic group has C_6 and C_8 alkyl groups attached to the β carbon, but in one the groups are both straight chain and in the other they are both branched, and finally, the analogous isomeric unsulfated alcohols $C_{16}H_{33}(OC_2H_4)_5OH$.

For binary surfactant mixtures in liquid-liquid systems, nonideal solution theory has been used to derive equations that predict interfacial mole fractions, and conditions for the existence of synergism or negative synergism, and the existence or absence of synergism or negative synergism in three phenomena: 1) interfacial tension reduction efficiency; 2) mixed micelle formation; and 3) interfacial tension reduction effectiveness. These equations involve the experimentally determined parameters, $\beta^{\sigma}{}_{LL}$ and $\beta^{M}{}_{LL}$, related to the molecular interactions between the two surfactants in the mixed monolayer at the liquid-liquid interface and in the mixed micelles, respectively. Experimental results are in good agreement with theoretical predictions. The effect of various factors on molecular interaction and synergism have been investigated. Factors investigated are: presence of the hydrocarbon and its structure, length of the surfactant hydrophobic group, branching of the surfactant hydrophobic group, number of EO groups in mixtures of POE nonionics, and surfactant head group type. Types of mixtures studied include: betaine/anionic, anionic/nonionic, and nonionic/nonionic.

To my mother

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CHAPTER I
INTRODUCTION

1.1 Surfactant/Hydrocarbon/Aqueous Systems

The modifying properties of surface active agents (surfactants) in hydrocarbon/aqueous systems have been known for a long time. Perhaps the first reference to the use of surfactants in hydrocarbon/aqueous systems was made by Galen (131 - c.201), a Greek physician (1), who noted the emulsifying power of beeswax.

Clayton (2), gives credit to Selmi (3) for the first modern definition of an emulsion. Selmi's definition in 1845, then, marks the beginning of scientific study of hydrocarbon/aqueous systems containing surfactants.

The major use of surfactants in these systems is for emulsification. Other uses with practical applications are for modeling biological systems (4-6) with biosurfactants such as proteins, steroids, or glycolipids, and for modeling oily soil removal in detergency (7-9). Three types of emulsions have been identified: 1) macroemulsions, which have droplet sizes in the range of 1000-10,000 nm, 2) microemulsions, which have droplet sizes from 10-100 nm, and 3) miniemulsions (10-13) which have an average droplet size of ≅ 200 nm. It is still not clear if miniemulsions have properties distinct from micro- and macroemulsions or whether they are just a borderline case between the two.

The emulsions referred to by Galen and Selmi, above, were macroemulsions. Macroemulsions, therefore, are the oldest known type of emulsions. In the 1800's, technological use of macroemulsions surged, but scientific studies aimed at explaining the underlying reasons for this phenomenon had to wait until the 1900's. Technologically, cosmetics (14), pesticides, margarine, ice cream, cutting oils, and textile processing oils (15) are macroemulsions. Scientifically, several books (16-20) have been written about macroemulsion, and researchers who have made major contributions in understanding macroemulsions include: Bancroft (21), who correlated surfactant solubility in each phase to the type of emulsion obtained ("Bancroft's rule"), and pointed out the importance of the interfacial film; Davies and Rideal (22), who adapted von Smoluchowski's theory (23,24) of the coagulation of colloids for use with macroemulsions; Derjaguin and Landau (25) and Verwey and Overbeek (26), who developed the "D.L.V.O." theory which explains the flocculation behavior of solid particles in dispersions, but which is equally valid for explaining flocculation of liquid droplets in macroemulsions; Griffin (27), who developed a method known as the HLB (Hydophile-Lipophile Balance) method which relates the surfactants structure to its emulsifying behavior; and Shinoda and Arai (28,29), who developed the PIT (Phase Inversion Temperature) method which not only relates surfactant structure to emulsifying behavior but also takes into account the temperature of the system, which the HLB method does not.

Like macroemulsions, microemulsions are technologically important. They are used in some pesticide formulations, pine oil cleaners, some cutting oils, flavor oil emulsions, some emulsion polymerization processes, floor polish products, and in flooding operations for tertiary oil recovery from oil wells. Microemulsions are related to macroemulsions in that both have one normally immiscible liquid phase dispersed in another, but differ in that microemulsions have much smaller dispersed droplet sizes, form spontaneously, are thermodynamicaly stable, and have very low interfacial tensions against both aqueous and hydrocarbon phases. Several books (30-32) and review articles (33-35) have been written about microemulsions.

The first microemulsion, made by George Rodawald in St. Louis, Missouri (U.S.A.) in 1928, was carnauba wax-in-water (36). Colloidal dispersions such as this were not identified as unique until 1943 by Hoar and Schulman (37). Schulman went on to publish many papers on the subject, notably one in 1955 (38) which greatly advanced the understanding of microemulsions. Other researchers who have contributed to microemulsion science include: Shinoda (23,24), whose PIT method is also applicable to microemulsions; Gogarty and Olsen (39), who began the use of microemulsions in tertiary oil recovery by filing a patent for such a process in 1962; Winsor (40), who worked on the phase behavior of microemulsions; Healy and coworkers (41,42), who studied the effect of salinity and cosurfactant on phase behavior; Wade and coworkers (43-45), who have studied the factors which lead to ultralow interfacial tensions; and those who have worked on models for formation and stability of microemulsions, e.g., Shah et al. (46) and Rosano (47) and Gerbacia (48), who modified Bowcott and

Schulman's (38) idea of a transient negative interfacial tension as the cause for spontaneous emulsification, and, Prince (49,50) and Robbins (51) who have developed theories about phase behavior and stability of microemulsions.

Despite the diverse technological utilization of surfactants for their modifying effects in hydrocarbon/aqueous systems, and the numerous studies on the various types of emulsions, and on the surfactants used (52-58) in their formation, relatively few studies of fundamental properties of highly purified, well characterized single (55,56,59-69) or mixed (62,70,71) surfactants in hydrocarbon/aqueous systems have been done. The done on emulsions have almost always involved commercial materials, with the result that the correlation between surfactant structure and emulsification is obscured by the presence of manufacturing and raw material impurities.

This thesis presents fundamental properties for highly purified, well characterized single and mixed surfactants in hydrocarbon/aqueous systems. Such studies of fundamental properties on highly purified surfactants are important for correlating surfactant structure with performance, allowing rational synthesis of new, more effective surfactants, and for allowing a scientific approach to the selection of surfactant mixtures for use in hydrocarbon/aqueous systems.

1.2 Thermodynamic and Interfacial Properties of Single Surfactants

This section will define, and give equations for the calculation of, some fundamental properties of single surfactants in hydrocarbon/aqueous systems. Such properties allow one to gain knowledge of surfactant performance, of the effects of structural and environmental factors, and of what is happening on a molecular scale, and are therefore valuable in making an overall assessment of a given surfactant for a particular application.

1.2.1 Interfacial Adsorption

By definition, a surfactant will, at low concentrations, spontaneously adsorb onto surfaces and interfaces, and substantially change the surface or interfacial free energy. Interface is defined as a boundry between any two immiscible phases; a surface occurs when one of the phases is a gas. Surfactants are invariably amphipathic molecules consisting of a hydrophobic portion that has very little attraction for water and a strong attraction for oil, and a hydrophilic portion that has a strong attraction for water and very little attraction for oil. When amphipathic molecules are dissolved in a hydrocarbon/aqueous system, the hydrophobic groups of the surfactant molecules in the aqueous phase disrupt the structure of the water and the hydrophilic groups of the surfactant molecules in the hydrocarbon phase disrupt the structure of the hydrocarbon. This disruption of solvent structure causes an increase in the free energy of the system. When the surfactant molecules move to the interface, the structure of either solvent is partially restored, lowering the free energy of the system. It is for this reason that these molecules adsorb so strongly at interfaces. In the mechanism of the adsorption process from an aqueous solution, the main driving force has been shown to be an increase in the entropy of the system upon release of water molecules attached (via van der Waals interactions) to the hydrophobic portion of the surfactant molecule. In certain cases an exothermic enthalpy of adsorption also contributes, presumably due to more hydrogen bonds being formed than broken when water molecules are released from the hydrophilic head groups.

1.2.1.1 Interfacial Excess Concentrations and Area per Surfactant Molecule

Following Gibbs (72), the adsorption process for dilute (i.e., $<10^{-2}$M) solutions of a nonionic surfactant, or a 1:1 ionic surfactant in the presence of a swamping amount of electrolyte containing a common nonsurfactant ion, at a liquid/liquid (or liquid/gas) interface is described by:

$$\Gamma = -(1/2.303RT)\,(\partial\gamma_I/\partial \log C_W)_T \qquad [1]$$

where Γ is the interfacial excess concentration in mol-cm^{-2}, R = 8.314 J/mol-K°, and $(\partial\gamma_I/\partial \log C_w)_T$ is the slope of the interfacial tension - log aqueous phase surfactant concentration plot at constant (absolute) temperature, T. For a 1:1 ionic surfactant in the absence of any added electrolyte, [1] becomes:

$$\Gamma = -(1/4.606RT)\ (\partial\gamma_I/\partial \log C_w)_T. \qquad [2]$$

The slope of a typical γ_I - log C_w plot is essentially constant below, but near the critical micelle concentration (cmc). In this region, the surface excess concentration has reached a constant maximum value and Γ calculated from [1] or [2] is labelled Γ_{max}.

From the maximum surface excess concentration, the minimum area per surfactant molecule at the interface in Å^2 may be calculated from the relationship:

$$A_{min} = 10^{16}/N\,\Gamma_{max} \qquad [3]$$

where N = Avogadro's number and Γ_{max} is in mol/cm^2.

1.2.1.2 Standard Thermodynamics of Adsorption

Posner et. al. (73), after Ward and Tordai (74,75), introduced the expression:

$$\Delta G^{\circ}_{ads} = -kT\ \{\ln (d\Pi/dC)_{C\to 0} - \ln (kT\delta)\} \qquad [4]$$

for the standard free energy of adsorption, where the standard state is unit concentration in the bulk and interfacial region, k is Boltzmann's constant, T is the absolute temperature, $(d\Pi/dC)_{C\to 0}$ is the slope in the linear, low concentration region of the γ_I (or $\Pi = \gamma^0_I - \gamma_I$, where γ^0_I is the interfacial tension between the two pure liquids) - bulk concentration curve, and δ is the monolayer thickness.

Betts and Pethica (76,77), have correctly criticized equation [4] on the grounds that the value taken for δ is no more than an estimation, and they have given a more sound equation:

$$\Delta G^{\circ}_{ads} = - RT \ln (d\Pi/dC)_{C \to 0} \qquad [5]$$

based on redefining the standard states for the surface and bulk phases as unit surface pressure (unit fugacity) and unit activity, respectively, where R= the gas constant.

A major problem with [4] and [5], however, is that reliable data in the limit of C→0 are difficult to obtain since, in this limit, trace amounts of impurities markedly affect interfacial tension values. Despite this, a study (56) on surfactants in L/L (liquid/Liquid) systems has used data in the C→0 limit.

An approach which uses interfacial tension (or surface) tension data over a much larger concentration range is based on the Szysykowski equation (78) :

$$\Pi = \gamma^{0}{}_{I} - \gamma_{I} = RT\Gamma_{max} \ln (C/B + 1), \qquad [6]$$

where C is the surfactant concentration in one of the bulk phases, and B is a constant. The standard state in this approach is defined as a half-filled interface, i.e., $\Gamma = \Gamma_{max}/2$, and [5] becomes:

$$\Delta G^{\circ}_{ads} = RT \ln B \qquad [7]$$

where B is obtained from [6]. The utility of [7] for a given system must be checked by calculating values of B over a wide range to ensure its constancy.

Recently, Rosen and Aronson (79) have introduced a method which allows calculation of the standard free energy of adsorption using interfacial tension data from the point at which the interface is saturated (Γ_{max}) up to the cmc. The standard state is defined as a hypothetical monolayer at saturation adsorption, but at zero interfacial pressure (Π). The expression is :

$$\Delta G°_{ads} = RT \ln (a_{\Pi}) - \Pi A_{min} \qquad [8]$$

where Π is the interfacial pressure (the difference between the interfacial tension between the pure solvents and the value at surfactant activity in a bulk phase, a_{Π}).

For dilute nonionic surfactants in hydrocarbon/water systems, [8] can be rewritten as :

$$\Delta G°_{ads} = RT \ln (C_{w\Pi}/\omega) - \Pi A_{min} \qquad [9]$$

where, $C_{w\Pi}$ = the surfactant concentration in the water phase after partition at interfacial pressure Π, and ω = mol of H_2O/dm^3 of H_2O at absolute temperature T (ω = 55.5 mol/dm^3 at 25.0° C).

For ionic surfactants in hydocarbon/aqueous systems in a swamping amount of electrolyte containing a common nonsurfactant ion, [8] becomes:

$$\Delta G°_{ads} = RT [\ln (C_{x+}/\omega) + \ln (f_{x+}) + \ln (C_{y-}/\omega) + \ln (f_{y-})] - \Pi A_{min} \qquad [10]$$

where the concentrations are for the aqueous phase, and f_{x+}, f_{y-} are the activity coefficients for the surfactant and counterion with appropriate signs. The activity coefficient may be calculated by using the extended Debye-Huckel equation (80) :

$$\log f_{ion} = - (B |Z^+Z^-| I^{1/2}) / (1 + 0.33\alpha I^{1/2}) \qquad [11]$$

where the total ionic strength of the solution is

$$I = 1/2 \ \Sigma_i \ C_i Z^2_i \ ,$$

B = 0.509 at 25.0° C, and α is the mean distance of approach of the ions in Å (81), and is taken as 0.3 Å, for counterions, and 0.6 Å for surfactant ions.

For ionic surfactants in hydrocarbon/water systems (i.e., in the absence of added electrolyte), [10] reduces to:

$$\Delta G^{\circ}_{ads} = 2RT \ln (C_{x+}/\omega) - \Pi A_{min} \cdot \qquad [12]$$

Standard entropies and enthalpies of adsorption can be calculated from [4], [5], [7], [9], [10], and [12] using the relationships (79) :

$$\Delta S^{\circ}_{ads} = - d(\Delta G^{\circ}_{ads})/dT \qquad [13]$$

and,

$$\Delta H^{\circ}_{ads} = \Delta G^{\circ}_{ads} + T\,\Delta S^{\circ}_{ads} \qquad [14]$$

respectively, where it is assumed in equation [13] that ΔH°_{ads} is constant with respect to changes in T over the range investigated. When ΔS°_{ads} is assumed to be constant over the T range investigated, then ΔH°_{ads} may be calculated from:

$$\Delta H^{\circ}_{ads} = -T^2\, d(\Delta G^{\circ}_{ads}/T)\,/\,dT \qquad [15]$$

and then ΔS°_{ads}, in turn, from equation [14].

1.2.2 Micelle Formation

After initial saturation (Γ_{max}) is achieved, the monomer concentration in the bulk phases increases with the addition of more surfactant to a point where either an insolubility limit is reached, or any additional monomers added aggregate into clusters called micelles. The concentration of monomers at the point of aggregation formation in the latter case is called the critical micelle concentration (cmc). When micelles form in water, the hydrophobic tail of the surfactant is in the interior of the micelle and the hydrophilic head is on the exterior; in nonaqueous media, the reverse is true. In hydrocarbon/aqueous systems, the micelles usually form in the aqueous phase. Micelles are technologically important since they are used for solubilization, detergency, micellar catalysis, and have recently been used for isolating proteins from cell membranes.

As in adsorption, the reason for micellization is the amphipathic structure of the surfactant molecule and the main driving force, in aqueous solution, is an increase in the entropy of the system upon release of the water molecules from the hydrophobic tails of the surfactant molecules when the tails cluster together in the interior of the micelle. Recently, Israelachvili et al. (82) have introduced a theory of self-assembly of surfactant molecules which predicts micellar type, size, and shape, for a given surfactant, and explains the effects of salt, temperature, and solubilized materials on micellization.

1.2.2.1 Detection of Micelle Formation

Many physical methods for the detection of cmcs in aqueous solution exist, since many physical properties change abruptly at this point. Among the physical properties that have been used are: surface tension, interfacial tension, osmotic pressure, light scattering, refractive index, and electrical conductance (for ionic surfactants only). The cmc is taken as the break point in the property - concentration (of surfactant) curve.

Detection of micelles in nonaqueous solvents is usually achieved by light scattering. Many of the properties used in aqueous solutions are unsuitable here for various reasons, e.g., surfactants do not significantly lower the surface tension of nonaqueous solvents, and there is no change in electrical conductivity with increasing ionic surfactant concentration since the ionic groups exist as nondissociated ion-pairs. These drawbacks leave light scattering as the most tractable method in these systems.

Since the break in the concentration - property curve is sharper with higher aggregation numbers (i.e., the number of monomer units per micelle), and aggregation numbers in nonaqueous solvents are lower than in aqueous systems, cmc values reported for nonaqueous systems have larger experimental error than those reported for aqueous systems.

1.2.2.2 Thermodynamics of Micelle Formation in Hydrocarbon/Aqueous Systems

Two general theories have been developed to calculate standard thermodynamic parameters of micellization.

The first is called the pseudo-phase separation model, and regards the micelle as a separate pseudo-phase (83-86). In this model, the standard free energy of micellization for a nonionic surfactant in a hydrocarbon/aqueous is given by:

$$\Delta G^{\circ}_{mic} = RT \ln (cmc_W/\omega) \qquad [16]$$

where, cmc_W = the concentration of surfactant in the water phase at the break point in the γ_I - log C_W plot. The standard initial, nonmicellar state is defined as a hypothetical state at unit mole fraction x, but with the individual molecules behaving ideally, and the standard final state is the micelle itself.

The second theory is called the mass action model, and is obtained from the consideration that the micelles and the monomers are in a rapid equilibrium (87-90). When the aggregation number, n , of the micelles is $\geq$ 20, the expression for the standard free energy of micellization of a nonionic surfactant in hydrocarbon/aqueous systems, according to this theory, is given by [16], where the standard initial state is the same as in the pseudo-phase separation model, and the standard final state is defined as a hypothetical state of a micelle of unit surfactant mole fraction x, but with the individual surfactant molecules behaving ideally.

The standard entropies and enthalpies of micellization can be calculated from [16] by equations analagous to [13] or [15], and [14].

1.2.3 Interfacial Tension Reduction

When a surfactant molecule replaces solvent molecules at an interface, the potential energy, and therefore the interfacial tension, of the interface is lowered. In order to compare the performance of surfactants, it is important to distinguish between the efficiency (91) of a surfactant, measured by the concentration of surfactant in a bulk phase required to produce some significant reduction in interfacial tension, and its effectiveness (92), measured by the maximum interfacial pressure (i.e., minimum interfacial tension) which the surfactant can attain at any bulk phase concentration. Because these two parameters can run parallel or counter to each other.

1.2.3.1 Efficiency of Interfacial Tension Reduction

This can be measured by the $pC_{30,w}$ (91) value which in hydrocarbon/aqueous systems is defined as the negative log of the concentration of surfactant in the water phase at interfacial pressure of 30 mN/m (i.e., $pC_{30,w} = -\log C_w$, at $\Pi=30$). At $\Pi = 30$ mN/m, saturation adsorption is achieved From [9], the relationship between this parameter and the standard free energy of adsorption may be seen from:

$$\Delta G^\circ_{ads} = -2.303RT\,(pC_{30,w} + \log \omega) - (30\mathrm{mN/m})(A_{min}) \qquad [17]$$

for a nonionic surfactant in a hydrocarbon/water system. From [17], the larger the $pC_{30,w}$, the more negative ΔG°_{ads} becomes. Similar equations to [17] can be expressed for ionic surfactants in a swamping amount of electrolyte and in pure water, with a hydrocarbon as the second phase, from [10] and [12], respectively. The effect of $pC_{30,w}$ on ΔG°_{ads} is the same as for a nonionic surfactant.

1.2.3.2 Effectiveness of Interfacial Tension Reduction

Effectiveness of interfacial tension reduction is measured by the maximum interfacial pressure, Π_{max} . When micelles form, $\Pi_{max} \approx \Pi_{cmc}$ since the interfacial tension generally does not decrease significantly, above the cmc. If an insolubility limit for the surfactant is reached before micelles form, then Π_{max} will occur at the insolubility limit. Π_{max} for a surfactant in a hydrocarbon/aqueous system can be expressed as (93):

$$\Pi_{max} = 30\ \text{mN/m} + \{2.303nRT\Gamma_{max} \log (\text{cmc}/C_{w,\Pi=30})\} \qquad [18]$$

where n = 1 for nonionic surfactants and ionic surfactants in a swamping amount of electrolyte with a common non-surfactant ion in the aqueous phase, and n = 2 for an ionic surfactant in the absence of any added electrolyte in the aqueous phase. The $\text{cmc}/C_{w\Pi=30}$ ratio in [18] is very useful in assessing the relationship between micellization and adsorption of surfactants (93).

1.3 Mixed Surfactant Systems

Mixed surfactant systems are of scientific and technological interest. In industrial applications, surfactants are almost always used as mixtures. Often, mixtures of surfactants exhibit fundamental and applied properties superior to those of either pure individual surfactant. The desire to understand and quantify these synergistic properties and to identify the surfactant mixtures that give rise to synergism has been the driving force behind much of the research in this area.

Most of the studies on surfactant mixtures have been done in aqueous surfactant/air systems and the references in this paragraph are to those systems. Early adsorption studies (94,95) were based on Hutchinson's method (96) of treating mixed surfactant monolayers. Lange (97) and Shinoda (98) presented pseudo-phase separation models for ideal mixed micelles, but the assumption of ideality of mixing was eventually shown to be incorrect and models (99-102) which accounted for nonideality were introduced. Since the early models were cumbersome, Rubingh's (102) model for nonideal mixed micelles has had the most use. Ingram (103), and Rosen and Hua (104), extended Rubingh's model to adsorption of mixed surfactants at the aqueous solution/air interface, and Hua and Rosen (105) derived equations for synergism in binary mixtures of surfactants from it.

Recently, Rosen and Gu (106) have derived equations for molecular interactions and synergism in interfacial tension reduction efficiency at the liquid/hydrophobic solid interface. In the next chapter, a derivation of equations for calculating molecular interaction and synergism for binary mixtures of surfactants in two-phase, liquid-liquid systems is given.

CHAPTER 2

THEORY

2.1 Equations for Calculating Mole Fractions of Individual Surfactants and Interaction Parameters in Binary Mixtures of Surfactants at the Liquid-Liquid Interface

In a system of two liquid phases and two surfactants (each after partition), the chemical potential of surfactant 1 at the interface of the two liquids can be expressed as:

$$\mu_{1,I} = \mu^{0}_{1,I} + RT \ln f_{1,I} X_{1,I} - \gamma_{I} A_{1,I} \qquad [19]$$

where $\mu_{1,I}$ is the chemical potential of surfactant 1 in the mixture at the interface, $\mu^{0}_{1,I}$ is the standard chemical potential of surfactant 1 in the interfacial region after partition (with the standard state defined as a monolayer of pure surfactant 1 at zero interfacial tension); $f_{1,I}$ is the activity coefficient of surfactant 1 in the mixture in the interfacial region, $X_{1,I}$ its mole fraction and $A_{1,I}$ its partial molar interfacial area there. The chemical potential $\mu_{1,W}$ of surfactant 1 in the mixture in the aqueous phase, after partition, can be expressed as:

$$\begin{aligned} \mu_{1,W} &= \mu^{\theta}_{1,W} + RT \ln a_{1,W} \\ &= \mu^{\theta}_{1,W} + RT \ln f_{1,W} C_{1,W} \qquad [20] \end{aligned}$$

where $\mu^{\theta}_{1,W}$ is the standard chemical potential of surfactant 1 in the aqueous phase (with the standard state defined as 1M solution, but behaving ideally), $f_{1,W}$ is the activity coefficient of surfactant 1 in the mixture after partition, and $C_{1,W}$ is the concentration of surfactant 1 in the same system on the molarity scale.

When equilibrium is reached, the chemical potentials of any given solute, in all phases, are equal. Therefore, eq. [19] is equal to eq. [20], which gives:

$$\mu^{0}_{1,I(\Pi)} - \mu^{\theta}_{1,W} = RT \ln (f_{1,W} C_{1,W} / f_{1,I} X_{1,I}) + \gamma_I A_{1,I} \qquad [21]$$

For a system of the same two phases containing only surfactant 1 (after partition) and at the same interfacial tension, γ_I, as the mixture:

$$\mu_{1,I,0} = \mu^{0}_{1,I} - \gamma_I A^{0}_{1,I} \qquad [22]$$

where $A^{0}_{1,I}$ is the molar interfacial area occupied by pure surfactant 1. In the water phase in a system of pure surfactant 1 after partition,

$$\begin{aligned}\mu_{1,W,0} &= \mu^{\theta}_{1,W} + RT \ln a^{0}_{1,W} \\ &= \mu^{\theta}_{1,W} + RT \ln f^{0}_{1,W} C^{0}_{1,W} ,\end{aligned} \qquad [23]$$

where $a^{0}_{1,W}$ is the aqueous phase activity of pure surfactant 1, after partition, required to produce the same interfacial tension, γ_I, as that of the mixture; $C^{0}_{1,W}$ is its aqueous phase molar concentration; and $f^{0}_{1,W}$ is its aqueous phase activity coefficient. At equilibrium, $\mu_{1,I,0} = \mu_{1,W,0}$, and from [22] and [23],

$$\mu^{0}_{1,I} - \mu^{\theta}_{1,W} = RT \ln f^{0}_{1,W} C^{0}_{1,W} + \gamma_I A^{0}_{1,I} \qquad [24]$$

Since [24] and [21] are equal,

$$RT \ln \frac{C_{1,W} f_{1,W}}{f_{1,I} X_{1,I} C^{0}_{1,W} f^{0}_{1,W}} = \gamma_I (A^{0}_{1,I} - A_{1,I}) \qquad [25]$$

By the same line of reasoning, one can obtain a similar relation for surfactant

2 in the mixture:

$$RT \ln \frac{C_{2,W}\, f_{2,W}}{f_{2,I}\; X_{2,I}\; C^{0}_{2,W}\, f^{0}_{2,W}} = \gamma_I\,(A^{0}_{2,I} - A_{2,I}) \qquad [26]$$

and since, only with two surfactants, $X_{2,I} = (1 - X_{1,I})$, [26] can be expressed as:

$$RT \ln \frac{C_{2,W}\, f_{2,W}}{f_{2,I}\;(1- X_{1,I})\; C^{0}_{2,W}\, f^{0}_{2,W}} = \gamma_I\,(A^{0}_{2,I} - A_{2,I}) \qquad [27]$$

When the concentrations of surfactants in the bulk phases are low, the ratios $f_{1,W}/ f^{0}_{1,W}$ and $f_{2,W}/ f^{0}_{2,W}$ in [25] and [27] , respectively, can be taken as equal to 1, and [25] and [27] become:

$$RT \ln \frac{C_{1,W}}{f_{1,I}\; X_{1,I}\; C^{0}_{1,W}} = \gamma_I\,(A^{0}_{1,I} - A_{1,I}) \qquad [28]$$

and

$$RT \ln \frac{C_{2,W}}{f_{2,I}\;(1- X_{1,I})\; C^{0}_{2,W}} = \gamma_I\,(A^{0}_{2,I} - A_{2,I}) \qquad [29]$$

respectively.

The activity coefficients of each surfactant at the interface ($f_{1,I}$ and $f_{2,I}$) can be approximated using the second term of the Margules expansion (the first term being equal to zero) (107), as:

$$f_{1,I} = \exp\{\beta^{\sigma}_{LL}(1- X_{1,I})^2\} \qquad [30]$$

and

$$f_{2,I} = \exp\{\beta^{\sigma}_{LL}(X_{1,I})^2\}, \qquad [31]$$

where β^{σ}_{LL} is a measure of the deviation from ideality in the interfacial region in the mixture and is related to the molecular interaction between surfactants 1 and 2 in that region. With these approximations, [28] and [39] become:

$$\beta^{\sigma}_{LL}(1- X_{1,I})^2 = \ln \frac{C_{1,W}}{X_{1,I}\, C^0_{1,W}} - \frac{\gamma_I\,(A^0_{1,I} - A_{1,I})}{RT} \qquad [32]$$

and

$$\beta^{\sigma}_{LL}(X_{1,I})^2 = \ln \frac{C_{2,W}}{(1-X_{1,I})\, C^0_{2,W}} - \frac{\gamma_I\,(A^0_{2,I} - A_{2,I})}{RT} \qquad [33]$$

respectively. If one lets:

$$B_1 = \frac{\gamma_I\,(A^0_{1,I} - A_{1,I})}{RT}$$

and,

$$B_2 = \frac{\gamma_I\,(A^0_{2,I} - A_{2,I})}{RT},$$

then one gets for [32] and [33],

$$\beta^{\sigma}_{LL}(1 - X_{1,I})^2 = \ln \frac{C_{1,W}}{X_{1,I}\, C^0_{1,W}} - B_1 \qquad [34]$$

and,

$$\beta^{\sigma}_{LL}(X_{1,I})^2 = \ln \frac{C_{2,W}}{(1-X_{1,I})\, C^0_{2,W}} - B_2 \qquad [35]$$

The partition coefficient for surfactant 1 can be expressed as:

$$K_1 = C_{1,B}/C_{1,W} \qquad [36]$$

where $C_{1,B}$ is the concentration of surfactant 1 in the oil phase of the two-phase system after partition and $C_{1,W}$ is the concentration of surfactant 1 in the aqueous phase after partition. The total concentration of surfactant 1, $C_{1,t}$, in the mixed system is then:

$$C_{1,t} = (C_{1,W}V_W + C_{1,B}V_B) / V_t \qquad [37]$$

where V_W, V_B, and V_t are the volumes of the aqueous phase, the oil phase, and the entire system, respectively. From [37],

$$C_{1,B} = (C_{1,t}V_t - C_{1,W}V_W) / V_B, \qquad [38]$$

and substitution of [38] into [36] gives:

$$K_1 = (C_{1,t}V_t - C_{1,W}V_W) / V_BC_{1,W}$$

from which,

$$C_{1,W} = \left(\frac{V_t}{K_1V_B + V_W}\right) C_{1,t} \qquad [39]$$

If $\varphi = V_B/V_W$, then $V_t = \varphi V_W + V_W$ and $V_B = \varphi V_W$. Substitution into [39] then yields:

$$C_{1,W} = \left(\frac{\varphi + 1}{K_1\varphi + 1}\right) C_{1,t} = F_1 C_{1,t} \qquad [40]$$

where $F_1 = (\varphi + 1) / (K_1\varphi + 1)$, the fraction of surfactant 1 in the aqueous phase of the surfactant mixture.

Similarly,

$$C_{2,W} = \left(\frac{\varphi + 1}{K_2\varphi + 1}\right) C_{2,t} = F_2 C_{2,t} \qquad [41]$$

where $F_2 = (\varphi + 1) / (K_2\varphi + 1)$, the fraction of surfactant 2 in the aqueous phase of the surfactant mixture. Hence,

$$C^0_{1,W} = \left(\frac{\varphi^0_1 + 1}{K^0_1\varphi^0_1 + 1}\right) C^0_{1,t} = F^0_1\, C^0_{1,t} \qquad [42]$$

where $F^0_1 = (\varphi^0_1 + 1) / (K^0_1\varphi^0_1 + 1)$, the fraction of surfactant 1 in the aqueous phase of the system containing only surfactant 1, and

$$C^0_{2,W} = \left(\frac{\varphi^0_2 + 1}{K^0_2\varphi^0_2 + 1}\right) C^0_{2,t} = F^0_2\, C^0_{2,t} \qquad [43]$$

where $F^0_2 = (\varphi^0_2 + 1) / (K^0_2\varphi^0_2 + 1)$, the fraction of surfactant 2 in the aqueous phase of the system containing only surfactant 2.

Here, again, the superscript ^{0} refers to systems containing only one surfactant. Substitution of [40] and [42] into [34], and of [41] and [43] into [35], respectively, gives:

$$\beta^{\sigma}_{LL}(1 - X_{1,I})^2 = \ln \frac{F_1\, C_{12,t}\, \alpha_1}{F^0_1\, X_{1,I}\, C^0_{1,W}} - B_1 \qquad [44]$$

and

$$\beta^{\sigma}_{LL}(X_{1,I})^2 = \ln \frac{F_2\, C_{12,t}\,(1-\alpha_1)}{F^0_2\,(1-X_{1,I})\, C^0_{2,W}} - B_2\,. \qquad [45]$$

where the relationships $C_{1,t} = C_{12,t}\,\alpha_1$ and $C_{2,t} = C_{12,t}\,(1-\alpha_1)$ were used for $C_{1,t}$ and $C_{2,t}$. $C_{12,t}$ is the total concentration of surfactant, 1 and 2 combined, in the mixed surfactant system, and α_1 is the mole fraction of surfactant 1 in the mixed surfactant. From [44] and [45],

$$\frac{(X_{1,I})^2 \ln \dfrac{F_1\, C_{12,t}\, \alpha_1}{F^0{}_1\, X_{1,I}\, C^0{}_{1,W}} - B_1}{(1-X_{1,I})^2 \ln \dfrac{F_2\, C_{12,t}\,(1-\alpha_1)}{F^0{}_2\,(1-X_{1,I})\, C^0{}_{2,W}} - B_2} = 1. \qquad [46]$$

Two assumptions about the molar areas of the surfactants in the mixed interfacial film are required. The first assumption is that $A_{1,I} \approx A^0{}_{1,I}$, and $A_{2,I} \approx A^0{}_{2,I}$ and thus that $B_1 = B_2 = 0$. In this case [44] and [46] become:

$$\beta^{\sigma}{}_{LL} = \frac{\ln (C_{12,t}\alpha_1 F_1 / C^0{}_{1,t}\, F^0{}_1\, X_{1,I})}{(1-X_{1,I})^2} \qquad [47]$$

and

$$\frac{(X_{1,I})^2 \ln (C_{12,t}\alpha_1 F_1/C^0_{1,t}\, F^0_1\, X_{1,I})}{(1-X_{1,I})^2 \ln (C_{12,t}(1-\alpha_1)F_2/C^0_{2,t}\, F^0_2(1-X_{1,I}))} = 1 \quad . \quad [48]$$

The second assumption (106) is that the ratio of the molar areas of the two surfactants in the interfacial film is equal to that in the individual monolayers, i.e. :

$$\frac{A_{1,I}}{A_{2,I}} = \frac{A^0_{1,I}}{A^0_{1,I}} \qquad [49]$$

In the mixed film,

$$X_{1,I}\, A_{1,I} + (1-X_{1,I})\, A_{2,I} = A_{av} \cdot \qquad [50]$$

From, [49] and [50],

$$A_{1,I} = \frac{A_{av}\, A^0_{1,I}}{X_{1,I}\, A^0_{1,I} + (1-X_{1,I})\, A^0_{2,I}}$$

and,

$$A_{2,I} = \frac{A_{av}\, A^0_{2,I}}{X_{1,I}\, A^0_{1,I} + (1-X_{1,I})\, A^0_{2,I}} \; .$$

From these,

$$B_1 = \frac{\gamma_I (A^0_{1,I} - A_{1,I})}{RT}$$

$$= \frac{\gamma_I \; A^0_{1,I} \; [1 - \dfrac{A_{av}}{X_{1,I} \; A^0_{1,I} + (1 - X_{1,I}) \, A^0_{2,I}}]}{RT} \qquad [51]$$

and,

$$B_2 = \frac{\gamma_I (A^0_{2,I} - A_{2,I})}{RT}$$

$$= \frac{\gamma_I \; A^0_{2,I} \; [1 - \dfrac{A_{av}}{X_{1,I} \; A^0_{1,I} + (1 - X_{1,I}) \, A^0_{2,I}}]}{RT} \qquad [52]$$

In this case, [44] and [46] become:

$$\beta^{\sigma}_{LL} = \frac{\ln \dfrac{F_1 \, C_{12,t} \, \alpha_1}{F^0_1 \, X_{1,I} \, C^0_{1,W}}}{(1 - X_{1,I})^2} - \frac{\gamma_I \, A^0_{2,I} \left[1 - \dfrac{A_{av}}{X_{1,I} \, A^0_{1,I} + (1 - X_{1,I}) \, A^0_{2,I}}\right]}{RT \, (1 - X_{1,I})^2} \qquad [53]$$

and

$$[\{X_{1,I} \bullet \ln(F_1 \, C_{12,t} \, \alpha_1 / F^0_1 \, X_{1,I} \, C^0_{1,W})\} - \{\gamma_I \, A^0_{1,I} \, [1 - (A_{av} / X_{1,I} \, A^0_{1,I} + (1 - X_{1,I}) \, A^0_{2,I})]/ RT\}] \, / \, [\{(1 - X_{1,I}) \bullet \ln[F_2 \, C_{12,t}(1 - \alpha_1) / F^0_2 \, (1 - X_{1,I}) \, C^0_{2,W}]\} - \{\gamma_I \, A^0_{2,I} \, [1 - (A_{av} / X_{1,I} \, A^0_{1,I} + (1 - X_{1,I}) \, A^0_{2,I})]/ RT\}] = 1 \qquad [54]$$

Two rough guides based on experimental results (106) as to whether equations obtained from the first or second assumption should be used are: 1) if $\beta^{\sigma}_{LL} \geq -5$, equations assuming $B_1 = B_2 = 0$ are good enough, and 2) if $\beta^{\sigma}_{LL} \leq -5$, equations employing the correction terms (B_1 and B_2) based on assuming that $A_{1,I} / A_{2,I} = A^0_{1,I} / A^0_{2,I}$ should be used.

Under certain conditions, the partition coefficient values may be eliminated from the pertinent equations since the ratios $F^0{}_1/F_1$ and $F^0{}_2/F_2$ become equal to 1. There are two such conditions :

1) $\varphi = \varphi^0{}_1 = \varphi^0{}_2$, $K_1 = K^0{}_1$, and $K_2 = K^0{}_2$. Then, $\varphi^0{}_1$, $\varphi^0{}_2$, and φ can be made equal to each other by using the same volume ratio V_B/V_W in the mixed and, pure surfactant systems. Considering the low surfactant concentrations normally used, $K^0{}_1$ and $K^0{}_2$ are frequently equal to K_1 and K_2, respectively.

2) $\varphi = \varphi^0{}_1 = \varphi^0{}_2$ and the $K\varphi$ values are << 1. Under this condition, $F^0{}_1/F_1 = F^0{}_2/F_2 \approx (\varphi +1)/1 \,/\, (\varphi +1)/1 = 1$. $K\varphi$ may be forced to become << 1 by using a small volume of oil relative to the aqueous phase which makes φ small. This method fails, however, when the surfactant is very oil soluble (i.e., K is very large).

A third condition applies only to the calculation of $X_{1,I}$, $X^M{}_1$, $\beta^\sigma{}_{LL}$, and $\beta^M{}_{LL}$ in equations [46] and [47] and the analogous equations for mixed micelles:

3) α_1 approaches zero or one. When the limit $\alpha_1 \rightarrow 1$, then $\alpha_1 C_{12,t} \rightarrow C^0{}_{1,t}$, $K_1 \rightarrow K^0{}_1$, and $F^0{}_1/F_1 \rightarrow 1$. When the limit $\alpha_1 \rightarrow 0$, then $F^0{}_1/F_1 \bullet \alpha_1 \rightarrow 0$ and the effect of $F^0{}_1/F_1$ on X_1 and $\beta^\sigma{}_{LL}$ (and, $X^M{}_1$ and $\beta^M{}_{LL}$) becomes negligible. Similar relationships hold for α_2.

If any of these three conditions apply, [47] and [48] reduce to:

$$\beta^\sigma{}_{LL} = \frac{\ln (C_{12,t}\alpha_1/C^0{}_{1,t}\ X_{1,I})}{(1- X_{1,I})^2} \qquad [55]$$

and

$$\frac{(X_{1,I})^2 \ln (C_{12,t}\alpha_1/C^0_{1,t}\; X_{1,I})}{(1-X_{1,I})^2 \ln \;(C_{12,t}(1-\alpha_1)/C^0_{2,t}\;(1-X_{1,I}))} = 1 \qquad [56]$$

and [53] and [54] reduce to:

$$\beta^{\sigma}_{LL} = \frac{\ln \dfrac{C_{12,t}\,\alpha_1}{X_{1,I}\;C^0_{1,W}}}{(1-X_{1,I})^2}$$

$$- \frac{\gamma_I\;A^0_{2,I}\;\left[1 - \dfrac{A_{av}}{X_{1,I}\;A^0_{1,I} + (1-X_{1,I})\,A^0_{2,I}}\right]}{RT\,(1-X_{1,I})^2} \qquad [57]$$

and

$$[\{X_{1,I} \bullet \ln(\,C_{12,t}\,\alpha_1 /\; X_{1,I}\;C^0_{1,W})\} - \{\,\gamma_I\;A^0_{1,I}\;[1 - (A_{av} / X_{1,I}\;A^0_{1,I} + (1-X_{1,I})\,A^0_{2,I}\,)] / RT\}] \;/\; [\{(1-X_{1,I}) \bullet \ln[\,C_{12,t}(1-\alpha_1) / (1-X_{1,I}\,)\,C^0_{2,W}]\} - \{\,\gamma_I\;A^0_{2,I}\;[1 - (A_{av} / X_{1,I}\;A^0_{1,I} + (1-X_{1,I})\,A^0_{2,I}\,)] / RT\}] = 1 \qquad [58]$$

respectively. Since $C_{12,t}$, α_1, $C^0_{1,t}$, and $C^0_{2,t}$ can be determined experimentally (as can K_1, K^0_1, K^0_2, K_2, φ, φ^0_1, φ^0_2, $A^0_{1,I}$, $A^0_{2,I}$, and A_{av}), [56] (or [58], [48], and [54]) can be solved numerically for $X_{1,I}$. Once $X_{1,I}$ is known, [55] (or [57], [47], and [53]) can be solved to obtain β^σ_{LL}.

2.2 Synergism and Negative Synergism in Interfacial Tension Reduction Efficiency

The efficiency of interfacial tension reduction by surfactants in a two-phase liquid-liquid system can be defined as the total surfactant concentration in the entire system required to produce a given interfacial tension reduction. Synergism in this respect is present in a surfactant mixture if a given interfacial tension (reduction) at a total mixed concentration lower than that required of either surfactant of the mixture by itself can be attained. Negative synergism in this respect is present when the mixture attains a given interfacial tension value at a concentration higher than that required for either surfactant of the mixture by itself.

For the case where $\beta^\sigma_{LL} \approx -5$ or less negative, $B_1 = B_2 = 0$ (i.e., $A_{1,I} \approx A^0_{1,I}$, and $A_{2,I} \approx A^0_{2,I}$), and equations [44] and [45] yield:

$$C_{12,t}\alpha_1 = \frac{F^0_1}{F_1} X_{1,I}\, C^0_{1,t} \cdot \exp\{\beta^\sigma_{LL}(1 - X_{1,I})^2\}, \qquad [59]$$

and,

$$C_{12,t}(1-\alpha_1) = \frac{F^0_2}{F_2}(1-X)C^0_{2,t} \cdot \exp\{\beta\sigma_{LL}(X)^2\}. \qquad [60]$$

respectively, where $X \equiv X_{1,I}$.

From [59]:

$$\ln C_{12,t} - \ln C^0_{1,t} = \ln X + \ln\frac{F^0_1}{F_1} + \beta\sigma_{LL}(1-X)^2 - \ln\alpha_1. \qquad [61]$$

Since, for synergism to be present, $C_{12,t}$ must be less than $C^0_{1,t}$ or less than $C^0_{2,t}$, a condition for synergism is:

$$\ln X + \ln\frac{F^0_1}{F_1} + \beta\sigma_{LL}(1-X)^2 - \ln\alpha_1 < 0. \qquad [62]$$

Since for negative synergism to be present, $C_{12,t}$ must be greater than $C^0_{1,t}$ or greater than $C^0_{2,t}$, a condition for negative synergism is:

$$\ln X + \ln\frac{F^0_1}{F_1} + \beta\sigma_{LL}(1-X)^2 - \ln\alpha_1 > 0. \qquad [63]$$

When either of the first two conditions for the elimination of partition coefficient values (p> 25) is satisfied, the conditions are for equation [62]:

$$\ln X + + \beta^{\sigma}{}_{LL}(1- X)^2 - \ln \alpha_1 < 0 \qquad [64]$$

and, for negative synergism, from equation [63],

$$\ln X + + \beta^{\sigma}{}_{LL}(1- X)^2 - \ln \alpha_1 > 0. \qquad [65]$$

When synergism (or negative synergism) in interfacial reduction efficiency exists, there will be a minimum (or maximum) in the $C_{12,t}$ vs α_1 curve and maximum synergism in this respect will be obtained where the $C_{12,t}$ vs α_1 curve shows a minimum (or maximum), i.e.

$$d\, C_{12,t}/d\alpha_1 = 0.$$

From [61],

$$\frac{d\, C_{12,t}}{d\alpha_1} = \frac{1}{X}\frac{dX}{d\alpha_1} - \frac{1}{\alpha_1} - 2\beta^{\sigma}{}_{LL}(1-X)\frac{dX}{d\alpha_1} \qquad [66]$$

where it assumed that K_1 does not change with α_1 at the low surfactant concentrations normally used. Since

$$\frac{d\,C_{12,t}}{d\alpha_1} = C_{12,t}\,\frac{d\ln C_{12,t}}{d\alpha_1},$$

[66] can be expressed as:

$$\frac{d\,C_{12,t}}{d\alpha_1} = C_{12,t}\cdot\left(\frac{1}{X}\frac{dX}{d\alpha_1} - \frac{1}{\alpha_1} - 2\beta^{\sigma}{}_{LL}(1-X)\,\frac{dX}{d\alpha_1}\right) = 0.$$

Since $C_{12,t} \neq 0$,

$$\frac{1}{X}\frac{dX}{d\alpha_1} - \frac{1}{\alpha_1} - 2\beta^{\sigma}{}_{LL}(1-X)\,\frac{dX}{d\alpha_1} = 0.$$

at the point of maximum synergism. From this,

$$\frac{dX}{d\alpha_1} = \frac{X}{\alpha_1\,(1 - 2\beta^{\sigma}{}_{LL}X + 2\beta^{\sigma}{}_{LL}X^2)}. \qquad [67]$$

Division of [59] by [60] followed by rearrangement gives:

$$\ln\frac{F_1F^0{}_2C^0{}_{2,t}}{F_2F^0{}_1C^0{}_{1,t}} + \ln\alpha_1 + \ln(1-X) - \beta^{\sigma}{}_{LL} + 2\beta^{\sigma}{}_{LL}X$$

$$- \ln(1-\alpha_1) - \ln X = 0. \qquad [68]$$

Differentiating with respect to α_1 gives:

$$\frac{1}{\alpha_1} - \frac{1}{(1-X)}\frac{dX}{d\alpha_1} + 2\beta^{\sigma}{}_{LL}\frac{dX}{d\alpha_1} + \frac{1}{(1-\alpha_1)} - \frac{1}{X}\frac{dX}{d\alpha_1} = 0 \quad [69]$$

where it is assumed that K_1 and K_2 do not change with change in α_1. Equation [69] can be expressed as:

$$\frac{dX}{d\alpha_1} = \frac{X(1-X)}{\alpha_1(1-\alpha_1)(1 - 2\beta^{\sigma}{}_{LL}X + 2\beta^{\sigma}{}_{LL}X^2)} \cdot \quad [70]$$

Combining [67] and [70],

$$\frac{X}{\alpha_1(1 - 2\beta^{\sigma}{}_{LL}X + 2\beta^{\sigma}{}_{LL}X^2)}$$

$$= \frac{X(1-X)}{\alpha_1(1-\alpha_1)(1 - 2\beta^{\sigma}{}_{LL}X + 2\beta^{\sigma}{}_{LL}X^2)}$$

or,

$$(1-\alpha_1) = (1-X)$$

and

$$\alpha^*{}_1 = X \quad [71]$$

where $\alpha^*{}_1$ is the mole fraction of surfactant 1 in the total surfactant in the entire system at the point of maximum synergism (or negative synergism) in interfacial reduction efficiency. Relationship [71] states that, at the point of maximum synergism (or negative synergism) in this respect, the mole fraction of either surfactant in the interfacial region is equal to its mole fraction in the entire system.

Substitution of [71] into [64] gives the first condition for synergism in this respect as:

$$\beta^{\sigma}{}_{LL}(1-X)^2 < 0\ , \qquad [72]$$

and substitution of [71] into [65] gives the first condition for negative synergism as:

$$\beta^{\sigma}{}_{LL}(1-X)^2 > 0\ , \qquad [73]$$

and since $(1-X)^2$ is always positive, $\beta^{\sigma}{}_{LL}$ must be negative for synergism, and positive for negative synergism, to exist.

From [71] and [68]:

$$\ln \frac{F_2F^0{}_1C^0{}_{1,t}}{F_1F^0{}_2C^0{}_{2,t}} = -\beta^{\sigma}{}_{LL}(1-2X). \qquad [74]$$

Since $0 < X < 1$ and $\beta^{\sigma}{}_{LL}$ must be negative, the second condition for synergism in interfacial tension reduction efficiency is:

$$\left| \ln \frac{F_2F^0{}_1C^0{}_{1,t}}{F_1F^0{}_2C^0{}_{2,t}} \right| < \left| \beta^{\sigma}{}_{LL} \right|\ , \qquad [75]$$

and since $\beta^{\sigma}{}_{LL}$ must be positive for negative synergism in this respect, the second condition for negative synergism to exist is:

$$\left| \ln \frac{F_2 F^0{}_1 C^0{}_{1,t}}{F_1 F^0{}_2 C^0{}_{2,t}} \right| < \beta^{\sigma}{}_{LL} \qquad [76]$$

When either of the first two conditions for the elimination of partition coefficient values is satisfied, the second condition for synergism, [75], becomes,

$$\left| \ln \frac{C^0{}_{1,t}}{C^0{}_{2,t}} \right| < \left| \beta^{\sigma}{}_{LL} \right| . \qquad [77]$$

and the second condition for negative synergism becomes:

$$\left| \ln \frac{C^0{}_{1,t}}{C^0{}_{2,t}} \right| < \beta^{\sigma}{}_{LL} \cdot \qquad [78]$$

Substitution of [71] into [61] gives:

$$\ln C_{12,t,\min(\max)} = \ln \frac{C^0{}_{1,t}F^0{}_1}{F_1} + \beta^\sigma{}_{LL}(1-X)^2 \,, \qquad [79]$$

where $C_{12,t,\min(\max)}$ is the minimum (or maximum, for negative synergism) total surfactant concentration required to produce a given interfacial tension (reduction). From [74],

$$X = \frac{\ln(\,F_2F^0{}_1C^0{}_{1,t}/\,F_1F^0{}_2C^0{}_{2,t}) + \beta^\sigma{}_{LL}}{2\,\beta^\sigma{}_{LL}} = \alpha^*{}_1 \qquad [80]$$

or, when either of the first two conditions for the elimination of partition coefficient values is satisfied:

$$X = \frac{\ln(C^0{}_{1,t}/\,C^0{}_{2,t}) + \beta^\sigma{}_{LL}}{2\,\beta^\sigma{}_{LL}} = \alpha^*{}_1 \,. \qquad [81]$$

Substitution of [80] into [79] gives:

$$C_{12,t,\min(\max)} = \frac{C^0{}_{1,t}F^0{}_1}{F_1} \cdot$$

$$\exp\left[\beta^\sigma{}_{LL}\left(\frac{\beta^\sigma{}_{LL} - \ln(\,F_2F^0{}_1C^0{}_{1,t}/\,F_1F^0{}_2C^0{}_{2,t})}{2\,\beta^\sigma{}_{LL}}\right)^2\right], \qquad [82]$$

and, when either of the first two conditions for the elimination of partition coefficient values is satisfied:

$$C_{12,t,min(max)} = C^0_{1,t} \cdot$$

$$\exp\left[\beta^\sigma_{LL}\left(\frac{\beta^\sigma_{LL} - \ln(C^0_{1,t}/C^0_{2,t})}{2\beta^\sigma_{LL}}\right)^2\right] \quad [83]$$

2.3 Synergism and Negative Synergism in Mixed Micelle Formation

Synergism in mixed micelle formation in binary mixtures of surfactants in a two-phase liquid-liquid system is present when the cmc of the mixture, $CMC_{12,t}$, is lower than the cmc of either surfactant comprising the mixture by itself in a similar liquid-liquid system. Negative synergism in this respect is present when the cmc of the mixture is higher than the cmc of either surfactant comprising the mixture by itself (in a similar liquid-liquid system). The cmc of the system is the total molar concentration of surfactant in the entire system at the point of intersection of the two almost linear portions of the interfacial tension vs log total (i.e., in the entire system) concentration curve in the region where micellization occurs in the system. From Eqs. [59] and [60], relationships analogous to those derived for synergism with respect to interfacial tension reduction efficiency can be obtained for synergism in mixed micelle formation.

For synergism to exist in this respect when either of the first two conditions for the elimination of partition coefficient values is satisfied, (i) $\beta^M{}_{LL}$ must be negative, and (ii) $|\ln CMC^0{}_{1,t}/ CMC^0{}_{2,t}|$ must be less than $|\beta^M{}_{LL}|$. For negative synergism to exist, (i) $\beta^M{}_{LL}$ must be positive, and (ii) $|\ln CMC^0{}_{1,t}/ CMC^0{}_{2,t}|$ must be less than $\beta^M{}_{LL}$, where $\beta^M{}_{LL}$ is the experimentally determined parameter related to molecular interaction between the two surfactants in the mixed micelles in the system, and $CMC^0{}_{1,t}$ and $CMC^0{}_{2,t}$ are the cmc's of individual surfactants 1 and 2, respectively, by themselves in similar two-phase, liquid-liquid systems. $\beta^M{}_{LL}$ is evaluated from equations analogous to Eqs. [47] and [55].

At the point of maximum synergism in this respect:

$$\alpha^{*,M} = X^M = \frac{\ln (CMC^0{}_{1,t}F_2F^0{}_1 \ / \ CMC^0{}_{2,t}F_1F^0{}_2) + \beta^M{}_{LL}}{2\,\beta^M{}_{LL}} \qquad [84]$$

When either of the first two conditions for the elimination of partition coefficient values is satisfied:

$$\alpha^{*,M} = X^M = \frac{\ln (CMC^0{}_{1,t}/CMC^0{}_{2,t}) + \beta^M{}_{LL}}{2\,\beta^M{}_{LL}}, \qquad [85]$$

and

$$CMC_{12,t,min(max)} = \frac{CMC^0_{1,t}F^0_1}{F_1} \cdot \exp\left[\beta^M_{LL}\left(\frac{\beta^M_{LL} - \ln(CMC^0_{1,t}F_2F^0_1/CMC^0_{2,t}F_1F^0_2)}{2\,\beta^M_{LL}}\right)^2\right] \qquad [86]$$

and, when either of the first two conditions for the elimination of partition coefficient values is satisfied:

$$CMC_{12,t,min(max)} = CMC^0_{1,t} \cdot \exp\left[\beta^M_{LL}\left(\frac{\beta^M_{LL} - \ln(CMC^0_{1,t}/CMC^0_{2,t})}{2\,\beta^M_{LL}}\right)^2\right]. \qquad [87]$$

2.4 Synergism and Negative Synergism in Interfacial Tension Reduction Effectiveness

The effectiveness of the interfacial tension reduction in a two-phase, liquid-liquid system can be defined as the interfacial tension reduction attained at the cmc of the system. Synergism in interfacial tension reduction effectiveness is, therefore, present in a liquid-liquid, binary surfactant system when the mixed surfactant system can attain a lower interfacial tension at its cmc, $CMC_{12,t}$, than either surfactant comprising the mixture can attain at its respective cmc, $CMC^0_{1,t}$ or $CMC^0_{2,t}$. Negative synergism in this respect is present when the mixture at its cmc has a surface tension value greater than either surfactant comprising the mixture can attain at its respective cmc.

The basic equations, analogous to [59] and [60], above, for adsorption at the liquid-liquid interface at the cmc, $CMC_{12,t}$, of the mixed surfactant system (when $B_1 = B_2 = 0$) are:

$$CMC_{12,t}\alpha_1 = \frac{F^0_1}{F_1} X\, C^{0,CMC}_{1,t} \cdot \exp[\,\beta^{\sigma}_{LL}(1-X)^2] \qquad [88]$$

and,

$$CMC_{12,t}(1-\alpha_1) = \frac{F^0_2}{F_2} (1-X)C^{0,CMC}_{2,t} \cdot \exp[\,\beta^{\sigma}_{LL}(X)^2] \qquad [89]$$

where $C^{0,CMC}_{1,t}$ and $C^{0,CMC}_{2,t}$ are the molar concentrations in the entire system of individual surfactants 1 and 2 , respectively, required to yield an interfacial tension equal to that obtained by any mixture of 1 and 2 at its cmc, i.e., $\gamma_{CMC,12,t}$. The linear portion of the interfacial tension, γ_I, vs C^0_t of each individual surfactant can hypothetically be extended to concentration values above the cmc to yield interfacial tension values equal to the interfacial tension, $\gamma_{CMC,12,t}$, of the mixture at its cmc. From this extrapolation:

$$\gamma_{CMC,12,t} = S'_1 + S_1 \ln\, C^{0,CMC}_{1,t} \qquad [90]$$

and,

$$\gamma_{CMC,12,t} = S'_2 + S_2 \ln C^{0,CMC}{}_{2,t} \qquad [91]$$

where S_1 and S_2 are the slopes of the γ vs ln $C^0{}_t$ plots of the individual surfactants and S'_1 and S'_2 are the hypothetical γ intercepts of the same plots.

From [88] and [90],

$$\gamma_{CMC,12,t} = S'_1 + S_1 \left[\ln \left(\frac{F_1}{F^0{}_1} CMC_{12,t}\alpha_1 \right) - \beta^{\sigma}{}_{LL}(1-X)^2 \right]. \qquad [92]$$

When synergism or negative synergism in interfacial tension reduction effectiveness exists, there will be a minimum or a maximum, respectively, in the $\gamma_{CMC,12,t}$ vs α_1 curve, or mathematically:

$$\frac{d\,\gamma_{CMC,12,t}}{d\alpha_1} = 0.$$

Thus,

$$\frac{d\,\gamma_{CMC,12,t}}{d\alpha_1} = S_1 \left(\frac{1}{\alpha_1} + \frac{d \ln CMC_{12,t}}{d\alpha_1} - \frac{1}{X}\frac{dX}{d\alpha_1} \right.$$

$$\left. + 2\beta^{\sigma}{}_{LL}(1-X)\frac{dX}{d\alpha_1} \right) = 0 , \qquad [93]$$

where it is assumed that K_1 and φ do not change with change in α_1. Since $S_1 \neq 0$:

$$\frac{1}{\alpha_1} + \frac{d \ln CMC_{12,t}}{d\alpha_1} - \frac{1}{X}\frac{dX}{d\alpha_1} + 2\,\beta^{\sigma}{}_{LL}(1-X)\frac{dX}{d\alpha_1} = 0$$

and

$$\frac{d \ln CMC_{12,t}}{d\alpha_1} = \left(\frac{1}{X} - 2\,\beta^{\sigma}{}_{LL}(1-X)\right)\frac{dX}{d\alpha_1} - \frac{1}{\alpha_1}\,. \qquad [94]$$

Following the same line of reasoning, one can derive, from [93] and [91]:

$$\frac{d \ln CMC_{12,t}}{d\alpha_1} = \left(\frac{1}{1-X} + 2\,\beta^{\sigma}{}_{LL}X\right)\frac{dX}{d\alpha_1} - \frac{1}{1-\alpha_1}\,, \qquad [95]$$

where it is assumed that K_2 and φ do not change with change in α_1.

Using the basic equations of nonideal solution theory, equations analogous to [59] and [60] can be derived for mixed micelle formation in a two-phase, liquid-liquid system:

$$CMC_{12,t}\alpha_1 = \frac{F^0{}_1}{F_1}\, CMC^0{}_{1,t}X^M \cdot \exp\, \beta^M{}_{LL}(1-X^M)^2 \qquad [96]$$

and

$$CMC_{12,t}(1-\alpha_1) = \frac{F^0_2}{F_2} CMC^0_{2,t}(1-X^M) \bullet \exp[\beta^M_{LL}(X^M)^2]. \quad [97]$$

Taking natural logs and differentiating [96] and [97] with respect to α_1 , one obtains :

$$\frac{d \ln CMC_{12,t}}{d\alpha_1} = \frac{-1}{\alpha_1} + \left(\frac{1}{X^M} - 2\beta^M_{LL}(1-X^M)\right)\frac{dX^M}{d\alpha_1} \quad [98]$$

and

$$\frac{d \ln CMC_{12,t}}{d\alpha_1} = \frac{-1}{1-\alpha_1} + \left(\frac{1}{1-X^M} - 2\beta^M_{LL}X^M\right)\frac{dX^M}{d\alpha_1}, \quad [99]$$

respectively, where it is assumed that K_1 and K_2 do not change with change in α_1.

From Eqs. [98], [94], [99], and [95], one obtains:

$$\frac{\dfrac{1}{X} - 2\beta^\sigma_{LL}(1-X)}{\dfrac{1}{1-X} - 2\beta^\sigma_{LL}X} = \frac{\dfrac{1}{X^M} - 2\beta^M_{LL}(1-X^M)}{\dfrac{1}{1-X^M} - 2\beta^M_{LL}X^M} \quad [100]$$

which reduces to:

$$X = X^M . \qquad [101]$$

Relationship [101] states that when a maximum or a minimum occurs in the $\gamma_{CMC,12,t}$ vs α_1 curve, the composition of the mixed monolayer at the liquid-liquid interface must equal the composition of the mixed micelles of the system.

Combining [88], [96], and [101], and taking natural logs yields:

$$\ln CMC^0_{1,t} - \ln C^{0,CMC}_{1,t} = (\beta^\sigma_{LL} - \beta^M_{LL})(1-X)^2 \qquad [102]$$

and combining [89], [97], and [101] gives:

$$\ln CMC^0_{2,t} - \ln C^{0,CMC}_{2,t} = (\beta^\sigma_{LL} - \beta^M_{LL})(X)^2 . \qquad [103]$$

Substituting [90] into [102] gives:

$$S'_1 + S_1 \ln CMC^0_{1,t} - \gamma_{CMC,12,t} = S_1 (\beta^\sigma_{LL} - \beta^M_{LL})(1-X)^2 .$$

Since,

$$\gamma^0_{CMC,1,t} = S'_1 + S_1 \ln CMC^0_{1,t} ,$$

where $\gamma^0_{CMC,1,t}$ is the interfacial tension in a pure surfactant 1 system at the critical micelle concentration for the entire system,

$$\gamma^0_{CMC,1,t} - \gamma_{CMC,12,t} = S_1 (\beta^\sigma_{LL} - \beta^M_{LL})(1-X)^2 \qquad [104]$$

By the same line of reasoning, using [91] in [103]:

$$\gamma^0_{CMC,2,t} - \gamma_{CMC,12,t} = S_2 (\beta^\sigma_{LL} - \beta^M_{LL})(X)^2 , \qquad [105]$$

where $\gamma^0_{CMC,2,t}$ is the interfacial tension in a pure surfactant 2 system at the critical micelle concentration for the entire system.

Conditions for the existence of synergism and negative synergism in interfacial tension reduction effectiveness.

1. Synergism in this respect is present in a system when $\gamma_{CMC,12,t}$ less than $\gamma^0_{CMC,1,t}$ and $\gamma^0_{CMC,2,t}$. From [104] and [105], since the slopes S_1 and S_2 are always negative and the quantities $(1-X)^2$ and $(X)^2$ are always positive, then the value of $(\beta^{\sigma}_{LL} - \beta^{M}_{LL})$ must be negative for synergism in interfacial tension reduction effectiveness to be present. When $\gamma_{CMC,12,t}$ is greater than $\gamma^0_{CMC,1,t}$ and $\gamma^0_{CMC,2,t}$, negative synergism in this respect exists. The necessary condition for negative synergism in this respect is that $(\beta^{\sigma}_{LL} - \beta^{M}_{LL})$ must be positive.

2. Combining [88] and [89] one obtains:

$$\ln C^{0,CMC}_{1,t} - \ln \alpha_1 + \ln X + \ln (F^0_1/F_1) + \beta^{\sigma}_{LL}(1-X)^2 =$$
$$\ln C^{0,CMC}_{2,t} - \ln (1-\alpha_1) + \ln(1-X) + \ln (F^0_2/F_2) + \beta^{\sigma}_{LL}(X)^2. \quad [106]$$

Combining [96] and[97] yields:

$$\ln CMC^0_{1,t} - \ln \alpha_1 + \ln X^M + \ln (F^0_1/F_1) + \beta^M_{LL}(1-X^M)^2 =$$
$$\ln CMC^0_{2,t} - \ln (1-\alpha_1) + \ln(1-X^M) + \ln (F^0_2/F_2) + \beta^M_{LL}(X^M)^2. \quad [107]$$

Combining [107], [106], and [101] gives:

$$\ln\left(\frac{C^{0,CMC}_{1,t}}{C^{0,CMC}_{2,t}} \cdot \frac{CMC^{0}_{2,t}}{CMC^{0}_{1,t}}\right) = (\beta^{\sigma}_{LL} - \beta^{M}_{LL})(2X-1) \ . \qquad [108]$$

From Eq. [108], since $|2X-1| < 1$, the second condition for either a minimum or a maximum to exist in the $\gamma_{CMC,12,t}$ vs α_1 is:

$$\left|\beta^{\sigma}_{LL} - \beta^{M}_{LL}\right| > \left|\ln\left(\frac{C^{0,CMC}_{1,t}}{C^{0,CMC}_{2,t}} \cdot \frac{CMC^{0}_{2,t}}{CMC^{0}_{1,t}}\right)\right| . \qquad [109]$$

Since, in relationship [109], β^{σ}_{LL} and the ratio $C^{0,CMC}_{1,t} / C^{0,CMC}_{2,t}$, change somewhat with γ_I, values are best calculated, when synergism occurs, at γ_I values less than both γ^{0}_{1} and γ^{0}_{2}; and when negative synergism occurs, at values greater than both γ^{0}_{1} and γ^{0}_{2}.

In summary, the conditions for the existence of synergism in intefacial tension reduction effectiveness, when the partition coefficients (K_1 and K_2) and the volume ratio (φ) do not change with α_1, are:

1. $\beta^{\sigma}_{LL} - \beta^{M}_{LL} < 0$
2. $\left|\beta^{\sigma}_{LL} - \beta^{M}_{LL}\right| > \left|\ln\left(\frac{C^{0,CMC}_{1,t}}{C^{0,CMC}_{2,t}} \cdot \frac{CMC^{0}_{2,t}}{CMC^{0}_{1,t}}\right)\right| .$

Condition 2 can be simplified by choosing $C^{0,CMC}_{t} = CMC^{0}_{t}$ (i.e. γ_I at the cmc) for the individual surfactant with the lower interfacial tension at the cmc. If this is surfactant 1, the condition reduces to:

2a. $$\left|\beta^{\sigma}{}_{LL}-\beta^{M}{}_{LL}\right| > \left|\ln\left(\frac{CMC^{0}{}_{2,t}}{C^{0,CMC}{}_{2,t}}\right)\right|,$$

and this situation is shown in Figure 1. If surfactant 2 has the lower interfacial tension value at the cmc, condition 2 becomes:

2b. $$\left|\beta^{\sigma}{}_{LL}-\beta^{M}{}_{LL}\right| > \left|\ln\left(\frac{C^{0,CMC}{}_{1,t}}{CMC^{0}{}_{1,t}}\right)\right|.$$

This situation is shown in Figure 2. The conditions for the existence of negative synergism in intefacial tension reduction effectiveness, when the partition coefficients (K_1 and K_2) and the volume ratio (φ) do not change with α_1, are:

1. $\beta^{\sigma}{}_{LL}-\beta^{M}{}_{LL} > 0$
2. $$\beta^{\sigma}{}_{LL}-\beta^{M}{}_{LL} > \left|\ln\left(\frac{C^{0,CMC}{}_{1,t}}{C^{0,CMC}{}_{2,t}}\cdot\frac{CMC^{0}{}_{2,t}}{CMC^{0}{}_{1,t}}\right)\right|.$$

In analogous fashion to condition 2 for synergism in this respect, condition 2 for negative synergism can be simplified by choosing γ_I at the cmc for the individual surfactant with the higher value (of γ_I at its cmc). If this is surfactant 1, the condition reduces to:

2a. $$\beta^{\sigma}{}_{LL}-\beta^{M}{}_{LL} > \left|\ln\left(\frac{CMC^{0}{}_{2,t}}{C^{0,CMC}{}_{2,t}}\right)\right|,$$

This situation is shown in Figure 3. When surfactant 2 has the higher value of γ_I at its cmc,

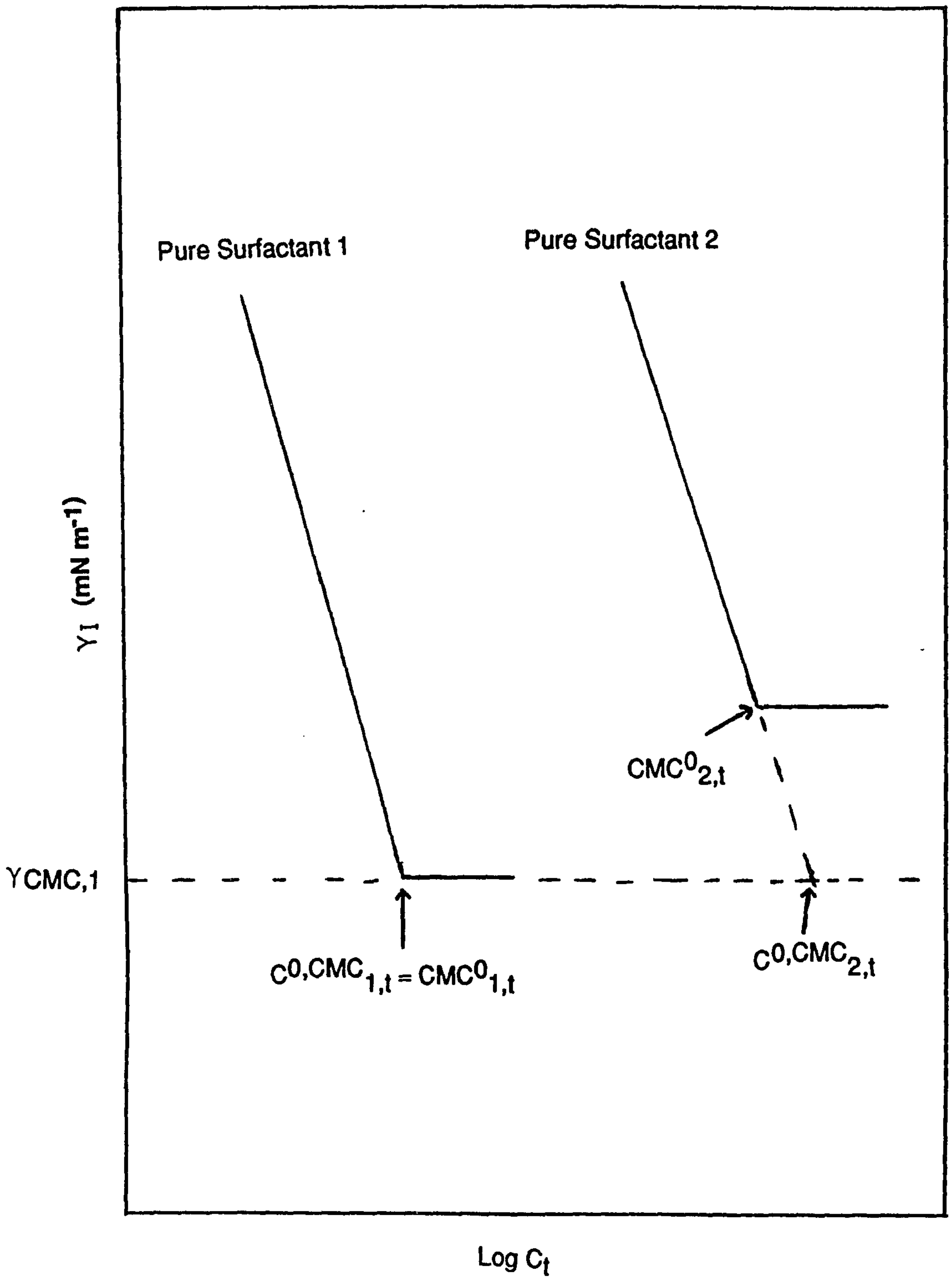

Figure 1. Method for determining $C^{0,CMC}_{1,t}$, $CMC^0_{1,t}$, $C^{0,CMC}_{2,t}$, and $CMC^0_{2,t}$ when $\gamma_{CMC,1}$ is less than $\gamma_{CMC,2}$ and synergism may exist.

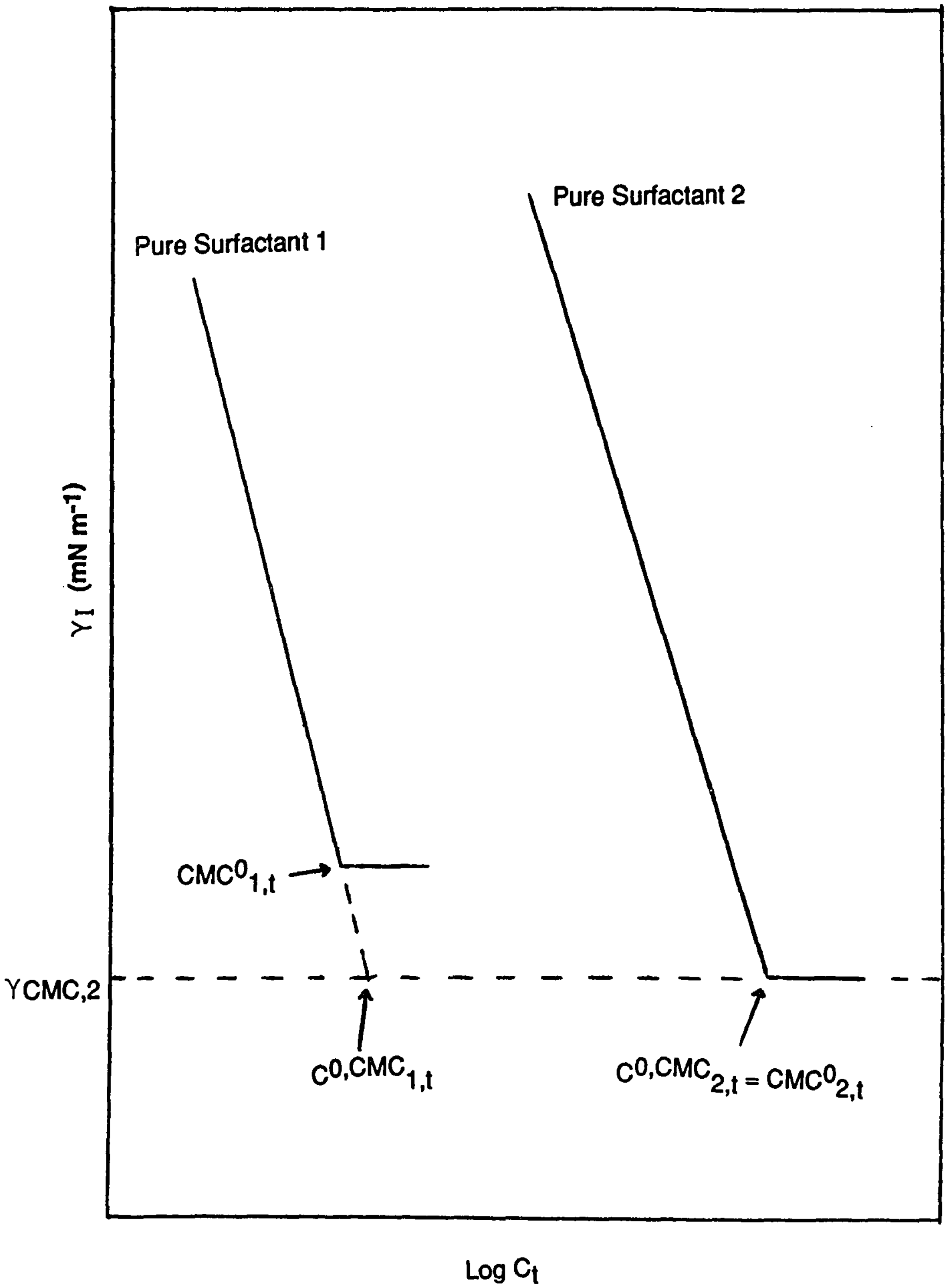

Figure 2. Method for determining $C^{0,CMC}_{1,t}$, $CMC^{0}_{1,t}$, $C^{0,CMC}_{2,t}$, and $CMC^{0}_{2,t}$ when $\gamma_{CMC,2}$ is less than $\gamma_{CMC,1}$ and synergism may exist.

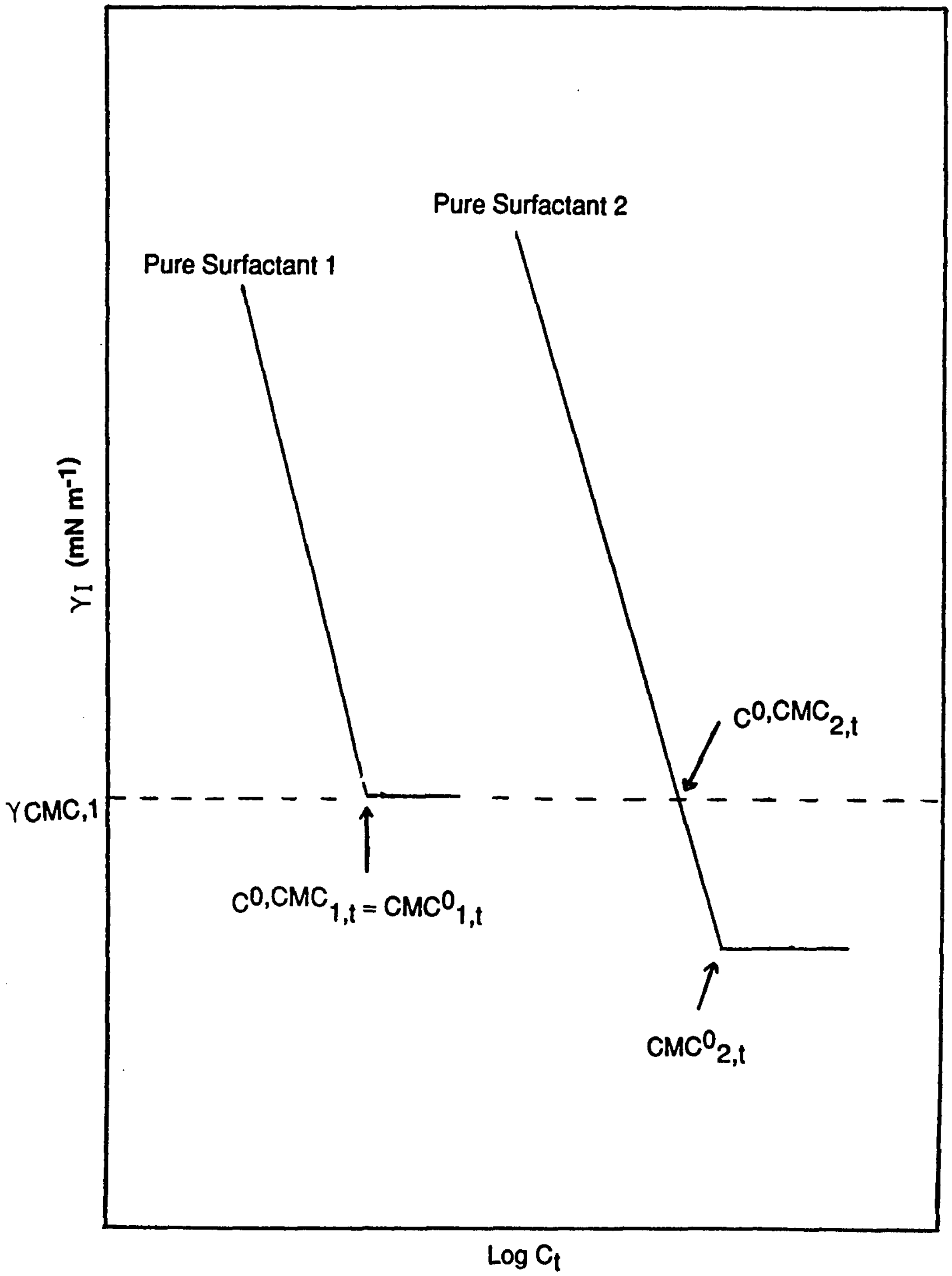

Figure 3. Method for determining $C^{0,CMC}_{1,t}$, $CMC^0_{1,t}$, $C^{0,CMC}_{2,t}$, and $CMC^0_{2,t}$ when $\gamma_{CMC,1}$ is greater than $\gamma_{CMC,2}$ and negative synergism may exist.

$$2b. \quad \beta^{\sigma}{}_{LL} - \beta^{M}{}_{LL} > \left| \ln\left(\frac{C^{0,CMC}{}_{1,t}}{CMC^{0}{}_{1,t}} \right) \right| .$$

This situation is shown in Figure 4.

Conditions at the point of maximum synergism.

Dividing Eq. [104] by Eq. [105], yields:

$$\frac{\gamma^{0}{}_{CMC,1,t} - S_1(\beta^{\sigma}{}_{LL} - \beta^{M}{}_{LL})(1-X^*)^2}{\gamma^{0}{}_{CMC,2,t} - S_2(\beta^{\sigma}{}_{LL} - \beta^{M}{}_{LL})(X^*)^2} = 1 \qquad [110]$$

where X^* is the mole fraction of surfactant 1 in the total surfactant at the liquid-liquid interface at the point of maximum synergism in this respect. Eq. [110] is solved numerically for X^* (Eq. [108] can be solved for X to give a first estimate of X^*). From Eq. [107],

$$\ln \frac{\alpha_1}{1-\alpha_1} = \ln \frac{CMC^{0}{}_{1,t}}{CMC^{0}{}_{2,t}} + \ln \frac{X^M}{1-X^M} + \beta^{M}{}_{LL}(1-2X^M)$$

$$+ \ln \frac{F^{0}{}_{1}F_2}{F^{0}{}_{2}F_1} , \qquad [111]$$

from which,

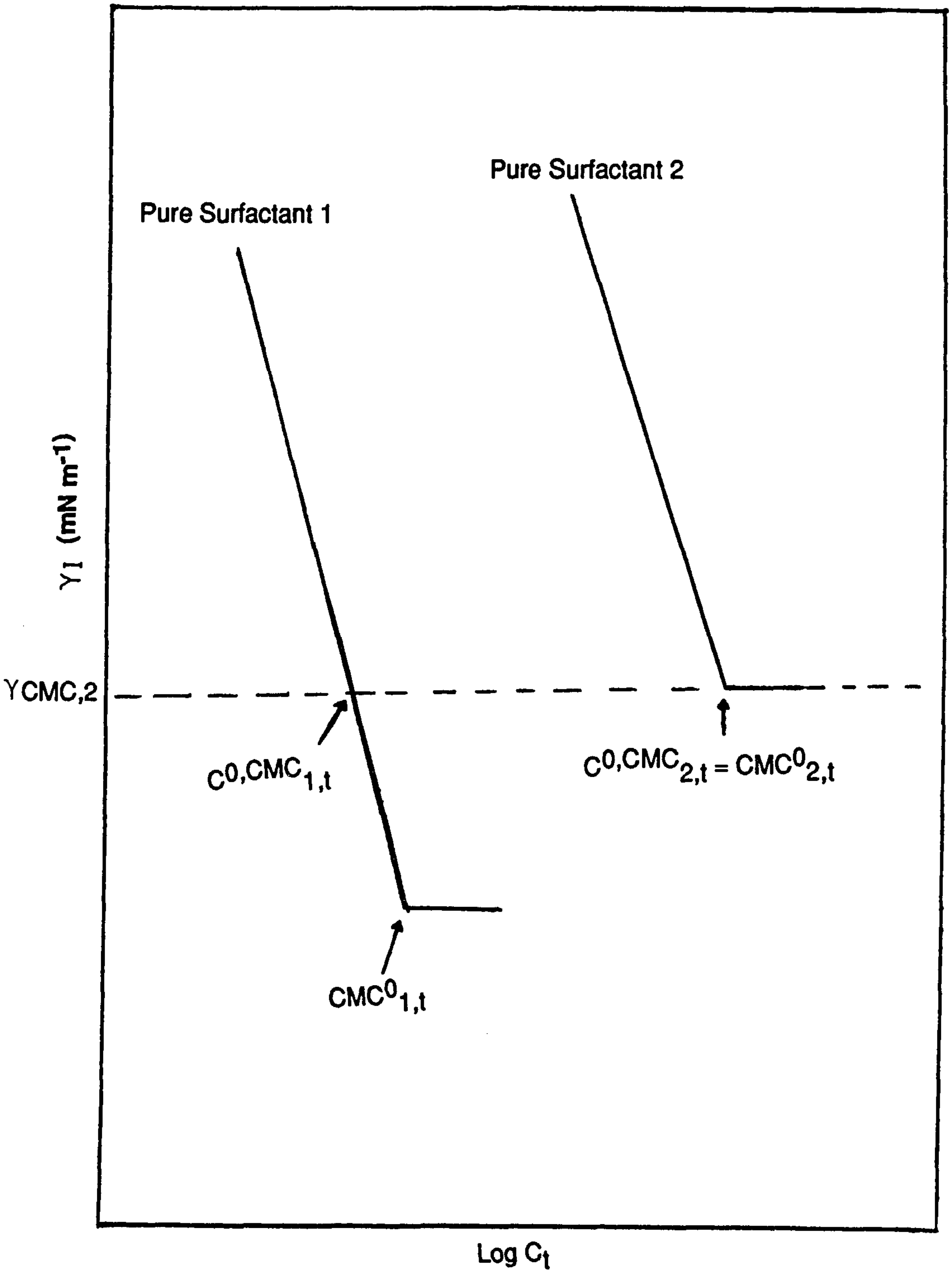

Figure 4. Method for determining $C^{0,CMC}_{1,t}$, $CMC^{0}_{1,t}$, $C^{0,CMC}_{2,t}$, and $CMC^{0}_{2,t}$ when $\gamma_{CMC,2}$ is greater than $\gamma_{CMC,1}$ and negative synergism may exist.

$$\alpha_1 = \frac{\dfrac{CMC^0_{1,t}}{CMC^0_{2,t}} \bullet \dfrac{F^0_1F_2}{F^0_2F_1} \bullet \dfrac{X^M}{1-X^M} \bullet \exp \beta^M_{LL}(1-2X^M)}{1 + \left(\dfrac{CMC^0_{1,t}}{CMC^0_{2,t}} \bullet \dfrac{F^0_1F_2}{F^0_2F_1} \bullet \dfrac{X^M}{1-X^M} \bullet \exp \beta^M_{LL}(1-2X^M)\right)} \quad . \quad [112]$$

Since relationship [101] applies at the point of maximum synergism, $X^* = X^M$ at this point, and substitution in [112] for X^M gives:

$$\alpha^{*,E}_1 = \frac{\dfrac{CMC^0_{1,t}}{CMC^0_{2,t}} \bullet \dfrac{F^0_1F_2}{F^0_2F_1} \bullet \dfrac{X^*}{1-X^*} \bullet \exp \beta^M_{LL}(1-2X^*)}{1 + \left(\dfrac{CMC^0_{1,t}}{CMC^0_{2,t}} \bullet \dfrac{F^0_1F_2}{F^0_2F_1} \bullet \dfrac{X^*}{1-X^*} \bullet \exp \beta^M_{LL}(1-2X^*)\right)} \quad , \quad [113]$$

where $\alpha^{*,E}_1$ is the mole fraction of surfactant 1 in the total mixed surfactant solution at the point of maximum synergism in this respect. When either of the first two conditions for the elimination of partition coefficient values is satisfied, [113] becomes:

$$\alpha^{*,E}_1 = \frac{\dfrac{CMC^0_{1,t}}{CMC^0_{2,t}} \bullet \dfrac{X^*}{1-X^*} \bullet \exp \beta^M_{LL}(1-2X^*)}{1 + \left(\dfrac{CMC^0_{1,t}}{CMC^0_{2,t}} \bullet \dfrac{X^*}{1-X^*} \bullet \exp \beta^M_{LL}(1-2X^*)\right)} \quad . \quad [114]$$

Substituting the values of X^* and $\alpha^{*,E}_1$ into Eq. [96] yields:

$$CMC^*_{12,t} = CMC^0_{1,t} \bullet \frac{F^0_1}{F_1} \bullet \frac{X^*}{\alpha^{*,E}_1} \bullet \exp\left[\beta^M_{LL}(1-X^*)^2\right] \qquad [115]$$

where $CMC^*_{12,t}$ is the critical micelle concentration for the entire system at the point of maximum synergism in interfacial tension resuction effectiveness. When either of the first two conditions for the elimination of partition coefficient values is satisfied, [101] becomes:

$$CMC^*_{12,t} = CMC^0_{1,t} \bullet \frac{X^*}{\alpha^{*,E}_1} \bullet \exp[\beta^M_{LL}(1-X^*)^2] \ . \qquad [116]$$

Substituting the values of x^* and $\alpha^{*,E}_1$ into Eq. [90] yields:

$$\gamma^*_{CMC,12,t} = \gamma^0_{CMC,1,t} - S_1 (\beta^\sigma_{LL} - \beta^M_{LL})(1-X^*)^2 \qquad [117]$$

where $\gamma^*_{CMC,12,t}$ is the lowest interfacial tension attainable at the cmc of any mixture of the two components.

When an ionic surfactant in a mixture is used in the absence of a swamping amount of electrolyte, the above method of solving [110] numerically for X^* gives erroneous results for $\alpha^{*,E}_1$, $CMC^*_{12,t}$, and $\gamma^*_{CMC,12,t}$, due to the lack of constant ionic strength at different α_1 values. Use of a cruder method, which assumes $X_1 = X_2 = 0.5$ (108) at the point of maximum synergism in interfacial and $\gamma^{*}_{CMC,12,t}$ in the absence of a swamping amount of electrolyte because this method is not as sensitive to the change in ionic strength with change in α_1. This is the only case where the cruder method is preferred for calculating the synergism parameters in interfacial tension reduction effectiveness. The equations for the calculation of synergism parameters when X is assumed to equal 0.5 are derived as follows. From, [96], [97], and [101]:

$$\alpha^{*,E}_1 = \frac{F_2 F^0_1 CMC^0_{1,t}}{F_2 F^0_1 CMC^0_{1,t} + F_1 F^0_2 CMC^0_{2,t}} \qquad [118]$$

When either of the first two conditions for the elimination of partition coefficient values is satisfied:

$$\alpha^{*,E}_1 = \frac{CMC^0_{1,t}}{CMC^0_{1,t} + CMC^0_{2,t}} \, . \qquad [119]$$

Introducing [118] into [96] or [97] gives:

$$CMC^{*}_{12,t} = \frac{F_2 F^0_1 CMC^0_{1,t} + F_1 F^0_2 CMC^0_{2,t}}{2F_1 F_2} \bullet \exp \frac{\beta^M_{LL}}{4} , \qquad [120]$$

or, when either of the first two conditions for the elimination of partition coefficient values is satisfied:

$$CMC^{*}_{12,t} = \frac{CMC^0_{1,t} + CMC^0_{2,t}}{2} \bullet \exp \frac{\beta^M_{LL}}{4} . \qquad [121]$$

Finally, from [104] and [105], and using the assumption X = 0.5:

$$\gamma^{*}_{CMC,12,t} = \gamma^{o}_{CMC,1(2),t} - \frac{S_{1(2)}(\beta^{\sigma}_{LL} - \beta^{M}_{LL})}{4} \qquad [122]$$

Best agreement between calculated $\gamma^{*}_{CMC,12,t}$ and experimental values is obtained when the individual surfactant having the larger (negative) slope in its γ_I vs $\ln C_t$ plot is used.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Surfactants

Sodium dodecanesulfonate, $C_{12}H_{25}SO_3^-Na^+$ ($C_{12}S$) > 99% purity (Research Plus, Bayonne, N.J.). N-dodecyl-N-benzyl-N-methylglycine, $C_{12}H_{25}N^+(CH_2C_6H_5)(CH_3)CH_2COO^-$ ($C_{12}BMG$) > 98% purity and synthesized in this laboratory (109). $C_{12}H_{25}(OC_2H_4)_xOH$ ($C_{12}EO_x$), where x=8,7,4,3,2, and $C_{16}H_{33}(OC_2H_4)_8OH$ ($C_{16}EO_8$), > 98% purity as indicated by gas chromatography (Nikko Chemical Co., Tokyo, Japan). $C_{12}H_{25}OH$ ($C_{12}OH$) purchased as reagent grade (Aldrich) and purified to > 99% purity (as measured by gas chromatography) by fractional distillation. N-dodecyl-2-pyrrolidine ($C_{12}P$), N-decyl-2-pyrrolidine ($C_{10}P$), and N-octyl-2-pyrrolidine (C_8P) > 99% purity as indicated by gas chromatography (GAF Corp. Wayne, N.J.). Two isomeric compounds $C_{16}H_{33}(OC_2H_4)_5SO_4Na$ where in both compounds the hydrophobic group has C_6 and C_8 alkyl groups attached to the β carbon, but in one ($C_{16}HGEO_5S$) the groups are both straight chain and in the other ($C_{16}EGEO_5S$) they are both branched. Both compounds are > 92% purity by titration. Analogous unsulfated alcohols $C_{16}HGEO_5OH$ and $C_{16}EGEO_5OH$ were > 95% purity (Exxon Research and Engineering, Annendale, N.J.)

Before being used for interfacial tension measurements, aqueous solutions of most of the surfactants (in water that had first been deionized and then distilled twice, the last time through a 1-m-high Vigreaux column with quartz condenser and receiver) were further purified by repeated passage (110) through minicolumns of octadecylsilanized silica gel to remove impurities more interfacially active than the parent compound. Surfactants not further purified in this way were $C_{12}EO_{2,3,4}$, $C_{12}OH$, $C_{12}P$, $C_{16}EO_8$, $C_{16}HGEO_5OH$, and $C_{16}EGEO_5OH$.

The surfactants used for the emulsion studies were not sent through the minicolumns.

The surfactants were analyzed for concentration as follows: anionics, by a two-phase, mixed-indicator (111) technique; zwitterionics, by UV spectroscopy ($\varepsilon_{C12BMG,263nm}$ = 355 (109)); nonionics, by UV spectroscopy ($\varepsilon_{C8P,\ 191nm}$ = 7.94 x 10^3; $\varepsilon_{C10P,\ 191nm}$ = 7.48 x 10^3), by surface tension, or by weight.

Hydrocarbons

The hydrocarbons used were hexadecane and heptamethylnonane, > 98% (Humphrey); dodecane and isooctane, > 99% (Aldrich); heptane, spectro grade (Eastman); cyclohexane and toluene, certified A.C.S. spectanalyzed (Fisher).

The UV absorbance of each of the saturated hydrocarbons was measured at 255nm against a blank of 95% ethanol when received. If the absorbance was less than 0.015, the saturated hydrocarbon was passed through a 31 x 3.4 cm column (Fisher and Porter Co.) of silica gel 922 (Will Corp.) that had been heated at 120°C for 3 hr. before use, until the absorbance was less than 0.015. The toluene was used as received.

3.2 Interfacial Tension Measurements

The spinning drop technique was used. The instrument used was a Model 500 interfacial tensiometer (University of Texas). For a droplet of oil inside an aqueous phase (i.e., density water > density oil), Vonnegut's equation (112):

$$\gamma_I = \frac{(5.21 \times 10^5)(\Delta \rho)(r^3{}_o)}{P^2} \qquad [123]$$

yields γ_I in dyne/cm, where $\Delta\rho$ is the density of the water minus the density of the oil in g/cm^3, r_o is the radius of the oil droplet in cm, and P^2 is the speed of the rotation in msec/rev. Equation [123] can only be used if the length of the oil droplet is four times its diameter. Readings were taken at 5 minute intervals after pre-equlibration until three consecutive readings coincided to within 0.1 mN/m. The density of water was taken as 0.9970 g/cm^3 and that of the oils (g/cm^3) as:

hexadecane, 0.773; dodecane 0.749; heptane, 0.684; cyclohexane, 0.779; isooctane, 0.692; heptamethylnonane, 0.793; toluene, 0.867.

3.3 Partition Coefficients (C_B/C_W)

Partition coefficient values for various surfactants are listed in Table 1. For pure C_{12}BMG, and in its mixture with C_{12}S, 100 ml of the surfactant solution was overlayed with 50 ml of heptane and this two-phase system was allowed to stand for 1 month to ensure that equilibrium was achieved (113). The partition coefficient of pure C_{12}BMG was obtained by determining the concentration in the initial aqueous solution by using UV spectroscopy, $\varepsilon_{C12BMG,263nm}$ = 355 L mol^{-1} cm^{-1} (109), then determining the concentration in the aqueous phase of the final two-phase system. The partition coefficient of C_{12}BMG in the presence of C_{12}S was determined the same way as for pure C_{12}BMG since C_{12}S does not absorb in the UV. (Data are listed in Table A1 in appendix A.)

For pure C_8P in the hexadecane/H_2O system, 25 ml of a 3 x 10^{-3}M aqueous solution was overlayed with 10 ml of hexadecane and allowed to partition to equilibrium (after 1 month aliquots of the aqueous phase were analyzed by UV spectrometry at 191 nm. No change in absorbance occurred after 1 month). The concentration of C_8P in the water phase was then determined by UV absorbance at 191 nm, $\varepsilon_{C8P,191nm}$ = 7.94 x 10^3 L mol^{-1} cm^{-1} (114), and its partition coefficient calculated. (Data are listed in Table A2.)

For pure C_8P and C_{10}P in hexadecane/aq. soln., 0.1M NaCl solution systems, known volumes and concentrations of C_8P and C_{10}P solutions in 0.1M NaCl were overlayed with measured volumes of hexadecane and allowed to partition to equilibrium (as described above). The concentration of C_8P or C_{10}P in the aqueous phase was determined from its UV absorbance at 191 nm (data are listed in Tables A2 and A3), compared to those of standard C_8P and C_{10}P solutions in 0.1M NaCl, since the ε values of these compounds change in the presence of electrolyte (Tables A4 and A5, and, Figures A1 and A2). The possibility of hexadecane dissolved in the

TABLE 1: Partition coefficient values at 25.0 ± 0.1°C

Surfactant 1 (surfactant 2)	Interface	$K_1(=C_B/C_W)$	α_1
$C_{12}BMG$	heptane/H_2O	$8.6_2 \times 10^{-3}$	–
$C_{12}BMG$ ($C_{12}S$)	heptane/H_2O	$6.9_3 \times 10^{-3}$	0.55_7
C_8P	hexadecane/H_2O	2.2×10^1	–
C_8P	hexadecane/aq. soln., 0.1M NaCl	3.0×10^1	–
C_8P ($C_{12}S$)	hexadecane/aq. soln., 0.1M NaCl	1.6×10^1	0.72
C_8P ($C_{12}S$)	hexadecane/aq. soln., 0.1M NaCl	2.0×10^1	0.62
$C_{10}P$	hexadecane/aq. soln., 0.1M NaCl	3.4×10^2	–
$C_{10}P$ ($C_{12}S$)	hexadecane/aq. soln., 0.1M NaCl	2.3×10^2	0.59
$C_{12}S$	hexadecane/aq. soln., 0.1M NaCl	<0.015	–
$C_{12}S$ (C_8P)	hexadecane/aq. soln., 0.1M NaCl	0.054	0.41
$C_{12}S$ ($C_{10}P$)	hexadecane/aq. soln., 0.1M NaCl	0.046	0.35
$C_{16}EGEO_5S$	hexadecane/aq. soln., 0.1M NaCl	0.037_7	

aqueous phase affecting the calculated concentrations after partitioning was eliminated by 1) using hexadecane-saturated water or hexadecane-saturated aqueous 0.1M NaCl solution as the blank and 2) saturating solutions of C_8P or $C_{10}P$ of known concentration with hexadecane and observing no change in ε values. For C_8P and $C_{10}P$, each in its mixture with $C_{12}S$, 12 mL of aqueous 0.1M NaCl containing the $C_{12}S$ was shaken intermittently over a period of two hours with 0.3 ml of hexadecane containing the C_8P or $C_{10}P$. The resulting emulsion was then broken by centrifugation and the optically clear aqueous phase was analyzed for the N-alkyl-2-pyrrolidone concentration by UV absorbance at 191 nm (further shaking produced no change in absorbance; data are listed in Tables A2 and A3). The $C_{12}S$ had no absorbance at 191 nm at the concentrations used. For the $C_{12}S$, 75 ml of an aqueous 0.1M NaCl solution of $C_{12}S$ was shaken with 10 ml of hexadecane containing the N-alkyl-2-pyrrolidone. The emulsion was allowed to break and 50 ml of the aqueous phase was analyzed by the two-phase titration technique (111) to determine the $C_{12}S$ concentration. (Data is listed in Table A6.)

For $C_{16}EGEO_5S$, 50 ml of $2.7_0 \times 10^{-4}$ M surfactant in 0.1M NaCl aqueous solution was overlayed with 25 ml of hexadecane and allowed to stand for one month after which a 25 ml aliquot of the aqueous phase was titrated for $C_{16}EGEO_5S$ concetration using the two-phase technique (111). (Data are listed in Table A7.)

3.4 Kφ and α Values

In all of the systems studied, φ was held constant such that $\varphi = \varphi^0{}_1 = \varphi^0{}_2 = 0.025$ (except $C_{12}EO7/C_{12}S$ which has $\varphi = \varphi^0{}_1 = \varphi^0{}_2 = 0.012_3$). One of the conditions for the elimination of partition coefficient values ($K\varphi << 1$ or that $\alpha_1 \rightarrow 0$ or 1) was met for all the systems investigated except the $C_8P, C_{10}P/C_{12}S$ systems. For these systems, $K\varphi$ for $C_{12}S$ was << 1, but for the N-alkyl-2-pyrrolidones, this was not true, and the K values measured in the mixtures (Table 1) were found to be different than in their pure systems. So, F_1, $F^0{}_1$, F_2, and $F^0{}_2$ were included in the pertinent equations for this system.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Interfacial Properties and Micellization of Pure, Individual Surfactants in Hydrocarbon/Aqueous Systems

4.1.1 Nonionic Surfactants

Plots of γ_I vs -log C_W (or -log C_t) for the nonionic surfactants $C_{12}EO_8$, $C_{12}EO_4$, $C_{12}EO_3$, $C_{12}EO_2$, $C_{16}EO_8$, $C_{16}HGEO_5OH$, $C_{16}EGEO_5OH$, C_8P, $C_{10}P$, and $C_{12}P$ are shown in figures B1-B5 (appendix B). These plots were constructed using the interfacial tension vs -log C_W (or -log C_t) data in Tables B1-B17.

The minimum areas per molecule, A_{min}, were calculated using equation [3]. Γ_{max} values were calculated using equation [1]. Values of A_{min}, Γ_{max}, and Π_{max} for the nonionic surfactants are listed in Table 2 (below).

Cmc_w values for $C_{12}EO_8$ were taken as the concentrations at the points of intersection of the two linear portions of the γ_I vs log C_W plots. Since $K(=C_B/C_W)$ of the $C_{12}EO_8$ is approximately equal to one (118) and the volume of the oil phase used was extremely small, all the $C_{12}EO_8$ can be considered to be in the water phase after partition. Table 4 lists the values of γ_{min}, cmc_w, $pC_{30,w}$, and cmc/C_{30} for the nonionic surfactants.

The standard free energy of adsorption, ΔG°_{ads}, and the free energy of micellization, ΔG°_{mic}, for $C_{12}EO_8$, C_8P, and $C_{10}P$ were calculated using equations [9] and [16], respectively. Values are listed in Table 5.

The A_{min} values (Table 2) for $C_{12}EO_8$ in the various hydrocarbon/water systems are found to be about 3Å^2 smaller than for the corresponding air/water system for the straight-chain hydrocarbon systems, and about the same value as for the corresponding air/water system for the branched and cyclic hydrocarbons. The 3Å^2 decrease in the straight-chain hydrocarbon/water systems has three consequences (119): 1) The head groups, which repel each other, are closer together. This is an energetically unfavorable change. 2) Surfactant hydrophobic tails have less conformational positions available to them, and surfactant tail-hydrocarbon interactions are reduced. This is a combination of two effects, both unfavorable. 3) The hydrocarbon/water interface becomes smaller. This is a favorable effect. Gruen and Haydon (119) suggest that compressing the head groups relative to the equilibrium A_{min} value in the air/water system is the largest barrier to contraction of the interfacial film in the liquid-liquid system. It therefore appears that the energy of interaction of the straight-chain hydrocarbon with the surfactant tails in the interfacial film (as measured by ΔG°_{ads}, Table 5) must supply the necessary energy for the compression of the EO_8 heads, resulting in the 3Å^2 contraction. With the branched chain and cyclic hydrocarbons, the bulkiness of these molecules intercalated between the $C_{12}EO_8$ tails in the interfacial film appears to cause a steric inhibition to contraction, and therefore the A_{min} value in the hydrocarbon/water system is about the same as for $C_{12}EO_8$ in the air/water system.

The effect on A_{min} of reducing the number of EO groups in the C_{12} polyoxyethylenated (POE) nonionics (down to $C_{12}EO_2$) (Table 2) in hexadecane/water systems is first the expected decrease with decrease in the length of the POE chain (similar to that found at the air/water interface (115)) , and then an increase at $C_{12}EO_2$ due to increased solubility of the surfactant in the oil phase. (Approximate partition coefficient values for nonionic surfactants can be calculated by using the cmc_t values from figures B3 and B4 and assuming that the concentration in the aqueous phase at this point equals cmc_w, values of which are known from references 115-117. This assumption is reasonable since it is known

TABLE 2: Interfacial properties of nonionic surfactants at 25.0°C. I: A_{min}, Γ_{max}, γ_{min}, Π_{max}. (Values in parentheses are at the corresponding air/aqueous solution interface.)

Surfactant	System	A_{min}/Å^2	$\Gamma_{max} \times 10^{10}$/ mol cm^{-2}	γ_{min} / mN m^{-1}	Π_{max}/ mN m^{-1}
$C_{12}EO_8$	hexadecane/H_2O	$63._0$ ($66._0$[a])	2.6_4	3.4_1	$48._7$($37._2$[a])
$C_{12}EO_8$	dodecane/H_2O	$62._1$ ($66._0$[a])	2.6_7	3.1_0	$48._9$($37._2$[a])
$C_{12}EO_8$	heptane/H_2O	$63._3$ ($66._0$[a])	2.6_2	1.7_0	$48._5$($37._2$[a])
$C_{12}EO_8$	cyclohexane/H_2O	$67._7$ ($66._0$[a])	2.4_5	1.2_7	$48._9$($37._2$[a])
$C_{12}EO_8$	isooctane/H_2O	$66._0$ ($66._0$[a])	2.5_2	2.2_0	$48._0$($37._2$[a])
$C_{12}EO_8$	heptamethylnonane/H_2O	$65._6$ ($66._0$[a])	2.5_3	3.0_0	$48._8$($37._2$[a])
$C_{12}EO_4$	hexadecane/H_2O	$52._6$($45._7$[a])	3.1_6	0.05	$52._1$($43._3$[a])
$C_{12}EO_3$	hexadecane/H_2O	$50._0$($41._8$[a])	3.3_2	0.18	$51._9$($44._1$[a])
$C_{12}EO_2$	hexadecane/H_2O	$55._6$($35._1$[a])	2.9_9	4.5_2	$47._6$($45._7$[a])
$C_{12}EO_2$	heptane/H_2O	$73._1$	2.2_7	6.5_0	$43._7$
$C_{16}EO_8$	hexadecane/H_2O	$54._7$(48[b])	3.0_4	1.5_0	$50._6$(37[b])
$C_{16}EGEO_5OH$	hexadecane/aq. soln., 0.1M NaCl	$70._0$(44[c])	2.3_7	1.2_8	$50._8$(39[c])
$C_{16}HGEO_5OH$	hexadecane/aq. soln., 0.1M NaCl	$65._2$	2.4_5	1.4_2	$50._7$
C_8P	hexadecane/H_2O	$42._4$($37._9$[e])	3.9_2	0.9	$51._2$($41._6$[d])
C_8P	hexadecane/aq. soln., 0.1M NaCl	$45._5$($38._9$[e])	3.6_5	-	$48._5$($41._1$[d])

TABLE 2: (Continued)

Surfactant	System	A_{min}/Å^2	$\Gamma_{max} \times 10^{10}$/ mol cm^{-2}	γ_{min} / mN m^{-1}	Π_{max}/ mN m^{-1}
$C_{10}P$	hexadecane/aq. soln., 0.1M NaCl	$61._2$	2.7_1	-	-
$C_{12}P$	hexadecane/H_2O	$58._4(32._7{}^{d})$	2.8_4	$2._4$	$49._7(45._6{}^{d})$

[a] Data from reference 115.

[b] Data from reference 116.

[c] Data from reference 117.

[d] Data from reference 114.

that saturated hydrocarbons affect cmc_w only slightly. Approximate K values are listed in Table 3.) In all of these shorter EO nonionics, the large partitioning into the oil causes the A_{min} to be larger at the liquid-liquid interface than at the water/air interface.

The A_{min} value for $C_{12}EO_2$ in the heptane water system is much larger than its value in the hexadecane/water system, presumably due to its greater oil solubility (Table 3), and greater intercalation between surfactant chains (119,120) in the former.

A_{min} values for $C_{16}EO_8$, $C_{16}EGEO_5OH$, $C_{16}HGEO_5OH$, C_8P, $C_{10}P$, and $C_{12}P$ are all larger in the hydrocarbon/aqueous systems than in the corresponding air/aqueous systems since these nonionics are very oil soluble (Tables 1 and 3). As expected, the more branched $C_{16}EGEO_5OH$ has a larger A_{min} value than the isomeric $C_{16}HGEO_5OH$, despite the fact that $C_{16}HGEO_5OH$ is more oil soluble.

The effectiveness of surfactant interfacial tension reduction can be measured by Π_{max} (Table 2). The values of this parameter in the hydrocarbon/aqueous systems are greater than the values in the corresponding air/aqueous systems for the nonionic surfactants studied. According to equation [18], this is primarily due to the larger cmc/C_{30} ratio values (Table 4) in the hydrocarbon/water systems. The Π_{max} values reflect the value of γ_{min}. In this respect, it is interesting to note that in the series $C_{12}EO_x$ in the hexadecane/water systems, when $x = 3$ or 4, the γ_{min} is very low (0.05mN m^{-1} for $x = 4$; 0.18 mN m^{-1} for $x = 3$) for a single pure surfactant slightly above the cmc. This is explained by a supplement (121) to the original theory of Israelachvilli et. al. (82), where it was shown that when $V_h/l_c a_o = 1$ (where V_h is the volume occupied by the surfactant hydrophobic tail, l_c is its length, and a_o is the area occupied by the hydrophilic head group), lamellar micelles are formed and the head-group curvature energy at the oil-water interface

TABLE 3: Approximate partition coefficient values at 25.0°C

Surfactant	System	$K=C_B/C_W$
$C_{12}EO_4$	hexadecane/H_2O	4×10^2
$C_{12}EO_3$	hexadecane/H_2O	1×10^3
$C_{12}EO_2$	hexadecane/H_2O	4×10^3
$C_{12}EO_2$	heptane/H_2O	7×10^3
$C_{16}EO_8$	hexadecane/H_2O	4×10^2
$C_{16}EGEO_5OH$	hexadecane/0.1M NaCl aq. soln.	7×10^3
$C_{16}HGEO_5OH$	hexadecane/0.1M NaCl aq. soln.	2×10^4

favors zero curvature, leading to very low interfacial tension. Since $V_h/l_c = a_c$ (where a_c is the area occupied by the hydrophobic tail (57)), when $V_hl_c/a_o = 1$, $a_c/a_o = 1$. This means that zero curvature is favored (and therefore low interfacial tension) when the hydrophilic head and the hydrophobic tail occupy the same area. Tiddy (122) has shown that, in water at room temperature, in the series $C_{12}EO_x$, when $x = 4$, lamellar micelles are formed, confirming that $V_h/l_ca_o = a_c/a_o = 1$ for this surfactant and explaining the low γ_I value obtained at the hexadecane/water interface.

Cmc_w values for $C_{12}EO_8$ (Table 4) in the hydrocarbon/water systems are all less than in the air/water system. As the solubilization of the saturated hydrocarbon into the core of the micelles increases, the micelle becomes a larger and larger swollen sphere (123), with the result that there is more room for each surfactant molecule and therefore a very slight decrease in the cmc_w. Thus, with heptane, which is solubilized to a greater extent than hexadecane, $C_{12}EO_8$ has a smaller cmc_w. Relating solubilization of the hydrocarbon into the micelle to cmc values was first proposed by Rehfeld (63). The results presented here are in agreement with his findings. Favorable interaction between the solubilizate and the hydrocarbon chains of the surfactant could also promote micellization.

The efficiency of surfactant interfacial tension reduction can be measured by $pC_{30,w}$ (Table 4). In air/aqueous systems, pC_{20} is usually used to measure a given surfactants efficiency in reducing surface tension; however, in hydrocarbon/aqueous systems, $pC_{30,w}$ is used to measure efficiency in interfacial tension reduction. The reason for this is that the measure of efficiency in this respect is usually taken at a Π value where saturation is achieved; this usually occurs at about $\Pi = 20$ mN m^{-1} in air/aqueous systems but not until about $\Pi =$

TABLE 4: Interfacial properties of nonionic surfactants at 25.0°C. II: cmc_w, $pC_{30,w}$, cmc/C_{30} (values in parentheses are for the corresponding air/aqueous solution systems)

Surfactant	System	$cmc_w \times 10^4/M$	$pC_{30,w}$	cmc/C_{30}
$C_{12}EO_8$	hexadecane/ H_2O	$1.0_2(1.0_9{}^a)$	$5.2_4(4.4_8{}^a)$	$17._5(3.3_1{}^a)$
$C_{12}EO_8$	dodecane/ H_2O	$1.0_0(1.0_9{}^a)$	$5.2_3(4.4_8{}^a)$	$17._0(3.3_1{}^a)$
$C_{12}EO_8$	heptane/ H_2O	$0.99(1.0_9{}^a)$	$5.2_7(4.4_8{}^a)$	$18._6(3.3_1{}^a)$
$C_{12}EO_8$	cyclohexane/ H_2O	$1.0_1(1.0_9{}^a)$	$5.3_4(4.4_8{}^a)$	$22._2(3.3_1{}^a)$
$C_{12}EO_8$	isooctane/ H_2O	$0.99(1.0_9{}^a)$	$5.2_5(4.4_8{}^a)$	$17._6(3.3_1{}^a)$
$C_{12}EO_8$	heptamethylnonane/H_2O	$1.0_5(1.0_9{}^a)$	$5.2_3(4.4_8{}^a)$	$17._8(3.3_1{}^a)$
$C_{12}EO_4$	hexadecane/ H_2O	b	b	$16._8(4._5{}^a)$
$C_{12}EO_3$	hexadecane/ H_2O	b	b	$14._5(4._3{}^a)$
$C_{12}EO_2$	hexadecane/ H_2O	b	b	$10._8(4._2{}^a)$
$C_{12}EO_2$	heptane/H_2O	b	b	$11._5$

TABLE 4: (Continued)

Surfactant	System	$cmc_w \times 10^4/M$	$pC_{30,w}$	cmc/C_{30}
$C_{16}EO_8$	Hexadecane/ H_2O	b	b	$20._0$
$C_{16}EGEO_5OH$	hexadecane/0.1 M NaCl aq. soln.	b	b	$43._7(2.7_3{}^c)$
$C_{16}HGEO_5OH$	hexadecane/0.1 M NaCl aq. soln.	b	b	$26._3$
C_8P	hexadecane/0.1 M NaCl aq. soln.	d	$3.2_2(2.8_2{}^e)$	-
C_8P	hexadecane/ H_2O	d	$2.9_9(2.7_3{}^e)$	-
$C_{10}P$	hexadecane/0.1 M NaCl aq. soln.	d	4.1_0	-

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[a] Data from reference 115.

[b] Only cmc_t and $pC_{30,t}$ obtainable; accurate partition coefficients not available.

[c] Data from reference 117.

[d] These compounds reach a solubiblity limit in the water phase before reaching cmc_w.

[e] Data from reference 114.

30 mN m^{-1} in hydrocarbon/aqueous systems. The $pC_{30,w}$ values are all greater (i.e., the surfactants are more efficient at reducing γ_I) in the hydrocarbon/aqueous systems than for the corresponding air/aqueous systems (pC_{30} values are used for the air/aqueous systems for comparison purposes). According to equation [17] and the data for $\Delta G°_{ads}$ (Table 5), this is due (in all cases) to the more negative $\Delta G°_{ads}$ values in the hydrocarbon/aqueous systems.

The relationship between micellization and adsorption can be measured by the cmc/C_{30} ratio (Table 4). Upon the introduction of some factor, if the cmc/C_{30} ratio increases, this indicates that micellization is inhibited more than adsorption or adsorption is facilitated more than micellization. A decrease in the cmc/C_{30} ratio indicates that adsorption is inhibited more than micellization or micellization is facilitated more than adsorption. Values for all the nonionic surfactants studied were larger in the hydrocarbon/aqueous systems than in the corresponding air/aqueous systems. As mentioned, below, in the discussion of the thermodynamic parameters of adsorption, adsorption is increased to a greater degree than micellization by the presence of the hydrocarbon phase. This may be due to the greater freedom experienced by the surfactant hydrophobic tails and hydrocarbon molecules at a planar interface than in the hydrocarbon core of a micelle, where the presence of the convex curved interface causes the core to be subject to a large Laplace pressure (124), permitting greater surfactant chain-hydrocarbon interaction in the former location. As a result, although cmc values in the hydrocarbon/aqueous systems are reduced, C_{30} values are reduced to a greater extent (i.e. introduction of the hydrocarbon facilitates adsorption more than micellization), resulting in larger cmc/C_{30} values.

For the shorter $C_{12}EO_x$ compounds, the ratio decreases as x decreases. For $C_{12}EO_4$ and $C_{12}EO_3$, the decrease in A_{min} (increase in Γ_{max}) in the γ_I vs log C_t slope (Figure B3) means that the C_{30} is being increased relative to cmc. For $C_{12}EO_2$, the γ_I vs log C_t slope decreases (i.e. C_{30} decreases relative to cmc), but the cmc decreases more than C_{30}.

The ΔG°_{mic} values in Table 5 for $C_{12}EO_8$ in the hydrocarbon/water systems are all very slightly more negative than for the air/water system. This is due to the slight decrease in cmc_w according to equation [16].

The ΔG°_{ads} values in Table 5 for the hydrocarbon/aqueous systems investigated are all considerably more negative than the values for the corresponding air/aqueous systems. This is probably due to the additional interaction (125) of the surfactant tails with the hydrocarbon phase. From the ΔG°_{mic} and ΔG°_{ads} values, it is apparent that, for $C_{12}EO_8$, adsorption is affected to a greater degree than micellization by the presence of the hydrocarbon phase.

4.1.2 Zwitterionic Surfactant

Plots of γ_I vs -log C_w for the zwitterionic surfactant C_{12}BMG are shown in figures B6-B11. These plots were constructed using the interfacial tension vs -log C_w data in Tables B18-B38.

Cmc_w values for C_{12}BMG were taken as the concentrations at the point of intersection of the two linear portions of the γ_I vs -log C_w plots. Values of the maximum interfacial excess concentrations, Π_{max}, were calculated using equation [1]. Minimum area per molecule values, A_{min}, were calculated using equation [3]. Values of cmc_w, Γ_{max}, and A_{min} for C_{12}BMG are listed in Table 6 (below).

The efficiency in interfacial tension reduction ($pC_{30,w}$), relationship between micellization and adsorption, cmc/C_{30}, minimum interfacial tension, γ_{min}, and maximum interfacial pressure, Π_{max}, values for C_{12}BMG are listed in Table 7.

The standard free energies (ΔG°_{mic}), entropies (ΔS°_{mic}), and enthalpies

TABLE 5: Standard free energies of micellization and adsorption at 25.0°C (values in parentheses are for the corresponding air/aqueous solution systems).

Surfactant	System	ΔG°_{ads}/ kJ mol^{-1}	ΔG°_{mic}/ kJ mol^{-1}
$C_{12}EO_8$	hexadecane/H_2O	$-51._{1}$ ($-47._{4}$[a])	$-32._{7}$ ($-32._{6}$[a])
$C_{12}EO_8$	dodecane/H_2O	$-51._{1}$ ($-47._{4}$[a])	$-32._{8}$ ($-32._{6}$[a])
$C_{12}EO_8$	heptane/H_2O	$-51._{5}$ ($-47._{4}$[a])	$-33._{0}$ ($-32._{6}$[a])
$C_{12}EO_8$	cyclohexane/H_2O	$-52._{8}$ ($-47._{4}$[a])	$-32._{8}$ ($-32._{6}$[a])
$C_{12}EO_8$	isooctane/H_2O	$-51._{8}$ ($-47._{4}$[a])	$-32._{8}$ ($-32._{6}$[a])
$C_{12}EO_8$	heptamethylnonane/ H_2O	$-52._{0}$ ($-47._{4}$[a])	$-32._{7}$ ($-32._{6}$[a])
C_8P	hexadecane/ H_2O	$-34._{6}$($-32._{4}$[b])	c
C_8P	hexadecane/0.1M NaCl aq. soln.	$-36._{5}$($-32._{9}$[b])	c
$C_{10}P$	hexadecane/0.1M NaCl aq. soln.	$-44._{2}$($\approx$ -38[b])	c

[a] Data from reference 115.

[b] Data from reference 114.

[c] This surfactant reached a solubility limit in the aqueous phase before forming micelles 114.

(ΔH°_{mic}), of micellization for C_{12}BMG were calculated using equation [16] and those analogous to [13] and [14], respectively. Values are listed in Table 8.

The standard free energies (ΔG°_{ads}), entropies (ΔS°_{ads}), and enthalpies (ΔH°_{ads}), of adsorption for C_{12}BMG were calculated using equatios [9], [13], and [14], respectively. Values are listed in Table 9.

The cmc_W values (Table 6) in the hydrocarbon/water systems are all less than in the air/water system. As found for $C_{12}EO_8$, the cmc_W value decreases as the solubilization of the saturated hydrocarbon into the core of the micelles increases. Thus, with heptane, which is solubilized to a greater extent than hexadecane, C_{12}BMG has a smaller cmc_W value. The aromatic hydrocarbon, toluene, is solubilized in the palisade layer of the micelle (126,127), which spreads out the surfactant molecules considerably and, thus lowers the cmc_W of the C_{12}BMG more than the saturated hydrocarbons. This is in agreement with the findings of Rehfeld (63).

The A_{min} values (Table 6) for C_{12}BMG are all greater at the hydrocarbon/water interfaces than at the air/water interface. Apparently, either the head group repulsions in this surfactant are too large, or its head group is too "hard" (i.e., not compressible enough), to allow contraction relative to the air/water system as found for $C_{12}EO_8$ in the straight-chain hydrocarbon/water systems and, in fact, expansion occurs with all the hydrocarbons investigated, despite the unfavorable increase in hydrocarbon/water interface.

The minimum area per molecule at the saturated hydrocarbon/water interface reflects the extent to which the hydrocarbon phase is inserted between the hydrophobic tails of C_{12}BMG. As the degree of intercalation increases, A_{min} increases.

The data at 25.0°C indicate that for C_{12}BMG, as the chain length of the

TABLE 6: Interfacial Properties of C_{12}BMG. I: $\mathrm{cmc_w}$, Γ_{max}, A_{min}

Second phase (against water)	T/°C	$\mathrm{cmc_w} \times 10^4$/ M	$\Gamma_{max} \times 10^{10}$/ mol cm^{-2}	A_{min}/Å^2
heptane	25	4.3_1	2.8_1	$59._2$
	35	4.0_8	2.7_3	$60._8$
	45	4.3_9	2.6_6	$62._4$
dodecane	25	4.8_2	2.8_3	$58._7$
	35	4.8_6	2.6_6	$62._4$
	45	5.2_4	2.5_9	$64._3$
hexadecane	25	5.1_9	2.9_0	$57._3$
	35	5.6_7	2.6_1	$63._6$
	45	5.6_8	2.5_6	$64._8$
isooctane	25	4.3_0	2.7_7	$60._0$
	35	4.3_5	2.5_9	$64._2$
	45	4.5_9	2.6_1	$63._6$
heptamethylnonane	25	4.9_5	2.7_8	$59._8$
	35	4.8_2	2.6_7	$62._2$
	45	5.0_7	2.6_4	$62._9$
cyclohexane	25	3.6_3	2.6_4	$62._9$
	35	3.4_7	2.5_8	$64._3$
	45	3.6_4	2.4_5	$67._7$
toluene	25	2.2_4	2.2_2	$74._7$
	35	2.1_8	2.1_5	$77._3$
	45	2.1_4	2.1_5	$77._3$

TABLE 6: (Continued)

Second phase (against water)	T/°C	$cmc_w \times 10^4$/ M	$\Gamma_{max} \times 10^{10}$/ mol cm^{-2}	A_{min}/Å^2
air[a]	10	6.0_4	3.0_0	$55._5$
	25	5.5_0	2.9_5	$56._0$
	40	5.4_5	2.7_8	$59._7$

[a] Data from reference 109.

hydrocarbon phase increases, A_{min} decreases. Thus, A_{min} decreases in the order: cyclohexane > isooctane > n-heptane > n-dodecane > n-hexadecane. With the exception of cyclohexane, this is the order of increasing cohesive energy density, δ (solubility parameter (128)) of the hydrocarbon (cyclohexane, 16.7; isooctane,14.0; n-heptane,15.2; n-hexadecane,16.3, in M $Pa^{1/2}$). This is resonable, since with increase in its cohesive energy density, there should be a decreased tendency for the hydrocarbon to intercalate between the hydrophobic tails of the C_{12}BMG molecules. These results are consistent with the theoretical calculations of Gruen and Haydon (119,120) on alkane-saturated lipid bilayers at room temperature that show that small alkanes penetrated farther into the alkyl chains of the lipids than did larger ones. The calculations of Gruen and Haydon imply that as the length of the alkane decreases, the equilibrium area per lipid molecule should increase. This general trend is observed in the experimental results given in a paper by White (129).

With increase to 45.0°C, there is the expected increase in A_{min} in all cases due to thermal agitation. However, again with exception of cyclohexane, the hydrocarbons with the largest cohesive energy densities, contrary to expectation, show the largest increase in A_{min}. Thus at 45.0°C, the order is n-hexadecane > n-dodecane > isooctane > n-heptane, almost exactly opposite to that at 25.0°C. This order at 45.0°C is in agreement with the findings of Rehfeld for sodium dodecyl sulfate (63) at 25.0°C, whereas the order at 25.0°C, above, is just opposite to his.

The aromatic hydrocarbon toluene, due to its attraction to water and the hydrophilic head of C_{12}BMG via its polarizable Π cloud, has the greatest concentration at the interface of the hydrocarbons investigated and produces the largest A_{min} for C_{12}BMG. This is in agreement with Rehfeld (63), and Vijayendran and Bursh (64).

The efficiency of C_{12}BMG in reducing interfacial tension is measured by $pC_{30,w}$ (Table7). These values are all greater in the saturated hydrocarbon/water

TABLE 7: Interfacial Properties of $C_{12}BMG$. II: $pC_{30,w}$, cmc/C_{30}, γ_{min}, Π_{max}

Second phase (against water)	T/°C	$pC_{30,w}$	cmc/C_{30}	γ_{min}/ mN m^{-1}	Π_{max}/ mN m^{-1}
heptane	25	4.5_0	14	1.8	48
	35	4.4_4	11	1.7	47
	45	4.3_4	10	1.4	46
dodecane	25	4.5_1	16	2.8	49
	35	4.5_1	16	2.6	48
	45	4.3_4	11	2.5	47
hexadecane	25	4.4_1	13	3.5	48
	35	4.4_5	16	3.1	47
	45	4.2_8	11	3.0	46
isooctane	25	4.5_2	14	2.0	48
	35	4.5_3	15	1.8	47
	45	4.3_2	10	1.7	46
heptamethylnonane	25	4.5_2	17	2.8	49
	35	4.4_4	14	2.6	48
	45	4.3_2	11	2.4	47
cyclohexane	25	4.6_8	18	0.8	49
	35	4.6_6	16	0.8	47
	45	4.5_1	12	0.7	46
toluene	25	4.1_1	2.8	0.3	35
	35	3.9_1	1.8	0.4	33
	45	3.7_1	1.1	0.5	30

TABLE 7: (Continued)

Second phase (against water)	T/°C	$pC_{30,w}$	cmc/C_{30}	γ_{min}/ mN m^{-1}	Π_{max}/ mN m^{-1}
air[a]	10	3.8_2	4.0	34	40
	25	3.8_1	3.3	33	39
	40	3.8_2	3.6	32	38

[a] Data from reference 109.

systems than the values in the air/water systems, in agreement with the findings for the nonionic surfactants. According to equation [17] and the data for ΔG°_{ads} (Table 8), this is due to the more negative ΔG°_{ads} values in the hydrocarbon/water systems in all cases. When the aromatic hydrocarbon toluene is the second phase against water, the C_{12}BMG efficiency (in interfacial tension reduction) is only slightly greater than in the air/water system. Although C_{12}BMG ΔG°_{ads} is more negative in the presence of toluene, it is not as efficient as in the saturated hydrocarbon/water systems because its A_{min} is larger in the toluene/water system, which tends to decrease the $pC_{30,w}$ value as seen in equation [17].

The relationship between micellization and adsorption can be measured by the cmc/C_{30} ratio (Table 7). The values for C_{12}BMG in the saturated hydrocarbon/water systems are all greater than the value in the air/water system. This is in agreement with the findings for the nonionic surfactants and is attributed to the C_{30} value being reduced to a larger extent than the cmc_w by the presence of the saturated hydrocarbon.

The cmc/C_{30} ratio of C_{12}BMG in the toluene/water system is slightly smaller than in the air/water system. This is because the cmc is reduced slightly more than the C_{30} value, due to solubilization of the toluene molecules in the palisade layer of the micelle (126,127).

The effectiveness of surfactant interfacial tension reduction can be measured by Π_{max}. The values of Π_{cmc} in the saturated hydrocarbon/water systems are all greater than for the air/water system (in agreement with the findings on nonionic surfactants). According to equation [18] this is due to the larger cmc/C_{30} ratio in these systems, since Γ_{max} does not vary very much. In the toluene/water system, Π_{max} of C_{12}BMG is less than in the air/water system. This is due to the combined effect of a decrease in Γ_{max} of $C_{12}BMG$ molecules at the toluene/water interface and the slight decrease in the cmc/C_{30} ratio.

The ΔG°_{mic} values (Table 8) for $C_{12}BMG$ in the hydrocarbon/water systems are all slightly more negative than for the air/water system. This is due to the slight decrease in the cmc upon solubilization of the hydrocarbon into the micelles. The ΔH°_{mic} and ΔS°_{mic} values reflect this small change. The slight differences for the various hydrocarbons investigated are not considered significant.

The ΔG°_{ads} values (Table 9) for $C_{12}BMG$ in the hydrocarbon/water systems are all considerably more negative (as seen above for $C_{12}EO_8$ and the N-alkyl-2-pyrrolidones) than the value for the air/water system. This is attributed to the additional interaction (125) of the surfactant tails with the hydrocarbon phase. It is apparent that the ΔG°_{mic} values are not affected as much as ΔG°_{ads} values by the presence of the hydrocarbon phase, showing (as seen above for the nonionic surfactants) that adsorption is affected to a greater degree than micellization by the presence of the hydrocarbon phase.

The ΔH°_{ads} values at 35.0°C become more negative and the ΔS°_{ads} values become less positive as the length of the hydrocarbon in the straight-chain alkane series decreases. This may be the result of increased interaction of the surfactant chains with the hydrocarbon phase as cohesive forces between the hydrocarbon molecules decrease. As pointed out by Gruen and Haydon (119,120), incorporation of alkanes into the hydrophobic tails of the surfactant molecules reduces the number of conformations available to both the alkanes and the tails and that smaller alkanes are incorporated to a larger extent than larger ones. The relatively large negative ΔH°_{ads} and small ΔS°_{ads} values for the branched alkanes are also consistent with this. In the case of toluene, the large ΔH°_{ads} and small ΔS°_{ads} values are also due to the increased hydration of the head groups accompanying the large increase in the value of A_{min}.

TABLE 8: Thermodynamic Parameters of Micellization for C_{12}BMG

Second phase (against water)	T/°C	ΔG°_{mic}/ kJ mol^{-1}	ΔH°_{mic}/ kJ mol^{-1}	ΔS°_{mic}/ kJ mol^{-1} K^{-1}
heptane	25	$-29._1$		
	35	$-30._3$	+0.5	0.09_9
	45	$-31._1$		
dodecane	25	$-28._9$		
	35	$-29._8$	- 3	0.08_7
	45	$-30._6$		
hexadecane	25	$-28._6$		
	35	$-29._4$	- 3	0.08_7
	45	$-30._4$		
isooctane	25	$-29._2$		
	35	$-29._8$	- 3	0.08_8
	45	$-31._0$		
heptamethylnonane	25	$-28._9$		
	35	$-29._8$	-0.5	0.09_5
	45	$-30._7$		
cyclohexane	25	$-29._5$		
	35	$-30._7$	+ 1	0.1_0
	45	$-31._6$		
toluene	25	$-30._8$		
	35	$-31._9$	+ 1	0.1_1
	45	$-33._0$		

TABLE 8: (Continued)

Second phase (against water)	T/°C	ΔG°_{mic}/ kJ mol^{-1}	ΔH°_{mic}/ kJ mol^{-1}	ΔS°_{mic}/ kJ mol^{-1} K^{-1}
air[a]	10	$-26._8$	-3	0.08_7
	25	$-28._6$		
	40	$-29._9$		

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[a] Data from reference 109.

TABLE 9: Thermodynamic Parameters of Adsorption for C_{12}BMG

Second phase (against water)	T/°C	ΔG°_{ads}/ kJ mol^{-1}	ΔH°_{ads}/ kJ mol^{-1}	ΔS°_{ads}/ kJ mol^{-1} K^{-1}
heptane	25	$-46._7$		
	35	$-47._5$	$-2._1 \times 10^1$	0.08_4
	45	$-48._3$		
dodecane	25	$-46._3$		
	35	$-47._9$	$-1._1 \times 10^1$	0.1_2
	45	$-48._6$		
hexadecane	25	$-45._5$		
	35	$-47._6$	-1	0.1_5
	45	$-48._4$		
isooctane	25	$-46._6$		
	35	$-48._3$	$-1._9 \times 10^1$	0.09_4
	45	$-48._5$		
heptamethylnonane	25	$-46._5$		
	35	$-47._8$	$-2._0 \times 10^1$	0.08_9
	45	$-48._3$		
cyclohexane	25	$-48._0$		
	35	$-49._0$	$-1._4 \times 10^1$	0.1_1
	45	$-50._3$		
toluene	25	$-46._9$		
	35	$-47._3$	$-2._4 \times 10^1$	0.07_7
	45	$-48._4$		

TABLE 9: (Continued)

Second phase (against water)	T/°C	ΔG°_{ads}/ kJ mol^{-1}	ΔH°_{ads}/ kJ mol^{-1}	ΔS°_{ads}/ kJ mol^{-1} K^{-1}
air[a]	10	$-40._{1}$	$-1._{4} \times 10^{1}$	0.09_{3}
	25	$-42._{0}$		
	40	$-43._{4}$		

[a] Data from reference 109.

4.1.3 Anionic Surfactants

Plots of γ_I vs -log C_w for the anionic surfactants $C_{12}S$, $C_{16}EGEO_5S$, and $C_{16}HGEO_5S$ are shown in figures B12-B14. These plots were constructed using the interfacial tension vs -log C_w data in Tables B39-B48.

For the anionic surfactants in 0.1M NaCl aqueous solution, the maximum interfacial excess concentration values (Γ_{max}) were calculated using equation [1]; for those without added NaCl, equation [2] was used. Minimum area per molecule values were calculated using equation [3]. The standard free energy of adsorption for anionic surfactants in systems with added salt were calculated using equations [10] and [11]; with systems without added salt, equation [12] was used. Values of cmc_w, Γ_{max}, A_{min}, and $\Delta G°_{ads}$ for the anionic surfactants are listed in Table 10.

Values for $pC_{30,w}$, cmc/C_{30}, γ_{min}, and Π_{max} are listed in Table 11.

As found for the nonionic and zwitterionic surfactants, all the cmc_w values (Table 10) for the anionic surfactants studied in the hydrocarbon/aqueous systems, except $C_{16}EGEO_5S$, were less than their corresponding values in the air/aqueous systems. There is not much decrease in the cmc_w values in the systems with saturated hydrocarbons relative to their values in the air/aqueous systems. However, with the aromatic hydrocarbon, toluene, the cmc_w value is decreased considerably. This agrees with the findings for $C_{12}BMG$ and of Rehfeld (63).

The A_{min} values (Table 10) for the anionic surfactant $C_{12}S$ in the hydrocarbon/water systems in the absence of electrolyte are all larger than the A_{min} value for $C_{12}S$ in the air/water system. The A_{min} values for $C_{12}S$, $C_{16}EGEO_5S$, and $C_{16}HGEO_5S$ in the hexadecane/0.1M NaCl aqueous solution systems

TABLE 10: Interfacial Properties of Anionic Surfactants at 25.0°C. I: cmc_w, Γ_{max}, A_{min}, $\Delta G°_{ads}$

Surfactant	system	cmc_w/M	$\Gamma_{max} \times 10^{10}$/ mol $^{-2}$ cm	A_{min}/Å^2	$\Delta G°_{ads}$/ kJ mol^{-1}
$C_{12}S$	heptane/H_2O	9.9×10^{-3}	2.4_4	$68._1$	$-60._3$
$C_{12}S$	dodecane/H_2O	9.7×10^{-3}	2.5_1	$66._0$	$-60._0$
$C_{12}S$	hexadecane/H_2O	$1.0_1 \times 10^{-2}$	2.8_0	$59._2$	$-57._8$
$C_{12}S$	isooctane/H_2O	9.5×10^{-3}	2.5_8	$64._3$	$-59._3$
$C_{12}S$	heptamethylnonane/ H_2O	9.7×10^{-3}	2.7_5	$60._4$	$-58._2$
$C_{12}S$	cyclohexane/H_2O	9.2×10^{-3}	2.3_9	$69._5$	$-61._3$
$C_{12}S$	toluene/H_2O	$5.4_8 \times 10^{-3}$	2.3_4	$70._9$	$-58._9$
$C_{12}S^a$	air/H_2O	$1.2_4 \times 10^{-2}$	2.9_3	$56._7$	$-52._8$
$C_{12}S$	hexadecane/0.1M NaCl aq. soln.	$2.0_0 \times 10^{-3}$	4.5_7	$36._4$	$-52._8$
$C_{12}S^a$	air/0.1M NaCl aq. soln.	$2.4_7 \times 10^{-3}$	3.7_6	$44._2$	$-51._9$
$C_{16}EGEO_5S$	hexadecane/0.1M NaCl aq. soln.	$3.8_0 \times 10^{-5}$	3.2_9	$50._5$	$-67._9$
$C_{16}EGEO_5S^b$	air/0.1M NaCl aq. soln.	$3.3_2 \times 10^{-5}$	2.8_0	$59._3$	$-68._3$
$C_{16}HGEO_5S$	hexadecane/0.1M NaCl aq. soln.	$1.0_5 \times 10^{-5}$	3.2_3	$51._4$	$-71._2$

TABLE 10: (Continued)

Surfactant system	cmc_w/M	$\Gamma_{max} \times 10^{10}$/ mol $^{-2}$ cm	A_{min}/Å^2	ΔG°_{ads} kJ mol^{-1}
$C_{16}HGEO_5S$[b] air/0.1M NaCl aq. soln.	$1.1_6 \times 10^{-5}$	3.0_7	$54._1$	$-69._2$

[a] Data from reference 130.

[b] Data from reference 117.

are all decreased relative to their values in the corresponding air/0.1M NaCl aqueous solution systems. When no electrolyte is added to the water phase, head group repulsions are large and the hydrocarbon molecule intercalates between the surfactant hydrophobic groups and spreads out the surfactant molecules. When 0.1M NaCl is added, head group repulsion is swamped out, enabling the energy of interaction of the hexadecane molecules with the hydrophobic tails (125) to contract the interfacial film relative to the corresponding air/0.1M NaCl aqueous solution system. In agreement with the findings on $C_{12}BMG$, as the degree of intercalation increases (119,120) for the straight-chain hydrocarbons, the A_{min} values for $C_{12}S$ (in the absence of added electrolyte) increase.

The $\Delta G°_{ads}$ values (Table 10) for $C_{12}S$ in the hydrocarbon/water systems are all much more negative than in the air/water system. This agrees with the findings on the nonionic and zwitterionic surfactants. $C_{12}S$, $C_{16}EGEO_5S$, and $C_{16}HGEO_5S$ in hexadecane/0.1M NaCl aqueous solution systems have $\Delta G°_{ads}$ values about the same as in the corresponding air/0.1M NaCl aqueous solution systems. Apparently, the excess energy of interaction of the hexadecane molecules with the surfactant hydrophobic tails is used in compressing the surfactant molecules closer together in the presence of electrolyte (i.e., when head group repulsions are swamped out) as indicated by the decrease in A_{min} in these systems relative to the values in the air/0.1M NaCl aqueous solution systems. The result is that in both the hexadecane/0.1M NaCl aqueous solution systems, and in the air/0.1M NaCl aqueous solution systems, $\Delta G°_{ads}$ is about the same, but in the former, A_{min} is smaller than in the latter.

The efficiency of interfacial tension reduction for the anionic surfactants as measured by $pC_{30,w}$ (Table 11) is greater in the hydrocarbon/water systems than the values in the air/water systems. This agrees with the findings on the other surfactant types.

TABLE 11: Interfacial Properties of Anionic Surfactants at 25.0°C. II: $pC_{30,w}$, cmc/C_{30}, γ_{min}, Π_{max}

Surfactant	system	$pC_{30,w}$	cmc/C_{30}	γ_{min}/ mN m^{-1}	Π_{max}/ mN m^{-1}
$C_{12}S$	heptane/H_2O	2.4_5	2.7_3	7.7	$42._5$
$C_{12}S$	dodecane/H_2O	2.6_0	3.8_6	9.4	$42._6$
$C_{12}S$	hexadecane/H_2O	2.3_9	2.4_7	9.8	$42._3$
$C_{12}S$	isooctane/H_2O	2.4_4	2.6_1	8.2	$42._0$
$C_{12}S$	heptamethylnonane /H_2O	2.4_1	2.4_9	9.6	$42._2$
$C_{12}S$	cyclohexane/H_2O	2.4_9	2.8_7	6.9	$43._3$
$C_{12}S$	toluene/H_2O	2.3_0	1.0_9	5.2	$30._9$
$C_{12}S^a$	air/H_2O	2.0_4	1.2_5	$39._0$	$33._0$
$C_{12}S$	hexadecane/0.1M NaCl aq. soln.	3.3_2	4.1_8	6.6	$45._7$
$C_{12}S^a$	air/0.1M NaCl aq. soln.	3.0_6	2.8_1	$35._9$	$36._4$
$C_{16}EGEO_5S$	hexadecane/0.1M NaCl aq. soln.	5.5_0	$11._9$	2.0	$50._4$
$C_{16}EGEO_5S^b$	air/0.1M NaCl aq. soln.	5.2_8	6.3_3	$29._5$	$42._8$
$C_{16}HGEO_5S$	hexadecane/0.1M NaCl aq. soln.	6.0_6	$11._9$	2.5	$42._1$

TABLE 11: (Continued)

Surfactant system	$pC_{30,w}$	cmc/C_{30}	γ_{min}/ mN m^{-1}	Π_{max} mN m^{-1}
$C_{16}HGEO_5S^b$ air/0.1M NaCl aq. soln.	5.6_3	4.95	$30._2$	$42._1$

[a] Data from reference 130.

[b] Data from reference 117.

The values of the relationship between micellization and adsorption for the anionic surfactants as measured by the cmc/C_{30} ratio are listed in Table 11. Values in the saturated hydrocarbon/water systems are all greater than the corresponding values in the air/water systems. For $C_{12}S$ in the toluene/water system, the cmc/C_{30} value is slightly less than the value for $C_{12}S$ in the air/water system. These results agree with the findings on the other surfactant types.

The effectiveness of interfacial tension reduction can be measured by Π_{max}. The values of Π_{max} (Table 11) for the anionic surfactants in the saturated hydrocarbon/water systems are all greater than for the air/water systems. $C_{12}S$ in the toluene/water system has a Π_{max} value less than in the air/water system. These results are consistent with the findings for the other surfactant types.

The γ_{min} values (Table 11) for $C_{12}S$ at the hydrocarbon/water interface are all greater than for nonionic or zwitterionic surfactants. This is due to a large head-group curvature energy for ionic surfactants (121) in the absence of added electrolyte. When 0.1M NaCl is added, the head-group curvature energy is reduced at the oil/water interface, and γ_{min} is reduced.

4.1.4 Summary of Effect of Surfactant Type on Interfacial Properties

CMC_w

The results on cmc_w values for all surfactant types studied (nonionic, zwitterionic, anionic) are in agreement. In saturated hydrocarbon/aqueous solution systems cmc_W values are slightly reduced relative to their values in air/aqueous solution systems (about 5% on average). In aromatic hydrocarbon/aqueous solution systems, the cmc_W values are considerably reduced compared to air/aqueous solution systems.

$\Delta G°_{mic}$

The results on this parameter for the nonionic and zwitterionic surfactants are in agreement. The values for the standard free energy of micellization in the hydrocarbon/aqueous solution systems are almost the same as in the corresponding air/aqueous solution systems.

$\Delta G°_{ads}$

In the absence of salt, the standard free energy of adsorption in the hydrocarbon/water systems is considerably more negative than in the corresponding air/water systems. For ionic surfactants in 0.1M NaCl, $\Delta G°_{ads}$ values in hexadecane/aqueous solution systems are comparable to those in corresponding air/0.1M NaCl aqueous solution systems. This is attributed to the excess energy of interaction of the hexadecane molecules with the (anionic) surfactant tails being used to compress the interfacial film.

A_{min}

For those nonionic surfactants that partition strongly into the oil phase, A_{min} is considerably greater in the hydrocarbon/aqueous solution system than in the air/aqueous solution system. Data in Table 12 on p,t-octylphenoxy di-ethenoxyethanol (OPE_2) are in agreement with this finding. For the nonionic surfactants (that partition preferentially into the water phase), and for ionic surfactants in 0.1M NaCl, A_{min} values in straight-chain hydrocarbon/aqueous solution systems are decreased relative to their values in air/aqueous solution systems. van Voorst Vader's data (62) on $C_{11}H_{23}COO^-Na^+$ in Table 12 is in

TABLE 12: A_{min} values from the literature at 25.0°C

Surfactant	system	$A_{min}/Å^2$	$A_{min}(air/H_2O)/Å^2$
OPE_{10}[a,b]	isooctane/H_2O	78	$74._5$
OPE_9[a]	isooctane/H_2O	71	66
OPE_8[a]	isooctane/H_2O	64	64
OPE_7[a]	isooctane/H_2O	58	58
OPE_6[a]	isooctane/H_2O	56	56
OPE_5[a]	isooctane/H_2O	53	53
OPE_4[a]	isooctane/H_2O	50	50
OPE_3[a]	isooctane/H_2O	48	45
OPE_2[a]	isooctane/H_2O	53	34
$C_{11}H_{23}COONa$[c]	heptane/0.1M NaCl aq. soln.	45	47

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[a] Data from reference 62.

[b] OPE = p,t-octylphenoxyethenoxyethanols. Subscript = polyoxyethylene (EO) chain length.

[c] Data from reference 60; at 20.0°C.

agreement with this finding. For nonionic surfactants in branched or cyclic hydrocarbon/water systems, and for the zwitterionic surfactant C_{12}BMG and ionic surfactants in the absence of added electrolyte in hydrocarbon/water systems, A_{min} is found to be unaffected or expanded relative to the corresponding air/water systems. In the case of the former, although the head group repulsion is small enough to allow contraction (as found with straight-chain hydrocarbons), the bulkiness of the branched or cyclic hydrocarbon between the surfactant tails prevents this from occuring (data agreeing with this by Crook et. al. (62) is given in Table 12). In the two latter cases, head group repulsions are too large with ionic surfactants, and head group repulsions are too large and/or the head group is too incompressible, for C_{12}BMG, to allow contraction of the interfacial film relative to the air/water system.

$pC_{30,W}$

For all surfactant types and under all conditions investigated, this parameter is larger in the hydrocarbon/aqueous solution systems than in the air/aqueous solution systems.

cmc/C_{30}

For all surfactant types studied in the saturated hydrocarbon/aqueous solution systems, cmc/C_{30} values are larger than in the air/aqueous solution systems since C_{30} is reduced to a greater extent than the cmc by the presence of the saturated hydrocarbon. When the aromatic hydrocarbon toluene is used as the hydrocarbon phase (with C_{12}BMG and C_{12}S), cmc and C_{30} values are both reduced considerably, leading to a cmc/C_{30} value that is about the same or slightly smaller than in the air/aqueous solution systems.

Π_{max}

In the saturated hydrocarbon/aqueous solution systems, all surfactant types studied yielded larger Π_{max} values than the values in the corresponding air/aqueous solution systems. When toluene is used as the hydrocarbon phase, Π_{max} is slightly smaller than in the air/aqueous solution system.

4.2 Molecular Interaction , Synergism, and Negative Synergism in Binary Surfactant Mixtures in Hydrocarbon/Aqueous Systems

4.2.1 Validity of the Theory

Plots of γ_I vs -log C_t for the mixed systems investigated (including $\alpha_1 = 0$ and $\alpha_1 = 1$ plots) are shown in Figures B15-B34. These plots were constructed using the interfacial tension vs -log total concentration data listed in tables B7-B93 (all data is at 25.0°C and $\varphi = \varphi^0{}_1 = \varphi^0{}_2 = 0.025$ for all the mixed systems except $C_{12}EO_7/C_{12}S$ which has $\varphi = \varphi^0{}_1 = \varphi^0{}_2 = 0.0123$). The data used to construct the curves in the nonionic-nonionic surfactant mixtures (Figures B25-B32) were produced without sending the surfactants through Sep-pak minicolumns since the oil soluble surfactant was not sufficiently soluble in water to allow analysis for its concentration in the effluent, and only aqueous solutions of the surfactants can be sent through. In Figure B21, the C_8P curve is constructed from data in Table B15 (Sep-pak purified C_8P data) ; in Figure B31, the C_8P curve is constructed from data in Table B90 (non-Sep-pak purified C_8P data). The data for $C_{12}EO_8$ in Tables B79 and B84 were produced without sending the $C_{12}EO_8$ through a Sep-pak (while for the data in Tables B1-B6, $C_{12}EO_8$ was passed repeatedly through a Sep-pak minicolumn).

Values of the molecular interaction parameter for the interfacial film, $\beta^{\sigma}{}_{LL}$, were calculated using equations [55] and [56] in all 20 mixed systems investigated (except the $C_8P/C_{12}S$ and $C_{10}P/C_{12}S$ systems for which equations [47] and [48] were used) and are listed in Table 13 (β^{σ} values at the air/aqueous

TABLE 13: Synergism in interfacial tension reduction efficiency at 25.0°C (values in parentheses are for the corresponding air/aqueous solution systems)

Surfactant1-2, system	β^{σ}_{LL}	$\lvert \ln C^0_{1,t}/C^0_{2,t} \rvert$	synergism predicted	synergism found(exp.)
$C_{12}EO_7$-$C_{12}S$, heptane/H_2O	$+0.1_9$	5.0	no	no
$C_{12}BMG$-$C_{12}S$, heptane/H_2O	$-4._7(-5._7{}^a)$	$4.2(4.0^a)$	yes	yes
$C_{12}BMG$-$C_{12}S$, dodecane/H_2O	$-4._8(-5._7{}^a)$	$4.0(4.0^a)$	yes	yes
$C_{12}BMG$-$C_{12}S$, hexadecane/H_2O	$-5._2(-5._7{}^a)$	$4.0(4.0^a)$	yes	yes
$C_{12}BMG$-$C_{12}S$, isooctane/H_2O	$-4._4(-5._7{}^a)$	$4.2(4.0^a)$	yes	yes
$C_{12}BMG$-$C_{12}S$, heptamethylnonane/H_2O	$-4._4(-5._7{}^a)$	$4.2(4.0^a)$	yes	yes
$C_{12}BMG$-$C_{12}S$, cyclohexane/H_2O	$-5._0(-5._7{}^a)$	$4.5(4.0^a)$	yes	yes
$C_{12}BMG$-$C_{12}S$, toluene/H_2O	$-3._2(-5._7{}^a)$	$4.6(4.0^a)$	no	no
C_8P-$C_{12}S$, hexadecane/ 0.1M NaCl aq. soln.	$-1._7(-3._1{}^b)$	$0.66^c(0.23^b)$	yes	yes

TABLE 13: (Continued)

Surfactant1-2, system	β^{σ}_{LL}	$\lvert \ln C^0_{1,t}/C^0_{2,t} \rvert$	synergism predicted	 found(exp.)
$C_{10}P$-$C_{12}S$, hexadecane/ 0.1M NaCl aq. soln.	$-2._3$	0.32^c	yes	yes
$C_{16}HGEO_5S$- $C_{16}HGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	$-1._2$	4.1	no	no
$C_{16}EGEO_5S$- $C_{16}EGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	$-2._2(-1._1{}^d)$	2.9	no	no
$C_{12}EO_8$-$C_{12}EO_4$, hexadecane/H_2O	$+0.5_5$	1.4	no	no
$C_{12}EO_8$-$C_{12}EO_3$, hexadecane/H_2O	$-0.7_1(-0.1_7{}^e)$	2.3	no	no
$C_{12}EO_8$-$C_{12}EO_2$, hexadecane/H_2O	$-2._2(-1._0)$	3.6	no	no
$C_{12}EO_8$-$C_{12}EO_2$, heptane/H_2O	$-1._6$	5.2	no	no
$C_{16}EO_8$-$C_{12}EO_2$, hexadecane/H_2O	$-1._4$	5.5	no	no
$C_{12}EO_8$-$C_{12}OH$, hexadecane/H_2O	$-5._2$	7.2	no	no

TABLE 13: (Continued)

Surfactant1-2, system	β^{σ}_{LL}	$\|\ln C^0_{1,t}/C^0_{2,t}\|$	synergism predicted	synergism found(exp.)
$C_{12}EO_8$-C_8P, hexadecane/H_2O	-0.5_2	4.5	no	no
$C_{12}EO_8$-$C_{12}P$, hexadecane/H_2O	$-2._0$	4.3	no	no

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[a] Data from reference 131.

[b] Data from reference 132.

[c] $|\ln F_1F^0_2C^0_{1,t}/F_2F^0_1C^0_{2,t}|$. $F_1F^0_2/F_2F^0_1 = 0.80_6$ for C_8P-$C_{12}S$ system and 0.71_1 for the $C_{10}P$-$C_{12}S$ system.

[d] Data from reference 117.

[e] Data from reference 104.

interface have been included for comparative purposes). In all 20 cases, the theoretical prediction for the existence or absence of synergism in interfacial tension reduction efficiency is in agreement with experimental results.

For the systems that did exhibit synergism in this respect, minimum concentration values, $C_{12,t,min}$, at the point of maximum synergism were calculated using equation [83] (equation [82] for the $C_8P/C_{12}S$, and $C_{10}P/C_{12}S$ systems), and mole fraction values, α^*_1, at the point of maximum synergism were calculated using equation [81] (equation [80] for the $C_8P/C_{12}S$, and $C_{10}P/C_{12}S$ systems). These calculated parameters are listed in Table 14 and the calculated $C_{12,t,min}$ values are compared with experimentally determined $C_{12,t,min}$ values (at experimental α values close to the α^* values) in Table 13. Calculated and experimental $C_{12,t,min}$ values are in good agreement.

For systems whose β^σ values at the air aqueous interface are listed in (Table 13), the β^σ_{LL} values (for those systems containing two water soluble surfactants ($C_{12}BMG/C_{12}S$, $C_{12}S/C_8P$)) at the hydrocarbon/aqueous solution interface are less negative than the β^σ values at the corresponding air/aqueous interface. This is attributed to intercalation of hydrocarbon molecules between surfactant molecules at the hydrocarbon/aqueous interface. For those systems where a water soluble surfactant is mixed with an oil soluble one ($C_{16}EGEO_5S/C_{16}EGEO_5OH$, $C_{12}EO_8/C_{12}EO_3$, and $C_{12}EO_8/C_{12}EO_2$), the β^σ_{LL} values at the hydrocarbon/aqueous solution interface are more negative than the β^σ values at the corresponding air/aqueous interface.

Molecular interaction parameters in the mixed micelles, β^M_{LL} values, were calculated for the systems in which both components exhibited cmc's (for the $C_{12}EO_8/C_8P$ and $C_{12}EO_8/C_{12}P$ systems, the cmc of C_8P and $C_{12}P$ was taken as the point of insolubility in the aqueous phase). Equations analogous to [55] and [56] (except the $C_8P/C_{12}S$ and $C_{10}P/C_{12}S$ systems for which equations analogous to [47] and [48] were used) give the values listed in Table 15 (β^M values for corresponding air/aqueous systems have been included for comparative purposes).

TABLE 14: Parameters at the Point of Maximum Synergism in Interfacial Tension Reduction Efficiency - $C_{12,t,min}$, α^* at 25.0°C

Surfactant1-2, system	$\alpha^*_{BMG,CxP}$ (calc.)	$C_{12,t,min}/M$ calc.	exp.($\alpha_{BMG,CxP}$)
$C_{12}BMG-C_{12}S$, heptane/H_2O	0.95	$1.1_1 \times 10^{-4}$	$1.0_7 \times 10^{-4}$ (0.94)
$C_{12}BMG-C_{12}S$, dodecane/H_2O	0.92	$1.4_2 \times 10^{-4}$	$1.4_4 \times 10^{-4}$ (0.94)
$C_{12}BMG-C_{12}S$, hexadecane/H_2O	0.88	$1.6_7 \times 10^{-4}$	$1.6_6 \times 10^{-4}$ (0.94)
$C_{12}BMG-C_{12}S$, isooctane/H_2O	0.98	$1.1_4 \times 10^{-4}$	$1.1_1 \times 10^{-4}$ (0.94)
$C_{12}BMG-C_{12}S$, heptamethylnonane/H_2O	0.97	$1.4_6 \times 10^{-4}$	$1.3_8 \times 10^{-4}$ (0.94)
$C_{12}BMG-C_{12}S$, cyclohexane/H_2O	0.95	$7.5_6 \times 10^{-5}$	$9.2_0 \times 10^{-5}$ (0.94)
$C_8P-C_{12}S$, hexadecane/0.1M NaCl aq. soln.	0.30	$1.2_1 \times 10^{-3}$	$1.3_0 \times 10^{-3}$ (0.23)
$C_{10}P-C_{12}S$, hexadecane/0.1M NaCl aq. soln.	0.43	$6.3_8 \times 10^{-4}$	$7.5_0 \times 10^{-4}$ (0.25)

TABLE 15: Synergism in Mixed Micelle Formation at 25.0°C (values in parentheses are for the corresponding air/aqueous systems)

Surfactant1-2, system	β^{M}_{LL}	$\|\ln CMC^{0}_{1,t}/CMC^{0}_{2,t}\|$	synergism	
			predicted	found(exp.)
$C_{12}EO_7$-$C_{12}S$, heptane/H_2O	-0.1_9	3.7	no	no
$C_{12}BMG$-$C_{12}S$, heptane/H_2O	$-4._0$($-5._0$[a])	3.1(3.0[a])	yes	yes
$C_{12}BMG$-$C_{12}S$, dodecane/H_2O	$-3._6$($-5._0$[a])	3.1(3.0[a])	yes	yes
$C_{12}BMG$-$C_{12}S$, hexadecane/H_2O	$-4._0$($-5._0$[a])	3.0(3.0[a])	yes	yes
$C_{12}BMG$-$C_{12}S$, isooctane/H_2O	$-4._0$($-5._0$[a])	3.1(3.0[a])	yes	yes
$C_{12}BMG$-$C_{12}S$, heptamethylnonane/H_2O	$-4._2$($-5._0$[a])	3.0(3.0[a])	yes	yes
$C_{12}BMG$-$C_{12}S$, cyclohexane/H_2O	$-2._1$($-5._0$[a])	3.3(3.0[a])	yes	yes
$C_{12}BMG$-$C_{12}S$, toluene/H_2O	$-2._1$($-5._0$[a])	3.3(3.0[a])	no	no
$C_{16}HGEO_5S$- $C_{16}HGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	-0.1_8	4.3	no	no

TABLE 15: (Continued)

Surfactant1-2, system	β^M_{LL}	$\lvert \ln CMC^0_{1,t}/CMC^0_{2,t} \rvert$	<u>synergism</u> predicted	found(exp.)
$C_{16}EGEO_5S$- $C_{16}EGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	$-1._5(+0.4^b)$	3.0	no	no
$C_{12}EO_8$-$C_{12}EO_4$, hexadecane/H_2O	$+0.3_3$	1.8	no	no
$C_{12}EO_8$-$C_{12}EO_3$, hexadecane/H_2O	-0.1_8	2.7	no	no
$C_{12}EO_8$-$C_{12}EO_2$, hexadecane/H_2O	$-2._7(+0.3_7)$	3.4	no	no
$C_{12}EO_8$-$C_{12}EO_2$, heptane/H_2O	$+0.4_1$	4.4	no	no
$C_{16}EO_8$-$C_{12}EO_2$, hexadecane/H_2O	$-5._2$	5.0	yes	no
$C_{12}EO_8$-C_8P, hexadecane/H_2O	-0.1_9	4.8	no	no
$C_{12}EO_8$-$C_{12}P$, hexadecane/H_2O	$-1._4$	4.5	no	no

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[a] Data from reference 131.

[b] Data from reference 132.

In 16 of the 17 cases, the theoretical prediction for the existence or absence of synergism in mixed micelle formation is in agreement with experimental results. For the one exception, the $C_{16}EO_8/C_{12}EO_2$ in a hexadecane/H_2O system, the condition for synergism that $|\beta^M{}_{LL}| > |\ln (CMC^0{}_{1,t}/CMC^0{}_{2,t})|$ was within experimental error of not being met since $\beta^M{}_{LL}$ values have an inherent error of ≈ ± 5%.

For the systems that did exhibit synergism in this respect, minimum concentration values at the cmc at the point of maximum synergism, $CMC_{12,t,min}$, were calculated using equation [87], and the mole fraction values, $\alpha^{*,M}{}_1$, at the point of maximum synergism were calculated using equation [85]. These calculated parameters are listed in Table 16 and the calculated $CMC_{12,t,min}$ values are compared with experimentally determined $CMC_{12,t,min}$ values (at experimental α_1 values close to the $\alpha^{*,M}{}_1$ values) in the Table. Calculated and experimental $CMC_{12,t,min}$ values are in good agreement.

For systems that air/aqueous β^M values have been included (Table 15), it is observed that for the $C_{12}BMG/C_{12}S$ systems, which contain two water soluble surfactants, the $\beta^M{}_{LL}$ values in the hydrocarbon/aqueous systems are less negative than the β^M value in the corresponding air/aqueous system. For those systems where a water soluble surfactant is mixed with an oil soluble one ($C_{16}EGEO_5S/C_{16}EGEO_5OH$, and $C_{12}EO_8/C_{12}EO_2$), the $\beta^M{}_{LL}$ values in the hydrocarbon/aqueous systems are more negative than the β^M values in the corresponding air/water systems.

With regard to synergism or negative synergism in interfacial tension reduction effectiveness, the theoretical prediction for its existence or absence is in agreement with experimental findings in 15 out of 17 cases as shown in Table 17. For the two cases ($C_{12}BMG/C_{12}S$ in a toluene/water system and $C_{16}EO_8/C_{12}EO_2$ in a hexadecane/water system) that are predicted to have synergism and negative synergism, respectively, in this respect but which do not exhibit it experimentally, the prediction of synergism or negative synergism is not a gross error since the

TABLE 16: Parameters at the Point of Maximum Synergism in Mixed Micelle Formation - $CMC_{12,t,min}$, $\alpha^{*,M}$ at 25.0°C and $\alpha_{BMG,\ exp.} = 0.94$

Surfactant1-2, system	$\alpha^{*,M}_{BMG}$ (calc.)	$CMC_{12,t,min}/M$ calc.	 exp.
$C_{12}BMG$-$C_{12}S$, heptane/H_2O	0.89	4.0×10^{-4}	3.2×10^{-4}
$C_{12}BMG$-$C_{12}S$, dodecane/H_2O	0.92	4.4×10^{-4}	3.7×10^{-4}
$C_{12}BMG$-$C_{12}S$, hexadecane/H_2O	0.88	4.6×10^{-4}	4.3×10^{-4}
$C_{12}BMG$-$C_{12}S$, isooctane/H_2O	0.98	4.0×10^{-4}	4.3×10^{-4}
$C_{12}BMG$-$C_{12}S$, heptamethylnonane/H_2O	0.97	4.8×10^{-4}	3.8×10^{-4}
$C_{12}BMG$-$C_{12}S$, cyclohexane/H_2O	0.95	3.4×10^{-5}	3.0×10^{-5}

TABLE 17: Synergism and Negative Synergism in Interfacial Tension Reduction Effectiveness at 25.0°C

Surfactant1-2, system	β^{σ}_{LL}- β^{M}_{LL}	$\lvert \ln CMC^0_{2,t}/C^0,CMC_{2,t} \rvert$	synergism(+) or negative(-) synergism predicted	found(exp.)
$C_{12}EO_7$-$C_{12}S$, heptane/H_2O	+0.3$_8$	0.39	no	no
$C_{12}BMG$-$C_{12}S$, heptane/H_2O	-0.7	0.45	yes(+)	yes(+)
$C_{12}BMG$-$C_{12}S$, dodecane/H_2O	-1.$_2$	0.45	yes(+)	yes(+)
$C_{12}BMG$-$C_{12}S$, hexadecane/H_2O	-1.$_2$	0.32	yes(+)	yes(+)
$C_{12}BMG$-$C_{12}S$, isooctane/H_2O	-0.4$_2$	0.41	yes(+)	yes(+)
$C_{12}BMG$-$C_{12}S$, heptamethylnonane/H_2O	-1.$_0$	0.43	yes(+)	yes(+)
$C_{12}BMG$-$C_{12}S$, cyclohexane/H_2O	-0.8	0.41	yes(+)	yes(+)
$C_{12}BMG$-$C_{12}S$, toluene/H_2O	-0.9	0.46	yes(+)	no
$C_{16}HGEO_5S$- $C_{16}HGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	-1.$_0$	0.15^a	yes(+)	yes(+)

TABLE 17: (Continued)

Surfactant1-2, system	$\beta^{\sigma}_{LL}-\beta^{M}_{LL}$	$\lvert\ln CMC^0_{2,t}/C^{0,CMC}_{2,t}\rvert$	synergism(+) or negative(-) synergism predicted	 found(exp.)
$C_{16}EGEO_5S$- $C_{16}EGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	-0.7	0.076[a]	yes(+)	yes(+)
$C_{12}EO_8$-$C_{12}EO_4$, hexadecane/H_2O	-0.2_2	0.46[a]	no	no
$C_{12}EO_8$-$C_{12}EO_3$, hexadecane/H_2O	-0.5_3	0.55[a]	no	no
$C_{12}EO_8$-$C_{12}EO_2$, hexadecane/H_2O	+0.5	0.12	yes(-)	no
$C_{12}EO_8$-$C_{12}EO_2$, heptane/H_2O	$-2._0$	0.78	yes(+)	yes(+)
$C_{16}EO_8$-$C_{12}EO_2$, hexadecane/H_2O	$+3._8$	0.75[a]	yes(-)	yes(-)
$C_{12}EO_8$-C_8P, hexadecane/H_2O	-0.3_3	0.43[a]	no	no
$C_{12}EO_8$-$C_{12}P$, hexadecane/H_2O	-0.6	0.06	yes(+)	yes(+)

[a] Parameter is for $\lvert\ln C^{0,CMC}_{1,t}/ CMC^0_{1,t}\rvert$.

conditions for synergism and negative synergism were barely met and within experimental error of not being met.

Among the systems that did exhibit synergism or negative synergism in interfacial tension reduction effectiveness, the cmc values at the point of maximum synergism, $CMC^*_{12,t}$, for the $C_{12}BMG/C_{12}S$ systems were calculated using equation [121] (since these systems contained an ionic surfactant in the absence of a swamping amount of electrolyte in the aqueous phase as discussed in section 2.4). For all the other systems the cmc values at the point of maximum synergism, or negative synergism ($C_{16}EO_8/C_{12}EO_2$ in a hexadecane/water system) were calculated using equation [116]. α^{*,E_1} values for the $C_{12}BMG/C_{12}S$ systems were calculated using equation [119], while α^{*,E_1} values for the other systems were calculated using equation [114]. The interfacial tensions at the point of maximum synergism, $\gamma^*_{CMC,12,t}$, for the $C_{12}BMG/C_{12}S$ systems were calculated using equation [122], while the values at the point of maximum synergism, or negative synergism, for the other systems were calculated using equation [117]. These calculated parameters are listed in Table 18. Again, there is good agreement between theoretical calculations and experimental results.

4.2.2 Effect of the Hydrocarbon Structure

This is demonstrated in Table 19 by the results for the $C_{12}BMG/C_{12}S$ mixture at various interfaces. The variation of the interaction with change in the nature of the hydrocarbon is slight, except for toluene, which shows a marked decrease in interaction at both the interface and in the micelles. This decrease in interaction is the result of the large increase in area per surfactant molecule, both at the toluene/aqueous solution interface and the micellar/aqueous solution interface, due to adsorption or solubilization, respectively, of toluene molecules. Although the variation in the interaction parameters among the saturated hydrocarbon/water systems is slight, it appears that the larger the cohesive energy density, δ, of the hydrocarbon, and thus the smaller its tendency to penetrate an interfacial film, the more negative is the β^{σ}_{LL} value. Thus, hexadecane and cyclohexane, which have larger δ values than isooctane or heptane, yield β^{σ}_{LL}

TABLE 18: Parameters at the Point of Maximum Synergism or Negative Synergism in Interfacial Tension Reduction Effectiveness - $\alpha^{*,E}$, $CMC^{*}_{12,t}$, $\gamma^{*}_{CMC,12,t}$

Surfactant1-2,	α^{*,M_1}	$CMC^{*}_{12,t}$ x 10^3/M		$\gamma^{*}_{CMC,12,t}$/ mN m^{-1}		
system	(calc.)	calc.	exp.	calc.	exp.	α_1,exp.
$C_{12}BMG$-$C_{12}S$, heptane/H_2O	0.042	1.8_5	1.6_2	0.6	1.1	0.051_6
$C_{12}BMG$-$C_{12}S$, dodecane/H_2O	0.044	2.0_5	2.0_0	0.7	1.8	0.051_6
$C_{12}BMG$-$C_{12}S$, hexadecane/H_2O	0.047	1.9_6	2.1_8	$1._4$	1.4	0.051_6
$C_{12}BMG$-$C_{12}S$, isooctane/H_2O	0.042	1.8_3	1.7_0	$1._3$	1.0	0.051_6
$C_{12}BMG$-$C_{12}S$, heptamethylnonane/H_2O	0.048	2.1_4	2.1_5	$1._1$	1.3	0.051_6
$C_{12}BMG$-$C_{12}S$, cyclohexane/H_2O	0.037	1.6_9	1.5_6	0	0.1	0.051_6
$C_{16}HGEO_5S$- $C_{16}HGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	9.8_4 x10^{-3}	0.44_7	0.36_3	0.08_6	0.13	0.013_8
$C_{16}EGEO_5S$- $C_{16}EGEO_5OH$, hexadecane/0.1M NaCl aq. soln.	3.6_5 x 10^{-2}	0.58_6	0.47_0	0.4_2	0.10	0.012_9
$C_{12}EO_8$-$C_{12}EO_2$, heptane/H_2O	2.3_5 x 10^{-2}	-	-	0.9_2	0.50	0.046_9

TABLE 18: (Continued)

Surfactant1-2,	$\alpha^{*,M}_1$	$CMC^{*}_{12,t} \times 10^3$/M		$\gamma^{*}_{CMC,12,t}$/ mN m^{-1}		
system	(calc.)	calc.	exp.	calc.	exp.	α_1,exp.
$C_{16}EO_8$-$C_{12}EO_2$, hexadecane/H_2O	$2.7_3 \times 10^{-3}$	-	-	$9._7$	$10._1$	0.0065_8
$C_{12}EO_8$-$C_{12}P$, hexadecane/H_2O	$3.4_4 \times 10^{-3}$	-	-	$1._9$	1.7	0.013_6

TABLE 19: Effect of the Hydrocarbon Structure on Molecular Interactions between $C_{12}BMG$ and $C_{12}S$

System	β^{σ}_{LL}	β^{M}_{LL}
heptane/H_2O	$-4._7$	$-4._0$
dodecane/H_2O	$-4._8$	$-3._6$
hexadecane/H_2O	$-5._2$	$-4._0$
isooctane/H_2O	$-4._4$	$-4._0$
heptamethylnonane/H_2O	$-4._4$	$-3._4$
cyclohexane/H_2O	$-5._0$	$-4._2$
toluene/H_2O	$-3._2$	$-2._1$

values that are more negative. No such trend is observed for the β^{M}_{LL} values.

Data that show the effect of hydrocarbon structure on synergism in interfacial tension reduction efficiency are listed in Table 20. The variation of $\alpha^{*}_{betaine}$ values with change in the hydrocarbon structure is slight. It does, however, appear that as the length of the straight-chain hydrocarbon is decreased, $\alpha^{*}_{betaine}$ values increase slightly. This follows from equation [81] and the data in Table 13, since as $\ln (C^{0}_{1,t}/C^{0}_{2,t}) \rightarrow \beta^{\sigma}_{LL}$, $\alpha^{*}_{1} \rightarrow 1$, and as the straight-chain hydrocarbon length is decreased, $\ln (C^{0}_{1,t}/C^{0}_{2,t})$ values are closer to their respective β^{σ}_{LL} values.

The quantity $(C^{0}_{1,t} - C_{12,t,min})/C^{0}_{1,t}$ $(= 1 - C_{12,t,min}/C^{0}_{1,t})$, where $C^{0}_{1,t} < C^{0}_{2,t}$ is a measure of the degree of synergism; the larger this quantity, the larger the synergistic effect. This quantity is related to equation [4], which determines the value of the $C_{12,t,min}/C^{0}_{1,t}$ ratio. As the difference between β^{σ}_{LL} and $\ln(C^{0}_{1,t}/C^{0}_{2,t})$ becomes larger, the $C_{12,t,min}/C^{0}_{1,t}$ ratio decreases and the degree of synergism increases. As indicated by the data in Table 13, the hexadecane/water system has the largest difference between β^{σ}_{LL} and $\ln(C^{0}_{1,t}/C^{0}_{2,t})$ and therefore the largest degree of synergism of the hydrocarbon/water systems studied, as shown in Table 20. For the straight-chain hydrocarbon phase systems, the synergistic effect in this respect becomes weaker as the chain becomes shorter.

Data that show the effect of hydrocarbon structure on synergism in mixed micelle formation are listed in Table 21. The variation of $\alpha^{*,M}_{betaine}$ values with change in the hydrocarbon structure is slight, and no trend is observed.

The quantity $(CMC^{0}_{1,t} - CMC_{12,t,min})/CMC^{0}_{1,t}$ $(= 1 - CMC_{12,t,min} / CMC^{0}_{1,t})$, where $CMC^{0}_{1,t} < CMC^{0}_{2,t}$, is a measure of the degree of synergism in this respect; the larger this quantity, the larger the synergistic effect. The variation of this parameter with change in the hydrocarbon structure is slight, and, in contrast to that observed in synergism in interfacial tension reduction efficiency, no correlation of the synergistic strength in this respect with length of the

TABLE 20: Effect of the Hydrocarbon Structure on Synergism in Interfacial Tension Reduction Efficiency in $C_{12}BMG/C_{12}S$ Mixed Surfactant Systems

System	$\alpha^{*}_{betaine}$	$1 - (C_{12,t,min}/C^{0}_{betaine,t})$
heptane/H_2O	0.95	0.01
dodecane/H_2O	0.92	0.03
hexadecane/H_2O	0.88	0.07
isooctane/H_2O	0.98	0.01
heptamethylnonane/H_2O	0.97	0.01
cyclohexane/H_2O	0.95	0.01

TABLE 21: Effect of the Hydrocarbon Structure on Synergism in Mixed Micelle Formation in $C_{12}BMG/C_{12}S$ Mixed Surfactant Systems

System	$\alpha^{*,M}_{betaine}$	$1 - (CMC_{12,t,min}/CMC^0_{betaine,t})$
heptane/H_2O	0.89	0.05
dodecane/H_2O	0.93	0.02
hexadecane/H_2O	0.87	0.08
isooctane/H_2O	0.89	0.04
heptamethylnonane/H_2O	0.94	0.01
cyclohexane/H_2O	0.89	0.05

straight-chain alkane is observed.

Data that show the effect on synergism in interfacial tension reduction effectiveness are listed in Table 22. The variation of $\alpha^{*,E}{}_{betaine}$ values with change in the hydrocarbon structure is slight.

The degree of synergism in this respect is measured by the $\gamma^{o}{}_{cmc, lowest}$ - $\gamma^{*}{}_{CMC,12,t}$ = $\Delta\gamma$ difference. The larger the $\Delta\gamma$ value the larger the synergistic effect. $\Delta\gamma$ is related to [117], viz.

$$\Delta\gamma = S_1 (\beta^{\sigma}{}_{LL} - \beta^{M}{}_{LL}) (1 - X^{*})^2 \qquad [124]$$

From this relation it is observed that $\Delta\gamma$ becomes larger when S_1 becomes more negative and/or $(\beta^{\sigma}{}_{LL} - \beta^{M}{}_{LL})$ becomes more negative. As shown in Table 22, the hexadecane/water system has the largest $\Delta\gamma$ value of the hydrocarbon/water systems studied. As the alkane length is shortened in the straight-chain alkane series, the $\Delta\gamma$ value becomes progressively smaller.

4.2.3 Effect of the Length of the Surfactant Hydrophobic Group

The effect of the length of the surfactant hydrophobic group is demonstrated by the results for the following six mixtures: $C_{16}EO_8$ or $C_{12}EO_8$/ $C_{12}EO_2$ and $C_{12}EO_8/C_8P$ or $C_{10}P$ in hexadecane/water systems, and C_8P, $C_{10}P$/ $C_{12}S$ in hexadecane/0.1M NaCl aqueous solution systems.

Data of the effect on molecular interactions are listed in Table 23. For the $C_{12}EO_8$ or $C_{16}EO_8$/ $C_{12}EO_2$ systems, increasing the length from C_{12} to C_{16} for the EO_8 compound causes $\beta^{\sigma}{}_{LL}$ to become less negative and $\beta^{M}{}_{LL}$ to become more negative. For the C_8P, $C_{10}P$/ $C_{12}S$ case, increasing the hydrophobic chain length

TABLE 22: Effect of the Hydrocarbon Structure on Synergism in Interfacial Tension Reduction Effectiveness in $C_{12}BMG/C_{12}S$ Mixed Surfactant Systems

System	$\alpha^{*,E}_{\text{betaine}}$	$\Delta\gamma$
heptane/H_2O	0.042	0.7
dodecane/H_2O	0.044	1.0
hexadecane/H_2O	0.047	2.1
isooctane/H_2O	0.042	1.0
heptamethylnonane/H_2O	0.048	1.5
cyclohexane/H_2O	0.037	0.9

TABLE 23: Effect of the Length of the Surfactant Hydrophobic Group on Molecular Interaction

Surfactant1-2	second phase (against hexadecane)	β^{σ}_{LL}	β^{M}_{LL}
$C_{12}EO_8$-$C_{12}EO_2$	H_2O	-2.2	-2.7
$C_{16}EO_8$-$C_{12}EO_2$	H_2O	-1.4	-5.2
C_8P-$C_{12}S$	0.1M NaCl aq. soln.	-1.7	-
$C_{10}P$-$C_{12}S$	0.1M NaCl aq. soln.	-2.3	-
C_8P-$C_{12}EO_8$	H_2O	-0.52	-0.19
$C_{12}P$-$C_{12}EO_8$	H_2O	-2.0	-1.4

from C_8 to C_{10} for the C_xP compound causes $\beta^{\sigma}{}_{LL}$ to become more negative. For the C_8P or $C_{12}P/C_{12}EO_8$ systems, increasing the length from C_8 to C_{12} for the C_xP compound causes both $\beta^{\sigma}{}_{LL}$ and $\beta^{M}{}_{LL}$ to become more negative. The interpretation of these results is that in the interfacial region, as the length of the hydrophobic tail is increased, hydrophobic bonding increases, and $\beta^{\sigma}{}_{LL}$ becomes more negative. This trend continues up to the point where the chain lengths in each surfactant are equal; beyond that point, however, $\beta^{\sigma}{}_{LL}$ then begins to become less negative (as seen in the $C_{12}EO_8$, $C_{16}EO_8/ C_{12}EO_2$ case). In the mixed micelles, $\beta^{M}{}_{LL}$ becomes consistently more negative as the chain length is increased, even beyond the point where the lengths in each surfactant are equal. Similar effects on β^{σ} and β^{M} are seen at the air/aqueous interface (133,134). These effects are probably due to the tighter packing experienced by the chains in the core of a micelle compared with a planar interface where the chains have more conformational freedom.

Data showing the effect on synergism in interfacial tension reduction efficiency is listed in Table 24. Since, as ln $(C^0{}_{1,t}/ C^0{}_{2,t}) \rightarrow \beta^{\sigma}{}_{LL}$, $\alpha^*{}_1 \rightarrow 1$ (equation [80]), and the difference between ln $(C^0{}_{1,t}/ C^0{}_{2,t})$ and $\beta^{\sigma}{}_{LL}$ (Table 13) is greater for the $C_{12}S$-$C_{10}P$ system than for the $C_{12}S$-C_8P system, $\alpha^*{}_1$ is smaller in the former system where the chain length of the C_xP compound is longer. This is expected since $\beta^{\sigma}{}_{LL}$ changes more rapidly with hydrophobic chain length (up to the point where the length of each surfactant is equal) than does ln $(C^0{}_{1,t}/ C^0{}_{2,t})$. The stength of the synergism in this respect, measured by $[1 - (C_{12,t,min}/ C^0{}_{1,t})]$, increases as the chain length of the C_xP compound increases. This trend would be expected to continue until the chain lengths of each surfactant are equal (since $\beta^{\sigma}{}_{LL}$ would reach its most negative value, for a given length, at that point).

TABLE 24: Effect of the Length of the Surfactant Hydrophobic Group on Synergism in Interfacial Tension Reduction Efficiency in Hexadecane/0.1M NaCl Aqueous Solution Systems

Surfactant1-2	α^*_1	$1 - (C_{12,t,min}/C^0_{1,t})$
$C_{12}S$-C_8P	0.70	0.14
$C_{12}S$-$C_{10}P$	0.57	0.35

4.2.4 Effect of Branching of the Hydrophobic Groups

The effect of branching of the hydrophobic groups is shown by the results for the $C_{16}HGEO_5S/C_{16}HGEO_5OH$ and $C_{16}EGEO_5S/C_{16}EGEO_5OH$ mixtures. Data are listed in Table 25. In both cases, in the hexadecane/0.1M NaCl aqueous solution systems, there is more surfactant interaction at the planar interface than there is in the micelle (i.e., $\beta^{\sigma}{}_{LL}$ is more negative than $\beta^{M}{}_{LL}$). This is attributed to more steric hinderence to surfactant interaction with these branched hydrophobic groups in the latter location due to more rigid packing requirements there, compared with a planar interface.

In these systems, there is enhanced interfacial adsorption of the oil soluble surfactant in the presence of the water soluble one. Enhanced interfacial adsorption of long-chain alcohols in the presence of sodium dodecyl sulfate in Nujol/water systems has been observed by Vold and Mittal (135). Data demonstrating enhanced adsorption, in the present case, are listed in Table 26. The contraction of 8.0Å^2, which is the difference between the A_{12} value calculated for $X_{C16EGEO5S} = 0.32$ (viz. (0.32)(50.$_4$Å^2) + (0.68)(70.$_0$Å^2) = 63.$_7$Å^2) and the actual value obtained at this X value (55.$_7$Å^2), shows that more surfactant is present at the interface than would be predicted by calculation assuming that the X_1 and X_2 values are correct. This contraction shows that there is enhanced adsorption in the mixed surfactant system . The A_{12} experimental value does not, however, mean that there is contraction relative to the L/A case. In fact, there is not; $A^0{}_{C16EGEO5S}$, L/A = 59.$_3$Å^2 , $A^0{}_{C16EGEO5OH}$, L/A = 44.$_0$Å^2, calculated A_{12} = (0.32)(59.$_3$Å^2) + (0.68)(44.$_0$Å^2) = 48.$_9$Å^2 (calculated at $X_{C16EGEO5S}$ =0.32). Since $\beta^{\sigma}{}_{LL}$ is more negative than $\beta^{M}{}_{LL}$ due to branching of the hydrophobic groups, $\beta^{\sigma}{}_{LL} - \beta^{M}{}_{LL}$ is rather large and negative. This combination is needed to meet the conditions for synergism in interfacial tension reduction effectiveness. Both systems therefore exhibit synergism in this respect. Data are listed in Table 31 (below).

TABLE 25: Effect of Branching of the Surfactant Hydrophobic Groups on Molecular Interaction

Surfactant1-2	system	β^{σ}_{LL}	β^{M}_{LL}
$C_{16}HGEO_5S/C_{16}HGEO_5OH$	hexadecane/0.1M NaCl aq. soln.	$-1._2$	-0.1_8
$C_{16}EGEO_5S/C_{16}EGEO_5OH$	hexadecane/0.1M NaCl aq. soln.	$-2._2$	$-1._5$

TABLE 26: Area per Molecule Data for Pure and Mixed $C_{16}EGEO_5S$ and $C_{16}EGEO_5OH$ in Hexadecane/0.1M NaCl Aqueous Solution Systems

Parameter	area/Å^2
A^0_{min} ($C_{16}EGEO_5S$)	$50._4$
A^0_{min} ($C_{16}EGEO_5OH$)	$70._0$
$A_{12,exp.}$ ($X_{EGS} = 0.32$)	$55._7$
$A_{12,calc.}$ at $X_{EGS} = 0.32$	$63._7$
contraction	**$8._0$**

4.2.5 Effect of the Number of EO Groups in Mixtures of POE Nonionics

Data illustrating the effect of the number of EO groups in mixtures of POE nonionics on molecular interactions are listed in Table 27. As the number of EO groups in the second surfactant is shortened from EO_4 to EO_0 in mixtures with $C_{12}EO_8$, both $\beta^{\sigma}{}_{LL}$ and $\beta^{M}{}_{LL}$ become more negative. It appears that molecular interaction at both the interface and in the micelles increases as the EO group of the second surfactant is shortened (and the surfactant becomes more oil soluble). This relationship is clearly indicated in Figure 5 where $\beta^{\sigma}{}_{LL}$ and $\beta^{M}{}_{LL}$ are plotted against number of EO groups.

Similar to the other systems (above) containing an oil-soluble and a water-soluble surfactant together in the mixture, there is enhanced adsorption at the interface in these systems in the presence of hexadecane. Data demonstrating this are listed in Table 28. If it is assumed that the values of X_1 and X_2 are correct, then as the EO number is reduced, the data indicate that the difference between experimental and calculated values (the "contraction") of the areas per surfactant molecule at the interface (in the mixed film relative to those in the individual films in the presence of hexadecane) becomes larger. As found with the $C_{16}EGEO_5S/C_{16}EGEO_5OH$ mixture, and as indicated in Table 28, the contraction shown in the L/L system does not mean that the interfacial film at the L/L interface is contracted relative to the film at the L/A interface ($44._5Å^2$ L/L; $41._9Å^2$ L/A; both for $X_{C12EO8} = 0.36_6$). It is interesting to note that experimental and calculated A_{min} values at the L/A interface ($42._9Å^2$ vs $43._1Å^2$, at $X_{C12EO8} = 0.59_4$) are very close, which is possibly the reason for the less negative β^{σ} value at the L/A interface than at the L/L interface where there is a substantial deviation from ideality ($44._5Å^2$ experimental vs $58._3Å^2$ calculated at $X_{C12EO8} = 0.36_6$).

Among the POE nonionic mixtures investigated, only two exhibit any type of synergism (see Tables 17 and 18). The $C_{16}EO_8/C_{12}EO_2$ system shows negative synergism in interfacial tension reduction effectiveness, although the interfacial

TABLE 27: Effect of the Length of the POE Groups on Molecular Interactions in POE Nonionic Mixtures in Hexadecane/H_2O Systems[a]

Surfactant1-2	β^{σ}_{LL}	β^{M}_{LL}
$C_{12}EO_8/C_{12}EO_4$	$+0.5_5$	$+0.3_3$
$C_{12}EO_8/C_{12}EO_3$	-0.7_1	-0.1_8
$C_{12}EO_8/C_{12}EO_2$	$-2._2$	$-2._7$
$C_{12}EO_8/C_{12}EO_0$[a]	$-5._2$	-

[a] $C_{12}EO_0 = C_{12}OH$.

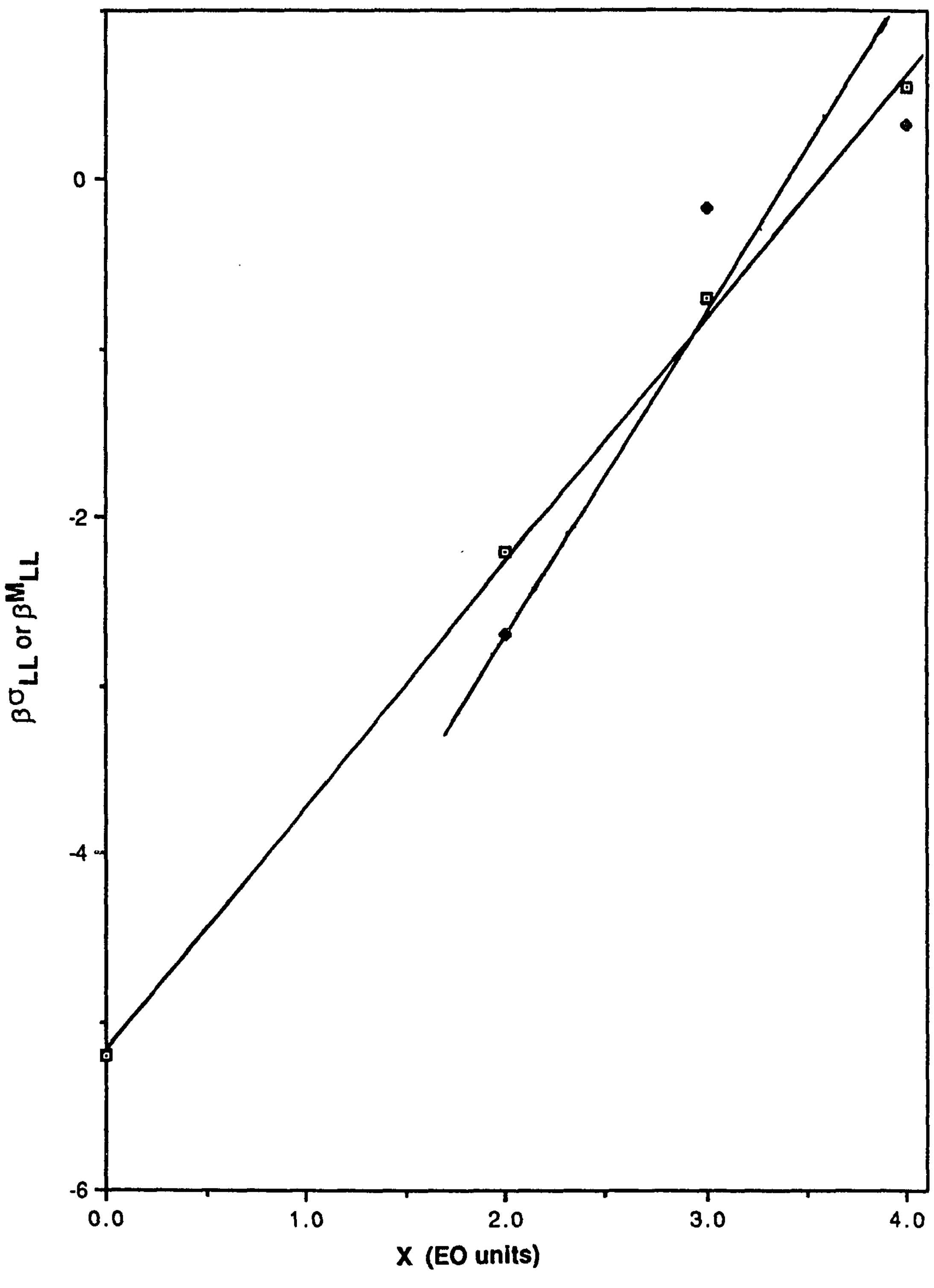

Figure 5. β^{σ}_{LL} or β^{M}_{LL} vs EO content in $C_{12}EO_x$ for $C_{12}EO_8/C_{12}EO_x$ mixtures in hexadecane/water systems. ▣, β^{σ}_{LL}; ◆, β^{M}_{LL}.

TABLE 28: Area per Molecule Data for Pure and Mixed POE Nonionic Surfactants in Hexadecane/H_2O Systems

Parameter/Å^2	$C_{12}EO_8$/ $C_{12}EO_4$	$C_{12}EO_8$/ $C_{12}EO_3$	$C_{12}EO_8$/ $C_{12}EO_2$	$C_{12}EO_8$/ $C_{12}EO_0$
$A^0_{1,min}$	$63._0$	$63._0$	$63._0$	$63._0$
$A^0_{2,min}$	$52._6$	$50._0$	$55._6$	$1.0_8 \times 10^2$
$A_{12,exp.}$	$59._8$	$54._8$	$44._5$	$59._1$
at X_{EO8}	0.58_5	0.46_8	0.36_6	0.77_0
$A_{12,calc.}$ at same X_{EO8}	$58._7$	$56._1$	$58._3$	$75._5$
contraction	**$-1._1$**	**$1._3$**	**$13._8$**	**$16._4$**
$A^0_{1,min}$ L/A	-	-	$60._9$	-
$A^0_{2,min}$ L/A	-	-	$30._9$	-
$A_{12,calc.}$ L/A at $X_{EO8} = 0.36_6$	-	-	$41._9$	-
$A_{12,exp}/A_{12,calc.}$ at $X_{EO8} = 0.59_4$, L/A	-	-	$42._9/43._1$	-

tension does continue to decrease slowly after the break in the γ_I vs -log C_t curve (Figure B29). In this case, micelle formation is enhanced since micelles form at a lower concentration than ideally predicted at the mole fraction investigated. A $C_{12}EO_8/C_{12}EO_2$ mixture in a heptane/water system exhibits synergism in interfacial tension reduction effectiveness (Table 17). In this system, micelle formation is hindered since micelles form at a higher concentration than ideally predicted at the mole fraction investigated. These two cases, however, are insufficient to yield conclusions of the effect of the EO number on synergism.

4.2.6 Effect of the Presence of the Hydrocarbon on Synergism

The effect of the presence of the hydrocarbon on synergism in interfacial tension reduction efficiency is shown in Table 29. The α^*_1 values for the hydrocarbon/aqueous systems are larger than their values in the corresponding air/aqueous systems. This follows from equation [81] and the data in Table 13, since as ln $(C^0_{1,t}/C^0_{2,t}) \rightarrow \beta^\sigma_{LL}$, $\alpha^*_1 \rightarrow 1$, and in the hydrocarbon/aqueous systems, ln $(C^0_{1,t}/C^0_{2,t})$ values are closer to their respective β^σ_{LL} values than in the air/aqueous systems.

The strength of the synergism in this respect (as measured by $1 - (C_{12,t,min}/C^0_{1,t})$ given in Table 29) is smaller in each of the hydrocarbon/aqueous systems studied compared with the corresponding air/aqueous systems. This is attributed to intercalation of hydrocarbon molecules between the surfactant hydrophobic tails at the hydrocarbon/aqueous interfaces.

The effect of the presence of the hydrocarbon on synergism in mixed micelle formation is shown in Table 30 for the $C_{12}BMG/C_{12}S$ systems. The $\alpha^{*,M}_{betaine}$ values in all the hydrocarbon/aqueous systems are greater than the value for the air/aqueous system. This follows from equation [85] and the data in Table 15 since as ln $(CMC^0_{1,t}/CMC^0_{2,t}) \rightarrow \beta^M_{LL}$, $\alpha^{*,M}_1 \rightarrow 1$.

The strength of the synergism in this respect (as measured by $1 - (CMC_{12,t,min}/CMC^0_{1,t})$ given in Table 30) is smaller in the

TABLE 29: Effect of the presence of the hydrocarbon on synergism in interfacial tension reduction efficiency

Surfactant1-2, system	α^*_1	$1 - (C_{12,t,min}/C^0_{1,t})$
C_{12}BMG/C_{12}S heptane/H_2O	0.95	0.01
C_{12}BMG/C_{12}S dodecane/H_2O	0.92	0.03
C_{12}BMG/C_{12}S hexadecane/H_2O	0.88	0.07
C_{12}BMG/C_{12}S isooctane/H_2O	0.98	0.01
C_{12}BMG/C_{12}S heptamethylnonane/H_2O	0.97	0.01
C_{12}BMG/C_{12}S cyclohexane/H_2O	0.95	0.01
C_{12}BMG/C_{12}S air/H_2O[a]	0.85	0.12
C_{12}S-C_8P, hexadecane/ 0.1M NaCl aq. soln.	0.70	0.14
C_{12}S-C_8P, air/ 0.1M NaCl aq. soln.[b]	0.53	0.49

[a] Data from reference 131.

[b] Data from reference 132.

TABLE 30: Effect of the presence of the hydrocarbon on synergism in mixed micelle formation. Data is for $C_{12}BMG/C_{12}S$ mixture

System	$\alpha^{*,M}{}_{betaine}$	$1 - (CMC_{12,t,min}/CMC^{0}{}_{betaine,t})$
heptane/H_2O	0.89	0.05
dodecane/H_2O	0.93	0.02
hexadecane/H_2O	0.87	0.08
isooctane/H_2O	0.89	0.04
heptamethylnonane/H_2O	0.94	0.01
cyclohexane/H_2O	0.89	0.05
air/H_2O[a]	0.80	0.18

[a] Data from reference 131.

hydrocarbon/aqueous systems than for the air/aqueous system.

The effect of the presence of the hydrocarbon on synergism in interfacial tension reduction effectiveness is shown in Table 31. The α^{*,E_1} values for the $C_{12}BMG/C_{12}S$ (both water soluble surfactants) in hydrocarbon/water systems are both above and below (0.048 in the heptamethylnonane/water system; 0.037 in the cyclohexane/water system) the value of 0.047 for the air/water system. For $C_{16}EGEO_5S/C_{16}EGEO_5OH$ (one water soluble surfactant and one oil soluble surfactant) in hexadecane/0.1M NaCl aqueous solution system, the α^{*,E_1} value is very small and much less than the value in the corresponding air/0.1M NaCl aqueous solution system. $C_{16}EGEO_5OH$ is very oil soluble which forces $CMC^0_{1,t} << CMC^0_{2,t}$, and therefore α^{*,E_1} to be very small for the L/L system because in equation [114], when $CMC^0_{1,t} << CMC^0_{2,t}$, $\alpha^{*,E_1} \rightarrow 0$. The α^{*,E_1} value for the L/A system is much larger because no oil phase is present to dissolve the $C_{16}EGEO_5OH$ molecules and, therefore, $CMC^0_{1,t}$ is not much less than $CMC^0_{2,t}$ ($CMC^0_{1,t} / CMC^0_{2,t} = 7.0$ in the L/A system (117), and 0.050 in the L/L system).

The strength of the synergism in this respect (as measured by $\Delta\gamma$ in Table 31) for the $C_{12}BMG/C_{12}S$ in hydrocarbon/water systems is less than for the corresponding air/water system. For the $C_{16}EGEO_5S/C_{16}EGEO_5OH$ in hexadecane/0.1M NaCl aqueous solution system, the synergism in this respect is slightly stronger than for the corresponding air/0.1M NaCl aqueous solution system due to a slightly larger (negative) slope for the pure anionic surfactant in the L/L system compared with the L/A system, in accordance with equation [124].

4.2.7 Summary of the Effect of the Hydrophilic Head on Molecular Interaction and Synergism

β^{σ}_{LL}

For the systems investigated, the order of decreasing surfactant interaction at the aqueous solution/hydrocarbon interface is:

TABLE 31. Effect of the presence of the hydocarbon on synergism in interfacial tension reduction effectiveness

Surfactant1-2	system	$\alpha^{*,E}_1$	$\Delta\gamma$(exp)
C_{12}BMG/C_{12}S	heptane/H_2O	0.042	0.7
C_{12}BMG/C_{12}S	dodecane/H_2O	0.044	1.0
C_{12}BMG/C_{12}S	hexadecane/H_2O	0.047	2.1
C_{12}BMG/C_{12}S	isooctane/H_2O	0.042	1.0
C_{12}BMG/C_{12}S	heptamethylnonane/H_2O	0.048	1.5
C_{12}BMG/C_{12}S	cyclohexane/H_2O	0.037	0.9
C_{12}BMG/C_{12}S	air/H_2O[a]	0.047	4.9
C_{16}HGEO_5S/C_{16}HGEO_5OH	hexadecane/0.1M NaCl aq. soln.	9.8×10^{-3}	1.3
C_{16}EGEO_5S/C_{16}EGEO_5OH	hexadecane/0.1M NaCl aq. soln.	3.6×10^{-2}	1.2
C_{16}EGEO_5S/C_{16}EGEO_5OH	air/0.1M NaCl aq. soln.[b]	0.87	1.0

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[a] Data from reference 131.

[b] Data from reference 117.

anionic-betaine ≥ anionic-nonionic(oil soluble) ≈ nonionic(water soluble)-nonionic(oil soluble) > anionic-nonionic(water soluble) > nonionic(water soluble)-nonionic(water soluble)

where the pyrrolidone group is included as a nonionic group. Only those aqueous/hydrocarbon systems consisting of a very oil soluble surfactant (K≈ > 4 x 10^3) mixed with a water soluble surfactant have more surfactant interaction than in the corresponding aqueous/air system. Based on the $\beta^{\sigma}{}_{LL}$ values in Table 13, it can be concluded that the pyrrolidone head group is equal to ≈ 2.5-3 EO groups.

$\beta^{M}{}_{LL}$

The order of decreasing interaction is similar to that given for $\beta^{\sigma}{}_{LL}$ above and only those L/L systems in which a water soluble surfactant is mixed with an oil soluble one show greater interaction than in the corresponding L/A case.

Synergism

Among the hydrocarbon/aqueous systems studied, the order of decreasing strength of synergism for all three types investigated is:

anionic-betaine > anionic-nonionic > nonionic-nonionic.

In the systems which contain two water soluble surfactants, the strength of the synergism in the L/A system is stronger than the synergism in the corresponding L/L system for all three types of synergism. For the systems containing a very oil soluble surfactant and a water soluble one, there are three cases where either synergism in interfacial tension reduction effectiveness is stronger in the L/L system than in the L/A system or synergism in this respect is present in the former and not in the latter. These systems are: $C_{16}EGEO_5S/C_{16}EGEO_5OH$ in hexadecane/aqueous 0.1M NaCl, $C_{12}EO_8/C_{12}EO_2$ in heptane/water, and $C_{12}EO_8/C_{12}P$ in hexadecane/water.

APPENDIX A

Partition Coefficient Data

TABLE A1: Data for calculating the partition coefficient of pure $C_{12}BMG$, and in its mixtures with $C_{12}S$, in heptane/water systems at 25.0°C (concentrations are for $C_{12}BMG$ only)

System	$C_w \times 10^{-3}/M$ (initial)	A (final)[a]	$C_w \times 10^{-3}/M$ (final)	$C_w \times 10^{-5}/M$ (final)
$C_{12}BMG$ (pure)				
run 1	0.27_3	0.096_5	0.27_2	0.2_3
run 2	0.27_3	0.096_5	0.27_2	0.2_3
$C_{12}BMG$ ($\alpha_{BMG}=0.55_7$)				
run 1	1.3_0	0.46_2	1.3_0	0.8
run 2	1.3_0	0.46_1	1.3_0	1

[a] A = absorbance of the water phase.

TABLE A2: Data for calculating the partition coefficient of pure C_8P, and in its mixtures with $C_{12}S$, at 25.0°C (concentrations are for C_8P only)

System	C_W x 10^{-3}/M (initial)	C_B x 10^{-2}/ M (initial)	A (final)	C_W x 10^{-4}/ (final)	C_B x 10^{-3}/ M (final)
C_8P (pure), hexadecane/ H_2O	3.0_0	0	0.22_0[a]	3.0_5	6.7_4
C_8P (pure), hexadecane/ 0.1M NaCl aq. soln.	3.0_0	0	0.19_6[b]	2.3_1	6.9_2
C_8P (α_{C8P}=0.72), hexadecane/ 0.1M NaCl aq. soln.	0	1.0_2	0.40_6	1.8_1	2.9_7
C_8P (α_{C8P}=0.62), hexadecane/ 0.1M NaCl aq. soln.	0	1.0_5	0.40_3	1.7_5	3.5

[a] Absorbance listed is for one ml of the final water phase diluted to 10ml.

[b] Absorbance listed is for 4 ml of the final aqueous phase diluted to 14 ml.

TABLE A3: Data for calculating the partition coefficient of pure $C_{10}P$, and in its mixture with $C_{12}S$, in hexadecane/0.1M NaCl aqueous solution systems at 25.0°C (concentrations are for $C_{10}P$ only)

System	C_W x 10^{-3}/M (initial)	C_B x 10^{-2}/ M (initial)	A (final)	C_W x 10^{-5}/ (final)	C_B x 10^{-2}/ M (final)
$C_{10}P$ (pure)	3.5_3	0	0.20_2	8.6_1	2.9_4
$C_{10}P$ (α_{C10P}=0.59)	0	2.6_9	0.19_1	9.9_3	2.2_9

TABLE A4: Absorbance vs concentration data for C_8P in 0.1M NaCl aqueuos solutions at 191 nm and at 25.0°C

C x 10^4/M	A
2.7_3	0.45_8
1.8_8	0.38_4
1.4_3	0.32_4
0.97	0.26_0
0.64_5	0.19_1

TABLE A5: Absorbance vs concentration data for $C_{10}P$ in 0.1M NaCl aqueuos solutions at 191 nm and at 25.0°C

$C \times 10^5$/M	A
$12._0$	0.29_1
8.6_1	0.20_1
6.0_2	0.14_4

TABLE A6: Data for calculating the partition coefficient of pure $C_{12}S$, and in its mixtures with C_8P and $C_{10}P$, in hexadecane/0.1M NaCl aqueous solution systems at 25.0°C (concentrations are for $C_{12}S$ only. Titrant is $1.0_2 \times 10^{-3}$M Hyamine and the ml's used represents the amount needed to titrate 50 ml of the aqueous phase; titration error = ± 0.045 ml)

System	C_W x 10^{-4}/M (initial)	ml titrant	C_W x 10^{-4}/ M (final)	C_B x 10^{-5}/ M (final)
$C_{12}S$	1.9_5	9.5_8	$\geq 1.9_4$	$\leq 2.8_8$
$C_{12}S/C_8P$ (α_{C12S}=0.41)	1.9_5	9.4_9	1.9_4	1.0_5
$C_{12}S/C_{10}P$(α_{C12S}=0.35)	1.9_5	9.5_0	1.9_4	0.90

TABLE A7: Data for calculating the partition coefficient of pure $C_{16}EGEO_5S$ in hexadecane/0.1M NaCl aqueous solution system at 25.0°C (titrant is $1.0_2 \times 10^{-3}$M Hyamine and the ml's used represents the amount needed to titrate 25 ml of the aqueous phase; titration error = ± 0.045 ml)

C_w/M (initial)	ml titrant	C_w/M (final)	C_B/M (final)
$2.7_0 \times 10^{-4}$	6.4_9	$2.6_5 \times 10^{-4}$	$1.0_0 \times 10^{-4}$

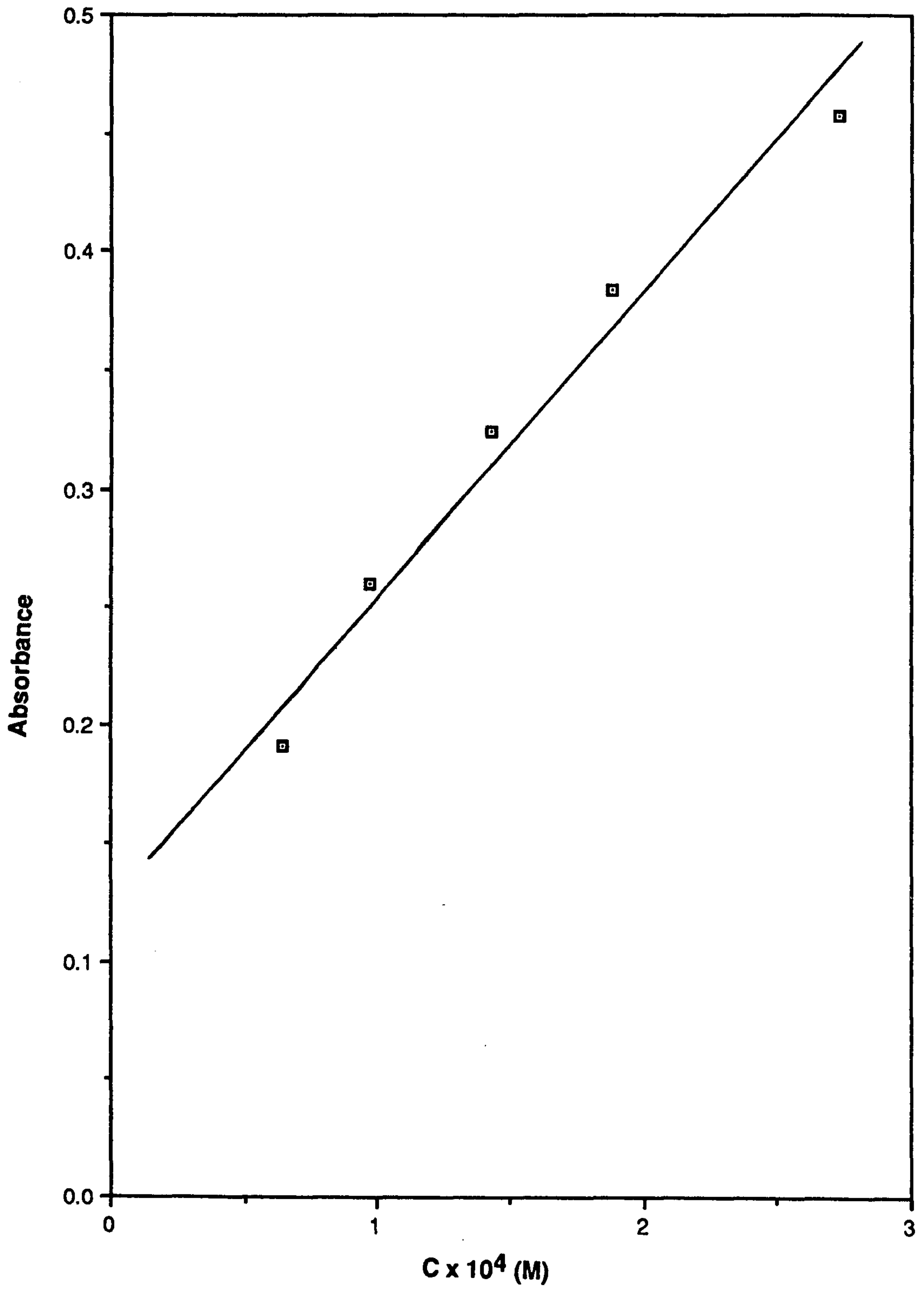

Figure A1. C_8P in 0.1M NaCl aqueous solution at 191nm and 25.0°C.

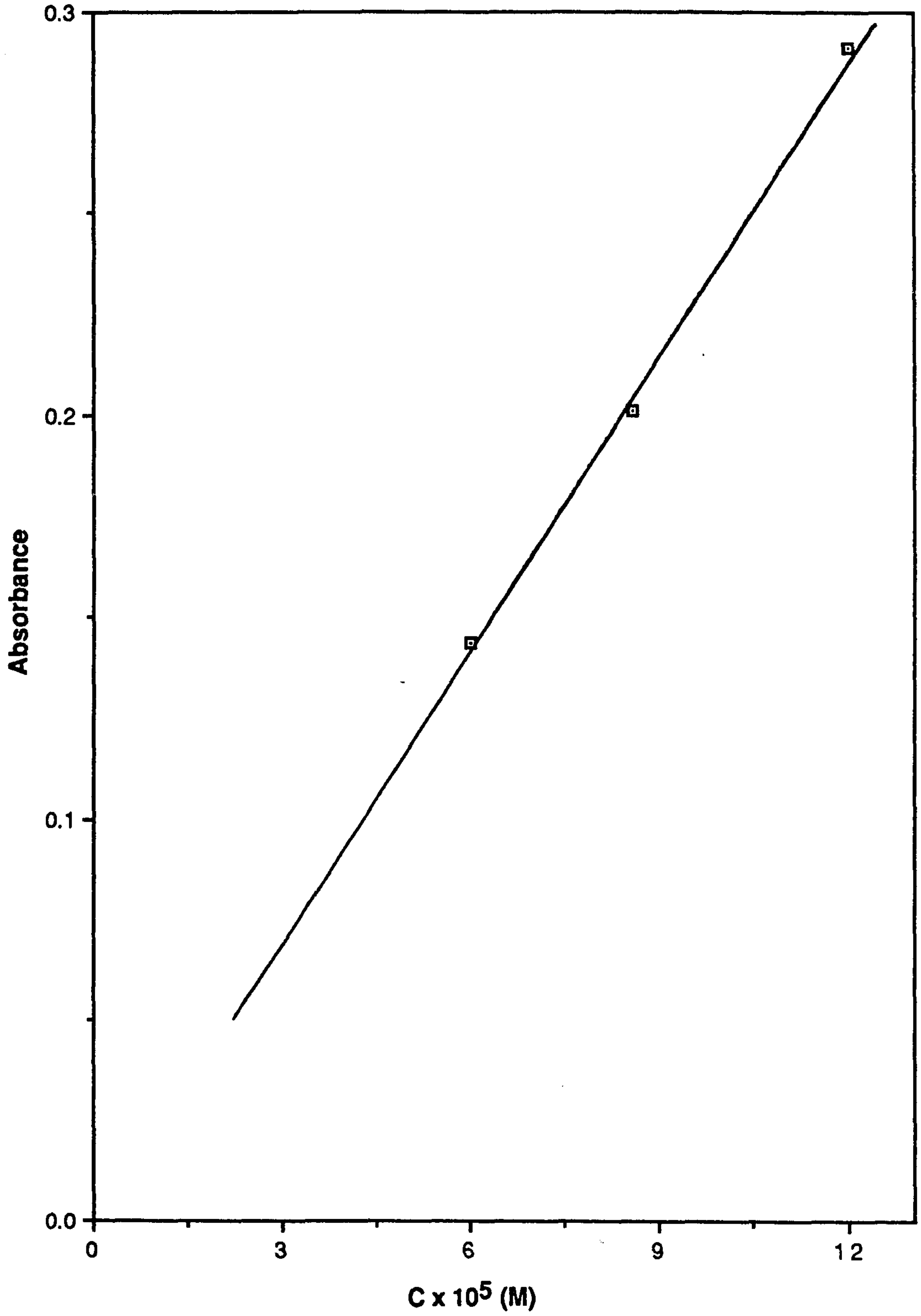

Figure A2. $C_{10}P$ in 0.1M NaCl aqueous solution at 191nm and 25.0°C

APPENDIX B

Interfacial Tension - Concentration Data

TABLE B1: Interfacial tension vs water phase concentration for $C_{12}EO_8$ in hexadecane/H_2O system at 25.0°C

$C_W \times 10^5$/M	-log C_W	γ_I/mN m^{-1}
$27._7$	3.55_8	3.3_3
$23._1$	3.63_6	3.4_5
6.9_2	4.16_0	6.0_5
5.1_9	4.28_5	7.8_2
3.4_4	4.46_3	$10._4$
2.3_1	4.63_6	$13._0$

TABLE B2: Interfacial tension vs water phase concentration for $C_{12}EO_8$ in dodecane/H_2O system at 25.0°C

$C_W \times 10^5$/M	-log C_W	γ_I/mN m^{-1}
$27._7$	3.55_8	3.2_9
$23._1$	3.63_6	3.0_9
6.4_8	4.18_8	5.8_9
4.8_6	4.31_3	7.7_8
3.2_4	4.48_9	$10._6$
2.1_6	4.66_6	$13._2$
1.6_2	4.79_0	$15._3$

TABLE B3: Interfacial tension vs water phase concentration for $C_{12}EO_8$ in heptane/H_2O system at 25.0°C

$C_W \times 10^5/M$	$-\log C_W$	$\gamma_I/mN\ m^{-1}$
$27._7$	3.55_8	1.7_6
$23._1$	3.63_6	1.7_7
6.9_2	4.16_0	3.4_0
5.1_9	4.28_5	5.6_3
3.4_4	4.46_3	7.9_3
2.3_1	4.63_6	$10._2$
1.7_3	4.76_2	$12._4$
1.1_5	4.93_9	$15._1$

TABLE B4: Interfacial tension vs water phase concentration for $C_{12}EO_8$ in cyclohexane/H_2O system at 25.0°C

$C_W \times 10^5$/M	$-\log C_W$	γ_I/mN m^{-1}
$27._7$	3.55_8	1.2_6
$23._1$	3.63_6	1.2_0
6.4_6	4.19_0	3.9_3
3.2_3	4.49_1	8.2_5
2.1_5	4.66_8	$10._6$
1.6_2	4.79_0	$12._2$

TABLE B5: Interfacial tension vs water phase concentration for $C_{12}EO_8$ in isooctane/H_2O system at 25.0°C

$C_W \times 10^5$/M	$-\log C_W$	γ_I/mN m^{-1}
$27._7$	3.55_8	2.1_0
$23._1$	3.63_6	2.1_4
6.4_4	4.19_1	5.5_7
4.8_2	4.31_7	6.2_9
3.2_2	4.49_2	9.4_9
2.1_4	4.67_0	$12._2$
1.6_1	4.79_3	$13._9$
1.0_8	4.96_7	$17._2$

TABLE B6: Interfacial tension vs water phase concentration for $C_{12}EO_8$ in heptamethylnonane/H_2O system at 25.0°C

$C_W \times 10^5$/M	$-\log C_W$	γ_I/mN m^{-1}
$27._7$	3.55_8	3.0_4
$23._1$	3.63_6	3.0_1
6.4_7	4.18_9	6.9_9
4.8_5	4.31_4	8.6_9
3.2_4	4.48_9	$11._1$
2.1_6	4.66_6	$13._9$
1.6_2	4.79_0	$15._2$
1.0_8	4.96_7	$18._4$

TABLE B7: Interfacial tension vs total concentration for $C_{12}EO_4$ in hexadecane/H_2O system at 25.0°C

$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
$11._1$	2.95_5	0.35
9.2_6	3.03_3	0.26
7.7_2	3.11_2	0.095
6.4_3	3.19_2	0.044
5.3_2	3.27_4	2.1_1
4.8_7	3.31_2	2.3_3
4.4_3	3.35_4	3.0_0
2.6_6	3.57_5	7.5_2
1.0_6	3.97_5	$14._4$
0.79_8	4.09_8	$16._4$

TABLE B8: Interfacial tension vs total concentration for $C_{12}EO_3$ in hexadecane/H_2O system at 25.0°C

$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
$37._0$	2.43_2	0.37
$22._2$	2.65_4	0.29
$11._1$	2.95_5	2.8_6
7.4_1	3.13_0	6.6_0
4.9_4	3.30_6	9.8_0
3.2_9	3.48_3	$13._0$

TABLE B9: Interfacial tension vs total concentration for $C_{12}EO_2$ in hexadecane/H_2O system at 25.0°C

$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
8.2_3	2.08_5	2.7_1
5.5_1	2.25_9	3.5_9
2.6_7	2.57_3	6.4_3
1.7_8	2.75_0	9.3_7
1.3_3	2.87_6	$11._3$
0.88_9	3.05_1	$14._4$
0.66_7	3.17_6	$16._7$

TABLE B10: Interfacial tension vs total concentration for $C_{12}EO_2$ in heptane/H_2O system at 25.0°C

$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
8.2_2	2.08_5	5.7_7
7.1_5	2.14_6	6.1_3
5.4_8	2.26_1	6.4_6
3.5_2	2.45_3	9.0_0
2.3_5	2.62_9	$11._1$
1.5_7	2.80_4	$13._2$
1.0_4	2.98_3	$15._8$
0.69_6	3.15_7	$18._2$

TABLE B11: Interfacial tension vs total concentration for $C_{16}EO_8$ in hexadecane/H_2O system at 25.0°C

$C_t \times 10^5/M$	$-\log C_t$	$\gamma_I/mN\ m^{-1}$
$27._5$	3.56_1	1.5_2
$22._0$	3.65_8	1.4_6
$15._2$	3.81_8	1.2_9
$10._2$	3.99_1	1.3_9
7.6_1	4.11_9	1.3_3
5.0_8	4.29_4	1.5_8
2.5_4	4.59_5	1.4_8
1.1_9	4.92_4	6.4_0
0.89_6	5.04_8	8.0_5
0.59_7	5.22_4	$11._0$
0.44_8	5.34_9	$12._7$
0.29_9	5.52_4	$15._7$

TABLE B12: Interfacial tension vs total concentration for $C_{16}EGEO_5OH$ in hexadecane/0.1M NaCl aq. soln. system at 25.0°C

$C_t \times 10^4$/M	$-\log C_t$	γ_I/mN m^{-1}
16.4	2.78_5	1.3_2
$10._9$	2.96_3	1.3_0
7.2_8	3.13_8	1.9_7
4.8_5	3.31_4	3.8_8
3.2_4	3.48_9	6.4_9
2.1_6	3.66_6	8.9_5

TABLE B13: Interfacial tension vs total concentration for $C_{16}HGEO_5OH$ in hexadecane/0.1M NaCl aq. soln. system at 25.0°C

$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
$13._4$	2.87_3	1.4_2
8.9_5	3.04_8	1.3_8
4.8_0	3.31_9	4.2_0
3.2_0	3.49_5	7.0_1
2.1_3	3.67_2	9.7_8
1.4_2	3.84_8	$12._1$
0.95	4.02_2	$14._6$
0.63_2	4.19_9	$16._8$

TABLE B14: Interfacial tension vs water phase concentration for C_8P in hexadecane/H_2O system at 25.0°C

$C_W \times 10^3$/M	-log C_W	γ_I/mN m^{-1}
3.4_8	2.45_8	$10._4$
2.4_4	2.61_3	$13._8$
1.8_9	2.72_4	$17._5$
1.5_7	2.80_4	$18._6$
1.2_6	2.90_0	$20._4$
1.0_2	2.99_1	$22._4$

TABLE B15: Interfacial tension vs concentration data for C_8P in hexadecane/0.1M NaCl aq. soln. system at 25.0°C

$C_W \times 10^3$/M	-log C_W	$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
2.9_3	2.55_3	5.1_3	2.29_0	7.4_2
2.3_2	2.63_5	4.0_6	2.39_1	$10._2$
1.8_8	2.72_6	3.2_9	2.48_2	$12._6$
1.6_2	2.79_0	2.8_3	2.54_8	$13._0$
1.2_6	2.90_0	2.2_0	2.65_9	$15._3$

TABLE B16: Interfacial tension vs concentration data for $C_{10}P$ in hexadecane/0.1M NaCl aq. soln. system at 25.0°C

$C_W \times 10^4$/M	-log C_W	$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
2.1_5	3.66_8	2.0_5	2.68_8	$15._8$
1.6_9	3.77_2	1.6_1	2.79_4	$17._6$
1.3_7	3.86_3	1.3_1	2.88_2	$19._0$
1.0_7	3.97_1	1.0_2	2.99_3	$20._7$
0.48_3	4.31_6	0.46_0	3.33_7	$25._9$

TABLE B17: Interfacial tension vs total concentration for $C_{12}P$ in hexadecane/H_2O system at 25.0°C

$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
$19._5$	1.71_0	1.6_0
$13._0$	1.88_6	2.1_0
9.7	2.01_3	2.8_8
6.4_8	2.18_8	5.2_3
4.3_2	2.36_5	7.8_5
2.8_8	2.54_1	$11._3$
1.9_2	2.71_7	$14._2$
1.2_8	2.89_3	$16._9$

TABLE B18: Interfacial tension vs concentration data for $C_{12}BMG$ in heptane/H_2O system at 25.0°C

$C_W \times 10^4$/M	-log C_W	$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
7.3_5	3.13_4	7.1_7	3.14_4	1.7_6
7.2_7	3.13_8	7.0_9	3.14_9	1.7_4
5.6_5	3.24_8	5.5_1	3.25_9	1.7_7
5.1_8	3.28_7	5.0_5	3.29_6	1.7_8
3.5_4	3.45_1	3.4_5	3.46_2	3.0_0
3.4_9	3.45_7	3.4_0	3.46_8	2.8_9
2.1_6	3.66_6	2.1_1	3.67_6	6.8_9
1.7_4	3.75_9	1.7_0	3.77_0	7.9_7
1.3_0	3.88_6	1.2_7	3.89_7	$10._4$
1.1_6	3.93_6	1.1_3	3.94_6	$10._8$
0.78	4.10_8	0.76	4.11_9	$14._3$
0.74	4.13_1	0.72_2	4.14_1	$13._6$

TABLE B19: Interfacial tension vs water phase concentration for C_{12}BMG in heptane/H_2O system at 35.0°C

$C_W \times 10^4$/M	$-\log C_W$	γ_I/mN m^{-1}
7.3_5	3.13_4	1.6_7
7.2_7	3.13_8	1.6_7
5.6_5	3.24_8	1.6_8
5.1_8	3.28_7	1.7_0
3.5_4	3.45_1	2.8_1
3.4_9	3.45_7	2.6_1
2.1_6	3.66_6	6.6_0
1.7_4	3.75_9	7.6_1
1.3_0	3.88_6	$10._2$
1.1_6	3.93_6	$10._4$
0.78	4.10_8	$13._8$
0.74	4.13_1	$13._2$

TABLE B20: Interfacial tension vs water phase concentration for C_{12}BMG in heptane/H_2O system at 45.0°C

$C_W \times 10^4$/M	-log C_W	γ_I/mN m^{-1}
7.3_5	3.13_4	1.5_1
7.2_7	3.13_8	1.5_6
5.6_5	3.24_8	1.5_5
5.1_8	3.28_7	1.5_6
3.5_4	3.45_1	2.8_9
3.4_9	3.45_7	3.0_0
2.1_6	3.66_6	6.7_2
1.7_4	3.75_9	8.0_7
1.3_0	3.88_6	$10._3$
1.1_6	3.93_6	$11._0$
0.78	4.10_8	$13._8$
0.74	4.13_1	$13._4$

TABLE B21: Interfacial tension vs concentration data for C_{12}BMG in dodecane/H_2O system at 25.0°C

$C_W \times 10^4$/M	-log C_W	$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
7.7_3	3.11_2	7.5_4	3.12_3	2.6_5
7.2_1	3.14_2	7.0_3	3.15_3	2.7_1
6.1_1	3.21_4	5.9_6	3.22_5	2.8_1
5.8_0	3.23_7	5.6_6	3.24_7	2.7_8
4.1_7	3.38_0	4.0_7	3.39_1	3.8_0
3.7_9	3.42_1	3.7_0	3.43_2	4.2_1
2.2_7	3.64_4	2.2_1	3.65_5	8.0_4
2.1_8	3.66_2	2.1_3	3.67_2	8.4_4
1.3_9	3.85_7	1.3_6	3.86_8	$12._1$
1.3_9	3.85_7	1.3_6	3.86_8	$11._5$
1.0_1	3.99_6	0.98_5	4.00_6	$13._6$
0.87	4.06_0	0.85	4.07_1	$14._5$

TABLE B22: Interfacial tension vs water phase concentration for C_{12}BMG in dodecane/H_2O system at 35.0°C

$C_W \times 10^4$/M	$-\log C_W$	γ_I/mN m^{-1}
7.7_3	3.11_2	2.5_9
7.2_1	3.14_2	2.5_9
6.1_1	3.21_4	2.6_3
5.8_0	3.23_7	2.6_4
4.1_7	3.38_0	3.4_7
3.7_9	3.42_1	3.9_8
2.2_7	3.64_4	7.6_5
2.1_8	3.66_2	8.1_7
1.3_9	3.85_7	$11._7$
1.3_9	3.85_7	$11._0$
1.0_1	3.99_6	$13._2$
0.87	4.06_0	$14._3$

TABLE B23: Interfacial tension vs water phase concentration for C_{12}BMG in dodecane/H_2O system at 45.0°C

$C_W \times 10^4$/M	$-\log C_W$	γ_I/mN m^{-1}
7.7_3	3.11_2	2.3_9
7.2_1	3.14_2	2.3_9
6.1_1	3.21_4	2.4_0
5.8_0	3.23_7	2.5_1
4.1_7	3.38_0	4.0_1
3.7_9	3.42_1	4.4_2
2.2_7	3.64_4	8.1_2
2.1_8	3.66_2	8.6_0
1.3_9	3.85_7	$12._0$
1.3_9	3.85_7	$11._5$
1.0_1	3.99_6	$13._6$
0.87	4.06_0	$14._6$

TABLE B24: Interfacial tension vs concentration data for C_{12}BMG in hexadecane/H_2O system at 25.0°C

$C_W \times 10^4$/M	-log C_W	$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
7.2_7	3.13_8	7.0_9	3.14_9	3.5_1
7.2_1	3.14_2	7.0_3	3.15_3	3.4_0
6.2_2	3.20_6	6.0_7	3.21_7	3.3_9
6.1_8	3.20_9	6.0_3	3.22_0	3.5_1
4.1_8	3.37_9	4.0_8	3.39_0	5.0_2
4.1_7	3.38_0	4.0_7	3.39_1	5.2_3
2.5_9	3.58_7	2.5_3	3.59_7	8.7_4
2.1_8	3.66_2	2.1_3	3.67_2	9.6_1
1.6_0	3.79_6	1.5_6	3.80_7	$12._3$
1.3_9	3.85_7	1.3_6	3.86_8	$13._0$
1.0_4	3.98_3	1.0_1	3.99_4	$15._2$
0.87	4.06_0	0.85	4.07_1	$15._9$

TABLE B25: Interfacial tension vs water phase concentration for C_{12}BMG in hexadecane/H_2O system at 35.0°C

$C_W \times 10^4$/M	-log C_W	γ_I/mN m^{-1}
7.2_7	3.13_8	3.2_1
7.2_1	3.14_2	3.1_6
6.2_2	3.20_6	3.2_0
6.1_8	3.20_9	3.2_5
4.1_8	3.37_9	4.7_6
4.1_7	3.38_0	4.7_9
2.5_9	3.58_7	8.4_7
2.1_8	3.66_2	9.3_7
1.6_0	3.79_6	$11._8$
1.3_9	3.85_7	$12._6$
1.0_4	3.98_3	$14._6$
0.87	4.06_0	$15._6$

TABLE B26: Interfacial tension vs water phase concentration for C_{12}BMG in hexadecane/H_2O system at 45.0°C

$C_W \times 10^4$/M	-log C_W	γ_I/mN m^{-1}
7.2_7	3.13_8	3.0_9
7.2_1	3.14_2	3.0_3
6.2_2	3.20_6	3.0_9
6.1_8	3.20_9	3.1_6
4.1_8	3.37_9	4.9_1
4.1_7	3.38_0	5.1_1
2.5_9	3.58_7	8.7_2
2.1_8	3.66_2	9.6_0
1.6_0	3.79_6	$12._2$
1.0_4	3.98_3	$15._0$
0.87	4.06_0	$15._8$

TABLE B27: Interfacial tension vs concentration data for C_{12}BMG in isooctane/H_2O system at 25.0°C

$C_W \times 10^4$/M	-log C_W	$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
7.2_1	3.14_2	7.0_3	3.15_3	1.9_7
6.1_7	3.21_0	6.0_2	3.22_0	1.9_3
4.1_7	3.38_0	4.0_7	3.39_1	2.1_2
2.1_8	3.66_2	2.1_3	3.67_2	6.7_0
1.3_9	3.85_7	1.3_6	3.86_8	$10._1$
0.85	4.07_1	0.83	4.08_1	$12._9$

TABLE B28: Interfacial tension vs water phase concentration for C_{12}BMG in isooctane/H_2O system at 35.0°C

$C_W \times 10^4$/M	-log C_W	γ_I/mN m^{-1}
7.2_1	3.14_2	1.8_3
6.1_7	3.21_0	1.8_1
4.1_7	3.38_0	1.9_3
2.1_8	3.66_2	6.2_2
1.3_9	3.85_7	9.7_9
0.85	4.07_1	$12._6$

TABLE B29: Interfacial tension vs water phase concentration for C_{12}BMG in isooctane/H_2O system at 45.0°C

$C_W \times 10^4$/M	-log C_W	γ_I/mN m^{-1}
7.2_1	3.14_2	1.6_4
6.1_7	3.21_0	1.6_4
4.1_7	3.38_0	2.0_4
2.1_8	3.66_2	6.5_7
1.3_9	3.85_7	$10._2$
0.85	4.07_1	$12._8$

TABLE B30: Interfacial tension vs concentration data for C_{12}BMG in heptamethylnonane/H_2O system at 25.0°C

$C_W \times 10^4$/M	$-\log C_W$	$C_t \times 10^4$/M	$-\log C_t$	γ_I/mN m^{-1}
7.2_7	3.13_8	7.0_9	3.14_9	2.6_1
7.2_1	3.14_2	7.0_3	3.15_3	2.6_6
6.3_4	3.19_8	6.1_9	3.20_9	2.6_5
5.7_7	3.23_9	5.6_3	3.25_0	2.7_1
5.1_8	3.28_6	5.0_5	3.29_6	2.8_1
4.1_8	3.37_9	4.0_8	3.39_0	4.0_1
4.1_7	3.38_0	4.0_7	3.39_1	3.3_7
2.5_9	3.58_7	2.5_3	3.59_7	7.6_4
2.1_8	3.66_2	2.1_3	3.67_2	8.0_8
1.6_0	3.79_6	1.5_6	3.80_7	$11._2$
1.3_9	3.85_7	1.3_6	3.86_8	$11._2$
0.85	4.07_1	0.83	4.08_1	$14._4$

TABLE B31: Interfacial tension vs water phase concentration for C_{12}BMG in heptamethylnonane/H_2O system at 35.0°C

$C_W \times 10^4$/M	$-\log C_W$	γ_I/mN m^{-1}
7.2_7	3.13_8	2.5_3
7.2_1	3.14_2	2.5_2
6.3_4	3.19_8	2.6_3
5.7_7	3.23_9	2.5_2
5.1_8	3.28_6	2.7_0
4.1_8	3.37_9	3.6_7
4.1_7	3.38_0	3.1_2
2.5_9	3.58_7	7.4_4
2.1_8	3.66_2	7.6_3
1.6_0	3.79_6	$11._0$
1.3_9	3.85_7	$10._9$
0.85	4.07_1	$14._0$

TABLE B32: Interfacial tension vs water phase concentration for C_{12}BMG in heptamethylnonane/H_2O system at 45.0°C

$C_W \times 10^4$/M	$-\log C_W$	γ_I/mN m^{-1}
7.2_7	3.13_8	2.4_0
7.2_1	3.14_2	2.3_4
6.3_4	3.19_8	2.4_8
5.7_7	3.23_9	2.3_7
5.1_8	3.28_6	2.5_9
4.1_8	3.37_9	3.9_4
4.1_7	3.38_0	3.6_3
2.5_9	3.58_7	7.6_0
2.1_8	3.66_2	8.1_7
1.6_0	3.79_6	$11._2$
1.3_9	3.85_7	$11._4$
0.85	4.07_1	$14._4$

TABLE B33: Interfacial tension vs concentration data for $C_{12}BMG$ in cyclohexane/H_2O system at 25.0°C

$C_W \times 10^4$/M	-log C_W	$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
5.7_7	3.23_9	5.6_3	3.25_0	0.89
5.1_8	3.28_6	5.0_5	3.29_6	0.82
4.1_8	3.37_9	4.0_9	3.39_0	0.83
4.1_7	3.38_0	4.0_7	3.39_1	0.98
2.5_9	3.58_7	2.5_3	3.59_7	3.0_8
2.1_8	3.66_2	2.1_3	3.67_2	3.9_3
1.6_0	3.79_6	1.5_6	3.80_7	6.5_7
1.3_9	3.85_7	1.3_6	3.86_8	7.2_4
1.0_4	3.98_3	1.0_1	3.99_4	9.5_5
0.85	4.07_1	0.83	4.08_1	$10._2$
0.56_1	4.25_1	0.54_7	4.26_2	$13._5$
0.51_6	4.28_7	0.50_3	4.29_8	$13._4$

TABLE B34: Interfacial tension vs water phase concentration for C_{12}BMG in cyclohexane/H_2O system at 35.0°C

$C_W \times 10^4$/M	-log C_W	γ_I/mN m^{-1}
5.7_7	3.23_9	0.77
5.1_8	3.28_6	0.73
4.1_8	3.37_9	0.75
4.1_7	3.38_0	0.80
2.5_9	3.58_7	2.6_0
2.1_8	3.66_2	3.6_2
1.6_0	3.79_6	6.1_2
1.3_9	3.85_7	6.7_2
1.0_4	3.98_3	9.0_6
0.85	4.07_1	9.7_3
0.56_1	4.25_1	$13._2$
0.51_6	4.28_7	$13._1$

TABLE B35: Interfacial tension vs water phase concentration for C_{12}BMG in cyclohexane/H_2O system at 45.0°C

$C_W \times 10^4$/M	$-\log C_W$	γ_I/mN m^{-1}
5.7_7	3.23_9	0.66
5.1_8	3.28_6	0.64
4.1_8	3.37_9	0.61
4.1_7	3.38_0	0.59
2.5_9	3.58_7	2.7_9
2.1_8	3.66_2	3.8_5
1.6_0	3.79_6	6.2_2
1.3_9	3.85_7	6.9_1
1.0_4	3.98_3	8.9_9
0.85	4.07_1	9.8_0
0.56_1	4.25_1	$13._1$
0.51_6	4.28_7	$13._0$

TABLE B36: Interfacial tension vs concentration data for C_{12}BMG in toluene/H_2O system at 25.0°C

$C_W \times 10^5$/M	-log C_W	$C_t \times 10^5$/M	-log C_t	γ_I/mN m^{-1}
$67._9$	3.16_8	$66._2$	3.17_9	0.30
$51._8$	3.28_6	$50._5$	3.29_6	0.28
$33._2$	3.47_9	$32._4$	3.49_0	0.23
$25._9$	3.58_7	$25._3$	3.59_7	0.38
$16._6$	3.78_0	$16._2$	3.79_1	1.1_6
$16._0$	3.79_6	$15._6$	3.80_7	2.3_8
8.3_0	4.08_1	8.1_0	4.09_2	5.5_6
7.7_7	4.11_0	7.5_8	4.12_0	6.8_5
3.8_7	4.41_2	3.7_8	4.42_3	9.9_0
3.7_1	4.43_1	3.6_2	4.44_1	$11._0$
2.3_5	4.62_9	2.2_9	4.64_0	$12._4$
1.7_3	4.76_2	1.6_9	4.77_3	$15._1$

TABLE B37: Interfacial tension vs water phase concentration for C_{12}BMG in toluene/H_2O system at 35.0°C

$C_W \times 10^5$/M	-log C_W	γ_I/mN m^{-1}
$67._9$	3.16_2	0.34
$51._8$	3.28_6	0.31
$33._2$	3.47_9	0.25
$25._9$	3.58_7	0.42
$16._6$	3.78_0	1.3_8
$16._0$	3.79_6	2.5_7
8.3_0	4.08_1	5.3_6
7.7_7	4.11_0	6.8_5
3.8_7	4.41_2	9.9_6
3.7_1	4.43_1	$11._0$
2.3_5	4.62_9	$12._2$
1.7_3	4.76_2	$14._8$

TABLE B38: Interfacial tension vs water phase concentration for C_{12}BMG in toluene/H_2O system at 45.0°C

$C_W \times 10^5$/M	-log C_W	γ_I/mN m^{-1}
$67._9$	3.16_8	0.39
$51._8$	3.28_6	0.42
$33._2$	3.47_9	0.31
$25._9$	3.58_7	0.48
$16._6$	3.78_0	1.5_8
$16._0$	3.79_6	3.1_1
8.3_0	4.08_1	5.7_0
7.7_7	4.11_0	7.0_8
3.8_7	4.41_2	$10._0$
3.7_1	4.43_1	$11._0$
2.3_5	4.62_9	$12._3$
1.7_3	4.76_2	$14._8$

TABLE B39: Interfacial tension vs concentration data for $C_{12}S$ in heptane/H_2O system at 25.0°C.

$C_W \times 10^3/M$	$-\log C_W$	$C_t \times 10^3/M$	$-\log C_t$	$\gamma_I/mN\ m^{-1}$
$13._6$	1.86_6	$13._3$	1.87_7	7.7_8
$12._6$	1.90_0	$12._3$	1.91_0	7.8_2
9.8_0	2.00_9	9.5_6	2.01_9	7.8_6
6.6_5	2.17_7	6.4_9	2.18_8	$12._8$
5.2_5	2.28_0	5.1_2	2.29_1	$15._8$
4.1_8	2.37_9	4.0_9	2.39_0	$18._1$

TABLE B40: Interfacial tension vs concentration data for $C_{12}S$ in dodecane/H_2O system at 25.0°C.

$C_W \times 10^3/M$	$-\log C_W$	$C_t \times 10^3/M$	$-\log C_t$	$\gamma_I/mN\ m^{-1}$
$13._6$	1.86_6	$13._3$	1.87_7	9.3_2
$12._6$	1.90_0	$12._3$	1.91_0	9.2_7
9.8_0	2.00_9	9.5_6	2.01_9	9.3_2
6.9_5	2.15_8	6.7_8	2.16_9	$13._1$
5.7_9	2.23_7	5.6_5	2.24_8	$15._2$
4.6_4	2.33_3	4.5_3	2.34_4	$17._6$
3.6_5	2.43_8	3.5_6	2.44_8	$21._1$

TABLE B41: Interfacial tension vs concentration data for $C_{12}S$ in hexadecane/H_2O system at 25.0°C.

$C_W \times 10^3$/M	-log C_W	$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
$15._8$	1.80_1	$15._4$	1.81_2	9.8_4
$12._6$	1.90_0	$12._3$	1.91_0	9.7_2
9.8_0	2.00_9	9.5_6	2.01_9	$10._6$
6.6_5	2.17_7	6.4_9	2.18_8	$14._8$
5.2_5	2.28_0	5.1_2	2.29_1	$19._4$
4.1_8	2.37_9	4.0_9	2.39_0	$22._2$

TABLE B42: Interfacial tension vs concentration data for $C_{12}S$ in isooctane/H_2O system at 25.0°C.

$C_W \times 10^3$/M	-log C_W	$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
$13._6$	1.86_6	$13._3$	1.87_7	8.2_1
$12._6$	1.90_0	$12._3$	1.91_0	8.3_1
9.8_0	2.00_9	9.5_6	2.01_9	8.3_3
6.6_5	2.17_7	6.4_9	2.18_8	$13._1$
5.2_5	2.28_0	5.1_2	2.29_1	$16._2$
4.1_8	2.37_9	4.0_9	2.39_0	$19._3$

TABLE B43: Interfacial tension vs concentration data for $C_{12}S$ in heptamethylnonane/H_2O system at 25.0°C.

$C_W \times 10^3$/M	-log C_W	$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
$13._{6}$	1.86_{6}	$13._{3}$	1.87_{7}	9.5_{8}
$12._{6}$	1.90_{0}	$12._{3}$	1.91_{0}	9.5_{8}
9.8_{0}	2.00_{9}	9.5_{6}	2.01_{9}	9.6_{9}
6.6_{5}	2.17_{7}	6.4_{9}	2.18_{8}	$14._{9}$
5.2_{5}	2.28_{0}	5.1_{2}	2.29_{1}	$17._{5}$
4.1_{8}	2.37_{9}	4.0_{9}	2.39_{0}	$21._{6}$

TABLE B44: Interfacial tension vs concentration data for $C_{12}S$ in cyclohexane/H_2O system at 25.0°C.

$C_W \times 10^3$/M	-log C_W	$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
$13._{6}$	1.86_{6}	$13._{3}$	1.87_{7}	6.3_{3}
$12._{6}$	1.90_{0}	$12._{3}$	1.91_{0}	6.4_{3}
9.8_{0}	2.00_{9}	9.5_{6}	2.01_{9}	6.5_{8}
6.6_{5}	2.17_{7}	6.4_{9}	2.18_{8}	$10._{4}$
5.2_{5}	2.28_{0}	5.1_{2}	2.29_{1}	$13._{0}$
3.7_{5}	2.42_{6}	3.6_{6}	2.43_{7}	$18._{1}$

TABLE B45: Interfacial tension vs concentration data for $C_{12}S$ in toluene/H_2O system at 25.0°C.

$C_W \times 10^3$/M	$-\log C_W$	$C_t \times 10^3$/M	$-\log C_t$	γ_I/mN m^{-1}
7.1_1	2.14_8	6.9_4	2.15_9	5.2_8
7.0_0	2.15_5	6.8_3	2.16_6	5.1_7
5.2_3	2.28_2	5.1_0	2.29_2	6.2_3
3.2_2	2.49_2	3.1_4	2.50_3	$11._2$
1.7_9	2.74_7	1.7_5	2.75_8	$18._7$

TABLE B46: Interfacial tension vs concentration data for $C_{12}S$ in hexadecane/0.1M NaCl aq. soln. system at 25.0°C.

$C_W \times 10^3$/M	-log C_W	$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
2.8_0	2.55_3	2.7_3	2.56_4	6.3_3
2.6_6	2.57_5	2.6_0	2.58_6	6.4_4
2.3_3	2.63_3	2.2_7	2.64_3	6.2_9
1.8_6	2.73_0	1.8_1	2.74_1	7.3_5
1.4_0	2.85_4	1.3_7	2.86_5	$10._0$
1.1_7	2.93_2	1.1_4	2.94_3	$13._2$
1.1_1	2.95_5	1.0_8	2.96_5	$11._5$
0.93	3.03_2	0.91	3.04_2	$15._7$
0.82	3.08_6	0.80	3.09_7	$16._4$
0.69_9	3.15_6	0.68_2	3.16_6	$18._2$

TABLE B47: Interfacial tension vs concentration data for $C_{16}EGEO_5S$ in hexadecane/0.1M NaCl aq. soln. system at 25.0°C.

$C_W \times 10^5$/M	-log C_W	$C_t \times 10^5$/M	-log C_t	γ_I/mN m^{-1}
6.7_5	4.17_1	6.5_9	4.18_1	1.8_9
4.4_9	4.34_8	4.3_8	4.35_8	2.1_3
2.8_1	4.55_2	2.7_4	4.56_2	3.7_9
1.8_0	4.74_5	1.7_6	4.75_5	8.4_0
1.1_2	4.95_0	1.0_9	4.96_2	$12._2$
0.67_5	5.17_1	0.65_9	5.18_1	$16._4$

TABLE B48: Interfacial tension vs concentration data for $C_{16}HGEO_5S$ in hexadecane/0.1M NaCl aq. soln. system at 25.0°C.

$C_W \times 10^6$/M	-log C_W	$C_t \times 10^6$/M	-log C_t	γ_I/mN m^{-1}
$27._0$	4.56_8	$26._3$	4.57_9	2.3_6
$18._0$	4.74_4	$17._6$	4.75_5	2.5_9
9.0	5.04_4	8.7_8	5.05_6	4.0_0
6.7_6	5.17_0	6.6_0	5.18_1	6.1_3
5.0_4	5.29_8	4.9_2	5.30_8	8.7_0

TABLE B49: Interfacial tension vs total concentration for $C_{12}EO_7$ in heptane/H_2O system

$C_t \times 10^5$/M	-log C_t	γ_I/mN m^{-1}
$44._{6}$	3.35_{1}	1.8_{2}
$23._{3}$	3.63_{3}	1.8_{2}
6.9_{8}	4.15_{6}	5.9_{0}
3.9_{4}	4.40_{5}	8.3_{0}
0.78_{7}	5.10_{4}	$16._{7}$
0.25_{2}	5.59_{9}	$23._{4}$

TABLE B50: Interfacial tension vs total concentration for $C_{12}EO_7$-$C_{12}S$ mixture at $\alpha_{C12EO7} = 3.7_5 \times 10^{-3}$ in heptane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
$20._{2}$	1.69_{5}	7.4_{0}
$14._{8}$	1.83_{0}	7.0_{3}
$12._{1}$	1.91_{7}	6.8_{5}
4.6_{9}	2.32_{9}	7.2_{7}
2.3_{4}	2.63_{1}	$12._{0}$
0.55_{3}	3.25_{7}	$18._{8}$

TABLE B51: Interfacial tension vs total concentration for $C_{12}EO_7$-$C_{12}S$ mixture at $\alpha_{C12EO7} = 0.24_9$ in heptane/H_2O system

$C_{12,t} \times 10^4$/M	$-\log C_{12,t}$	γ_I/mN m^{-1}
$26._6$	2.57_5	4.6_5
$13._8$	2.86_0	4.5_0
5.5_3	3.25_7	4.0_0
2.6_0	3.58_5	6.5_7
1.5_4	3.81_2	9.5_6
0.57_1	4.24_3	$14._8$

TABLE B52: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at $\alpha_{C12BMG} = 0.027_7$ in heptane/H_2O system

$C_{12,t} \times 10^3$/M	$-\log C_{12,t}$	γ_I/mN m^{-1}
5.2_1	2.28_3	2.7_8
3.2_5	2.48_8	2.1_1
2.6_0	2.58_4	1.6_2
1.7_6	2.75_6	3.8_0
1.3_2	2.88_0	5.0_1
0.75_7	3.12_1	$11._4$
0.51_8	3.28_6	$14._7$

TABLE B53: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.051_3 in heptane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.8_3	2.41_6	2.7_9
2.8_9	2.54_0	2.5_1
2.0_2	2.69_5	1.6_5
1.4_4	2.84_1	2.3_1
1.0_2	2.99_1	5.8_7
0.73_2	3.13_5	8.7_9
0.54_6	3.26_3	$12._4$
0.37_7	3.42_3	$15._0$

TABLE B54: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.94 in heptane/H_2O system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
7.4_0	3.13_0	2.3_5
4.9_5	3.30_5	2.5_3
2.6_6	3.57_5	3.8_0
1.6_4	3.78_5	7.7_9
1.0_9	3.96_2	$10._1$
0.76_2	4.12_9	$13._8$

TABLE B55: Interfacial tension vs total concentration for C_{12}BMG-C_{12}S mixture at $\alpha_{C12BMG} = 0.027_7$ in dodecane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
5.2_1	2.28_3	3.4_6
3.8_0	2.42_0	2.7_8
2.6_0	2.58_4	2.3_3
1.7_6	2.75_6	5.5_7
1.3_2	2.88_0	8.1_4
0.75_7	3.12_1	$13._4$

TABLE B56: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.051_6 in dodecane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.8_3	2.41_6	3.6_3
2.8_9	2.54_0	2.8_8
2.0_2	2.69_5	2.6_1
1.3_3	2.87_6	5.6_3
1.0_2	2.99_1	8.3_2
0.73_2	3.13_5	$11._4$
0.54_6	3.26_3	$14._4$
0.37_7	3.42_3	$17._9$

TABLE B57: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.94 in dodecane/H_2O system

$C_{12,t} \times 10^4/M$	$-\log C_{12,t}$	$\gamma_I/mN\ m^{-1}$
7.4_0	3.13_0	3.4_0
4.9_5	3.30_5	3.5_0
3.2_5	3.48_8	4.6_3
2.3_5	3.63_0	7.2_7
1.4_8	3.82_9	$10._9$
0.94	4.02_8	$14._1$

TABLE B58: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.027_7 in hexadecane/H_2O system

$C_{12,t} \times 10^3/M$	$-\log C_{12,t}$	$\gamma_I/mN\ m^{-1}$
5.2_1	2.28_3	3.4_2
3.8_0	2.42_0	3.0_0
2.6_0	2.58_4	2.5_0
1.7_6	2.75_6	5.4_2
1.3_2	2.88_0	8.6_3
0.75_7	3.12_1	$15._1$

TABLE B59: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at $\alpha_{C12BMG} = 0.051_6$ in hexadecane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.8_3	2.41_6	3.5_1
2.8_9	2.54_0	2.4_3
2.0_2	2.69_5	2.4_2
1.4_4	2.84_1	5.2_5
1.0_2	2.99_1	8.2_5
0.73_2	3.13_5	$12._3$
0.54_6	3.26_3	$15._8$
0.37_7	3.42_3	$19._0$

TABLE B60: Interfacial tension vs total concentration for C_{12}BMG-C_{12}S mixture at α_{C12BMG} = 0.94 in hexadecane/H_2O system

$C_{12,t}$ x 10^4/M	-log $C_{12,t}$	γ_I/mN m^{-1}
8.7_5	3.05_8	3.2_5
6.1_9	3.20_9	3.4_1
3.8_1	3.41_8	4.4_2
2.9_4	3.53_2	6.5_1
1.8_0	3.74_6	$10._3$
1.0_9	3.96_2	$14._0$

TABLE B61: Interfacial tension vs total concentration for C_{12}BMG-C_{12}S mixture at α_{C12BMG} = 0.027_7 in isooctane/H_2O system

$C_{12,t}$ x 10^3/M	-log $C_{12,t}$	γ_I/mN m^{-1}
5.2_1	2.28_3	3.1_6
3.5_9	2.44_6	2.2_3
2.6_0	2.58_4	1.6_6
1.7_6	2.75_6	3.8_0
1.3_2	2.88_0	5.9_9
0.75_7	3.12_1	$12._4$
0.51_8	3.28_6	$14._7$

TABLE B62: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.051_6 in isooctane/H_2O system

$C_{12,t}$ x 10^3/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.8_3	2.41_6	3.1_3
2.8_9	2.54_0	2.3_1
2.0_2	2.69_5	2.0_3
1.3_3	2.87_6	3.0_6
1.0_2	2.99_1	6.0_5
0.73_2	3.13_5	9.5_2
0.54_6	3.26_3	$12._8$
0.37_7	3.42_3	$15._6$

TABLE B63: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.94 in isooctane/H_2O system

$C_{12,t}$ x 10^4/M	-log $C_{12,t}$	γ_I/mN m^{-1}
7.4_0	3.13_0	2.5_9
4.9_5	3.30_5	2.7_2
2.6_6	3.57_5	4.4_2
1.6_4	3.78_5	8.2_2
1.0_9	3.96_2	$11._2$

TABLE B64: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at $\alpha_{C12BMG} = 0.027_7$ in heptamethylnonane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
5.2_1	2.28_3	3.5_7
3.8_0	2.42_0	2.5_8
2.6_0	2.58_4	2.5_8
1.7_6	2.75_6	5.1_0
1.3_2	2.88_0	7.4_0
0.75_7	3.12_1	$14._3$

TABLE B65: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at $\alpha_{C12BMG} = 0.051_6$ in heptamethylnonane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.8_3	2.41_6	3.6_9
2.8_9	2.54_0	2.5_1
2.0_2	2.69_5	2.6_8
1.3_3	2.87_6	5.4_7
1.0_2	2.99_1	7.9_3
0.73_2	3.13_5	$11._4$
0.54_6	3.26_3	$14._9$
0.37_7	3.42_3	$17._8$

TABLE B66: Interfacial tension vs total concentration for C_{12}BMG-C_{12}S mixture at α_{C12BMG} = 0.94 in heptamethylnonane/H_2O system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
7.4_0	3.13_0	3.2_0
4.9_5	3.30_5	3.4_0
3.3_9	3.47_0	4.2_5
2.7_4	3.56_2	5.8_9
1.6_8	3.77_5	9.6_0
0.98	4.01_1	$13._4$

TABLE B67: Interfacial tension vs total concentration for C_{12}BMG-C_{12}S mixture at α_{C12BMG} = 0.027_7 in cyclohexane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.4_7	2.45_9	1.3_6
2.3_9	2.62_2	1.0_4
1.5_1	2.82_0	1.9_5
1.3_1	2.88_4	3.1_7
0.79_7	3.09_8	8.0_2
0.44_9	3.35_8	$14._5$

TABLE B68: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.051_6 in cyclohexane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.8_3	2.41_6	2.0_0
2.8_8	2.54_1	1.7_4
2.0_2	2.69_5	0.80
1.4_4	2.84_1	0.90
1.0_2	2.99_1	3.7_2
0.73_2	3.13_5	6.9_0
0.54_6	3.26_3	$10._0$
0.37_7	3.42_3	$13._2$

TABLE B69: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.94 in cyclohexane/H_2O system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
5.7_6	3.24_0	1.5_1
4.0_2	3.39_6	1.3_7
2.1_5	3.66_7	3.4_1
1.3_3	3.87_7	6.9_8
0.90	4.04_6	9.5_7
0.50_8	4.29_4	$13._4$

TABLE B70: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.027_7 in toluene/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.4_7	2.45_9	1.0_3
2.4_5	2.61_1	0.82_8
1.7_4	2.76_0	1.4_6
0.79_7	3.09_8	6.1_3
0.43_8	3.35_8	$10._8$
0.23_9	3.62_2	$14._8$

TABLE B71: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.051_6 in toluene/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.8_3	2.41_6	1.4_6
2.8_8	2.54_1	1.2_3
2.0_2	2.69_5	0.92
1.4_4	2.84_1	1.4_2
1.0_2	2.99_1	3.2_7
0.73_2	3.13_5	5.2_2
0.54_6	3.26_3	6.9_4
0.37_7	3.42_3	9.9_8

TABLE B72: Interfacial tension vs total concentration for $C_{12}BMG$-$C_{12}S$ mixture at α_{C12BMG} = 0.94 in toluene/H_2O system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.2_5	3.48_8	0.44_0
2.3_5	3.63_0	0.23_0
1.2_1	3.91_7	3.8_0
0.61_9	4.20_9	7.4_0
0.37_2	4.43_0	$10._6$
0.19_5	4.71_0	$14._2$

TABLE B73: Interfacial tension vs total concentration for $C_{12}S$-C_8P mixture at α_{C12S} = 0.27_5 in hexadecane/0.1M NaCl aqueous solution system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.1_0	2.50_8	3.8_5
2.4_1	2.61_7	5.6_1
1.7_2	2.76_4	8.9_0
1.2_4	2.90_6	$12._4$
0.89_6	3.04_8	$15._0$

TABLE B74: Interfacial tension vs total concentration for $C_{12}S$-C_8P mixture at $\alpha_{C12S} = 0.77_1$ in hexadecane/0.1M NaCl aqueous solution system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
2.7_5	2.56_0	3.8_2
2.2_9	2.63_9	4.3_0
1.7_8	2.75_0	6.5_3
1.2_6	2.89_9	$10._2$
0.91_8	3.03_7	$13._4$
0.68_8	3.16_2	$16._4$

TABLE B75: Interfacial tension vs total concentration for $C_{12}S$-$C_{10}P$ mixture at $\alpha_{C12S} = 0.41_6$ in hexadecane/0.1M NaCl aqueous solution system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
7.0_3	3.15_3	$15._1$
5.5_7	3.25_4	$16._2$
4.4_0	3.35_7	$19._3$
3.5_2	3.45_4	$20._9$

TABLE B76: Interfacial tension vs total concentration for $C_{12}S$-$C_{10}P$ mixture at $\alpha_{C12S} = 0.74_8$ in hexadecane/0.1M NaCl aqueous solution system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
$11._2$	2.95_2	$10._2$
9.1_5	3.03_9	$12._2$
7.1_1	3.14_8	$14._6$
5.4_9	3.26_1	$16._9$
4.3_7	3.36_0	$18._9$
3.4_6	3.46_2	$21._1$
2.7_4	3.56_2	$23._4$
2.0_3	3.69_2	$25._6$

TABLE B77: Interfacial tension vs total concentration for $C_{16}HGEO_5S$-$C_{16}HGEO_5OH$ mixture at $\alpha_{C16HGEO5S} = 0.013_8$ in hexadecane/0.1M NaCl aqueous solution system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
7.1_2	3.14_7	0.40
4.7_5	3.32_4	0.27
3.1_6	3.50_0	1.3_6
2.1_1	3.67_6	3.8_1
1.4_2	3.84_6	7.3_8

TABLE B78: Interfacial tension vs total concentration for $C_{16}EGEO_5S$-$C_{16}EGEO_5OH$ mixture at $\alpha_{C16HGEO5S} = 0.012_9$ in hexadecane/0.1M NaCl aqueous solution system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
6.3_1	3.20_1	0.25
5.4_8	3.26_1	0.13
4.2_0	3.37_7	1.2_5
2.8_0	3.55_3	3.7_8
1.8_9	3.72_3	6.7_1
1.2_6	3.90_0	9.9_2
0.84_0	4.07_6	$13._0$

TABLE B79: Interfacial tension vs total concentration for $C_{12}EO_8$ in hexadecane/H_2O system

$C_t \times 10^4$/M	$-\log C_t$	γ_I/mN m^{-1}
2.4_2	3.61_6	3.6_8
1.6_5	3.78_2	3.6_6
1.2_4	3.90_7	3.6_6
1.0_0	3.99_8	3.8_7
0.55_0	4.25_9	8.8_2
0.31_6	4.50_0	$11._4$
0.17_2	4.76_5	$15._4$
0.10_3	4.98_6	$17._8$

TABLE B80: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}EO_4$ mixture at $\alpha_{C12EO8} = 0.25_5$ in hexadecane/H_2O system

$C_{12,t} \times 10^4$/M	$-\log C_{12,t}$	γ_I/mN m^{-1}
7.2_9	3.13_8	0.92
6.0_7	3.21_7	1.1_9
4.7_6	3.32_3	1.5_8
4.3_6	3.36_1	1.9_1
3.9_6	3.40_2	2.1_2
2.3_8	3.62_4	4.1_6
1.5_9	3.80_0	6.9_3
1.1_9	3.92_5	7.9_9
0.81_2	4.09_0	$10_{.6}$
0.39_6	4.40_2	$14_{.3}$

TABLE B81: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}EO_3$ mixture at α_{C12EO8} = 0.079_9 in hexadecane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
1.3_4	2.87_2	0.19
1.0_1	2.99_7	0.48
0.80_5	3.09_4	0.84
0.67_1	3.17_3	1.6_0
0.40_2	3.39_5	5.2_8
0.26_8	3.57_1	8.7_1
0.17_9	3.74_7	$11._4$
0.11_9	3.92_4	$14._6$

TABLE B82: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}EO_2$ mixture at α_{C12EO8} = $8.9_2 \times 10^{-3}$ in hexadecane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
4.1_7	2.38_0	0.32
2.7_8	2.55_6	1.9_7
2.0_9	2.68_1	3.4_5
1.5_4	2.81_1	4.4_5
1.2_8	2.89_2	7.1_1
1.0_4	2.98_2	8.1_6
0.77_0	3.11_3	$11._5$
0.51_3	3.29_0	$15._0$

TABLE B83: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}EO_2$ mixture at α_{C12EO8} = 0.38_7 in hexadecane/H_2O system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
$10._9$	2.96_3	1.6_1
5.4_4	3.26_4	2.8_6
2.7_2	3.56_5	3.7_1
1.8_1	3.74_2	4.6_4
1.1_0	3.95_9	8.9_0
0.72_5	4.13_9	$11._2$
0.48_4	4.31_5	$14._0$

TABLE B84: Interfacial tension vs total concentration for $C_{12}EO_8$ in heptane/H_2O system

$C_t \times 10^4$/M	-log C_t	γ_I/mN m^{-1}
2.4_3	3.61_5	2.0_7
1.8_2	3.74_0	1.9_2
1.2_1	3.91_6	2.0_2
0.80_9	4.09_2	2.0_3
0.27_6	4.55_9	7.0_7
0.16_6	4.78_1	$10._2$
0.11_0	4.95_7	$12._2$
0.073_5	5.13_3	$15._3$

TABLE B85: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}EO_2$ mixture at $\alpha_{C12EO8} = 0.046_9$ in heptane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
2.1_6	2.66_6	0.10
1.6_7	2.79_1	0.33
1.0_8	2.96_7	1.0_5
0.71_9	3.14_3	3.8_6
0.48_0	3.31_9	6.2_1
0.32_0	3.49_5	8.9_2

TABLE B86: Interfacial tension vs total concentration for $C_{16}EO_8$-$C_{12}EO_2$ mixture at α_{C16EO8} = $6.5_8 \times 10^{-3}$ in hexadecane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
2.7_2	2.56_5	0.54
1.8_1	2.74_1	2.7_1
1.2_1	2.91_8	4.4_5
0.89_0	3.05_1	6.6_7
0.68_0	3.16_7	9.0_0
0.55_5	3.25_6	$10._2$
0.45_3	3.34_4	$10._6$
0.30_2	3.52_0	$14._5$
0.20_2	3.69_6	$18._8$
0.13_4	3.87_2	$22._4$

TABLE B87: Interfacial tension vs total concentration for $C_{12}OH$ in hexadecane/H_2O system

$C_t \times 10^2$/M	-log C_t	γ_I/mN m^{-1}
2.7_2	1.56_5	$14._3$
1.8_2	1.74_1	$15._8$
1.2_1	1.91_7	$17._4$
0.80_7	2.09_3	$18._6$
0.53_8	2.26_9	$20._1$

TABLE B88: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}OH$ mixture at $\alpha_{C12EO8} = 2.0_2 \times 10^{-3}$ in hexadecane/H_2O system

$C_{12,t} \times 10^2$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
1.6_4	1.78_6	8.8_1
1.0_9	1.96_2	9.2_9
0.72_8	2.13_9	$10._2$
0.48_5	2.31_4	$11._3$
0.32_4	2.49_0	$12._6$
0.21_6	2.66_6	$14._0$

TABLE B89: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}OH$ mixture at $\alpha_{C12EO8} = 0.035_3$ in hexadecane/H_2O system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
5.6_3	3.25_0	$10._6$
3.7_5	3.42_6	$13._5$
2.5_0	3.60_2	$16._2$
1.6_7	3.77_8	$19._2$

TABLE B90: Interfacial tension vs total concentration for C_8P in hexadecane/H_2O system

$C_t \times 10^3$/M	-log C_t	γ_I/mN m^{-1}
$19._4$	1.71_2	0.72
$16._1$	1.79_4	0.75
9.8_3	2.00_7	3.2_7
7.3_1	2.13_6	6.0_7
5.0_4	2.29_8	9.9_8
2.5_2	2.59_9	$16._2$
1.6_8	2.77_5	$20._2$

TABLE B91: Interfacial tension vs total concentration for $C_{12}EO_8$-C_8P mixture at $\alpha_{C12EO8} = 0.042_8$ in hexadecane/H_2O system

$C_{12,t} \times 10^3/M$	$-\log C_{12,t}$	$\gamma_I/mN\ m^{-1}$
4.1_0	2.38_8	2.1_7
3.4_1	2.46_7	2.4_0
2.7_3	2.56_4	2.6_0
2.0_5	2.68_9	3.1_6
1.3_7	2.86_5	5.0_2
1.0_2	2.99_0	7.5_9
0.68_3	3.16_6	$10._2$
0.45_5	3.34_2	$12._8$

TABLE B92: Interfacial tension vs total concentration for $C_{12}EO_8$-C_8P mixture at α_{C12EO8} = 0.52_3 in hexadecane/H_2O system

$C_{12,t} \times 10^4$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
3.3_0	3.48_1	3.8_0
2.6_4	3.57_8	3.8_5
1.7_6	3.75_4	4.9_8
1.3_5	3.86_8	6.1_8
0.99	4.00_4	8.1_2
0.66_0	4.18_0	9.9_4
0.44_0	4.35_6	$12._4$

TABLE B93: Interfacial tension vs total concentration for $C_{12}EO_8$-$C_{12}P$ mixture at $\alpha_{C12EO8} = 0.013_6$ in hexadecane/H_2O system

$C_{12,t} \times 10^3$/M	-log $C_{12,t}$	γ_I/mN m^{-1}
$13._2$	1.88_0	0.43
8.7_8	2.05_7	0.08
5.8_5	2.23_3	0.22
3.9_0	2.40_9	1.1_5
2.6_0	2.58_5	3.2_1
1.7_3	2.76_1	6.5_2
1.1_4	2.94_2	9.9_3
0.76_2	3.11_8	$13._0$

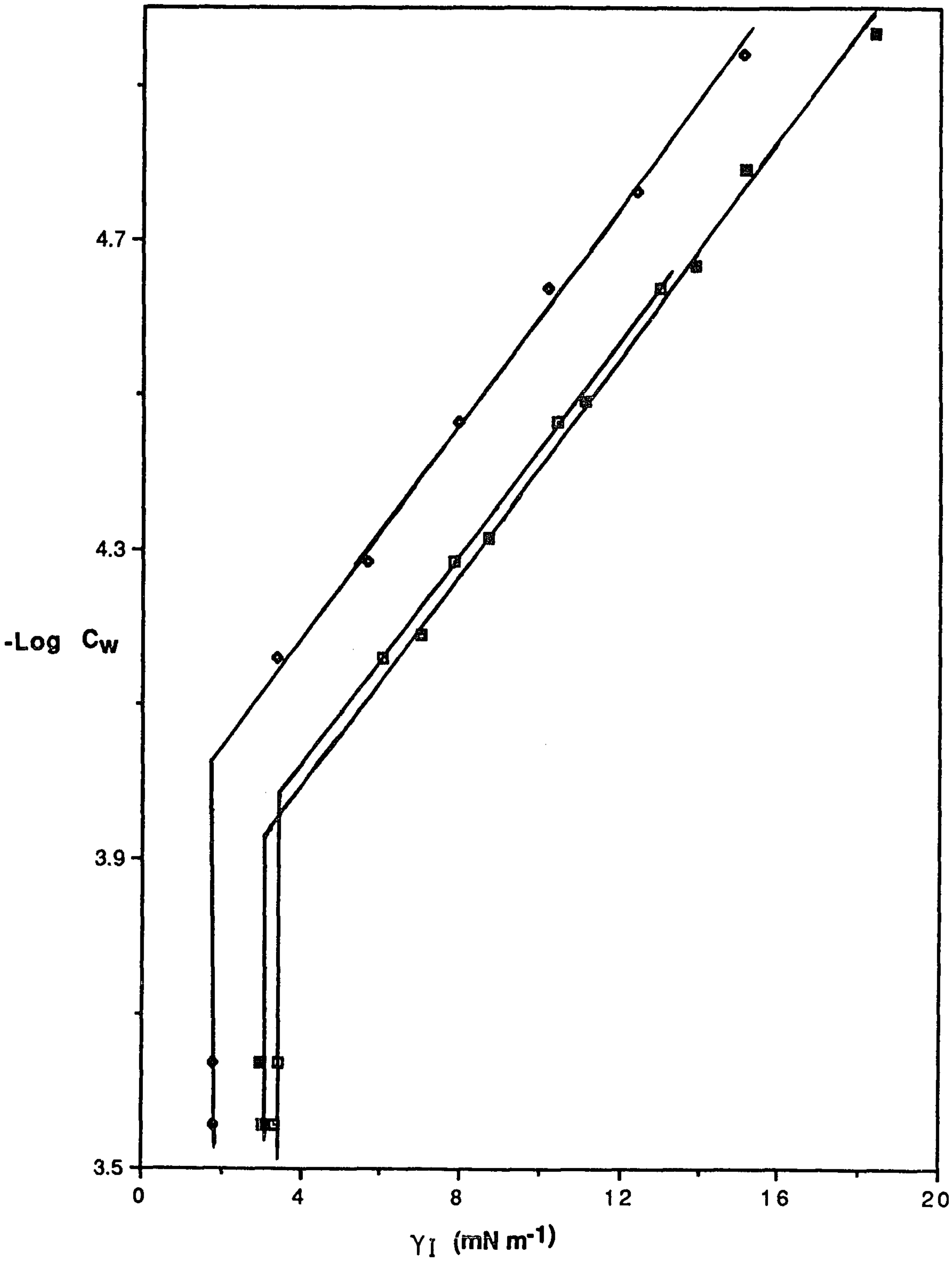

Figure B1. $C_{12}EO_8$ in hydrocarbon/H_2O systems at 25.0°C. Hydrocarbon phase: hexadecane (◻), heptamethylnonane (■), and heptane (◇).

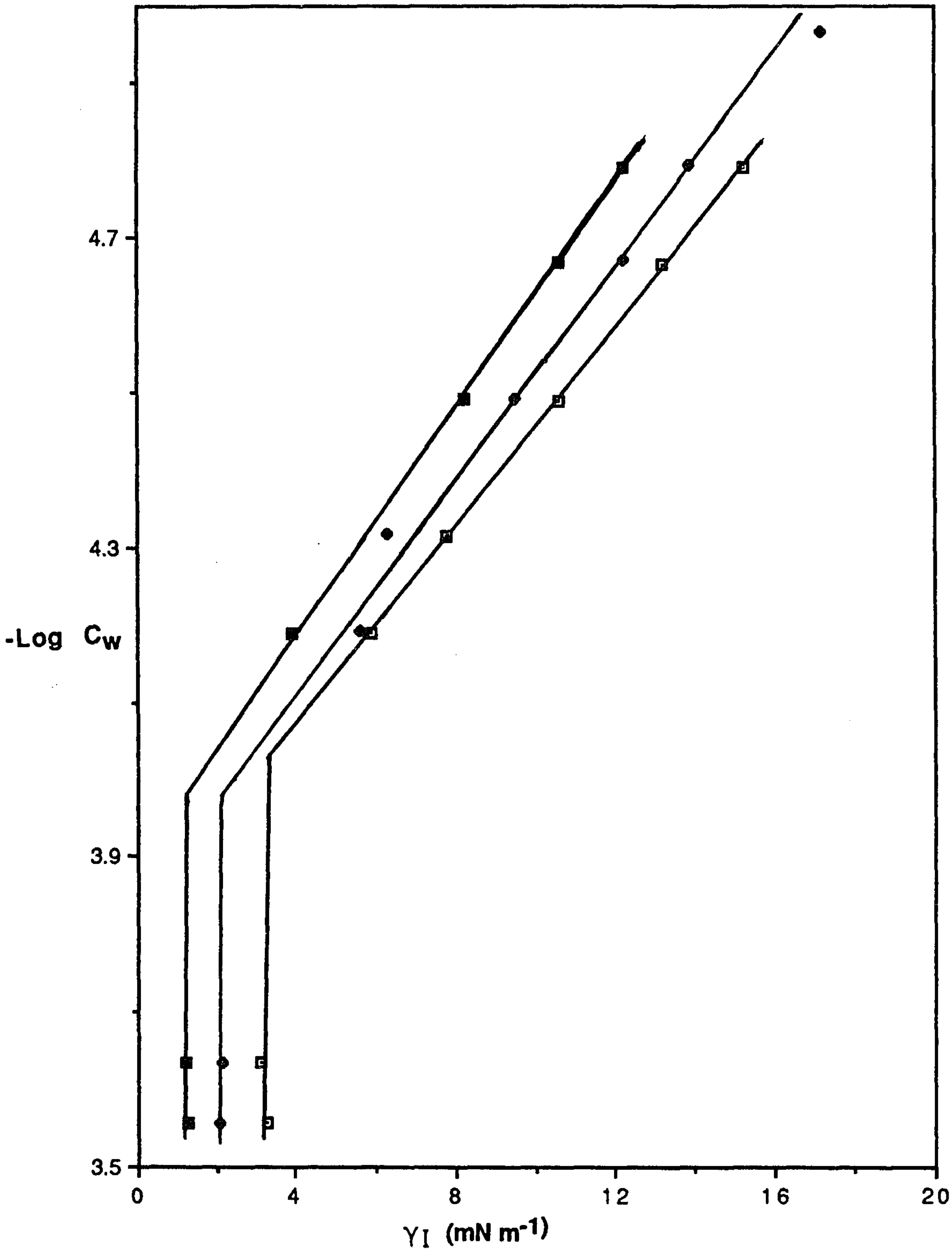

Figure B2. $C_{12}EO_8$ in hydrocarbon/H_2O systems at 25.0°C. Hydrocarbon phase: dodecane (□), isooctane (◆), and cyclohexane (■).

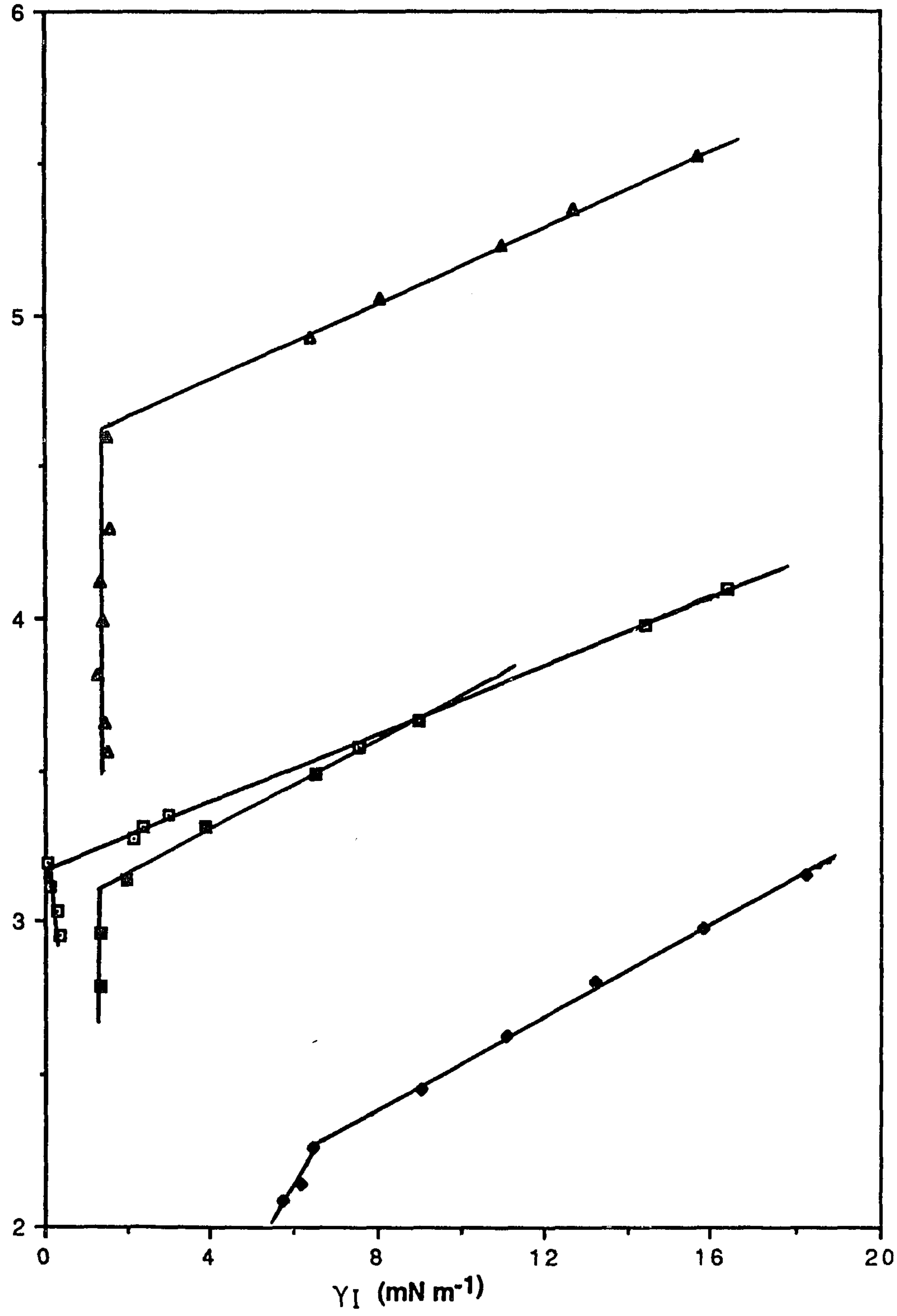

Figure B3. Nonionic surfactants in hydrocarbon/aqueous systems at 25.0°C. Surfactant/hydrocarbon/aqueous phase: $C_{12}EO_4$/hexadecane/H_2O (□), $C_{12}EO_2$/heptane/H_2O (◆), $C_{16}EGEO_5OH$/hexadecane/0.1M NaCl (■), and $C_{16}EO_8$/hexadecane/H_2O (▲).

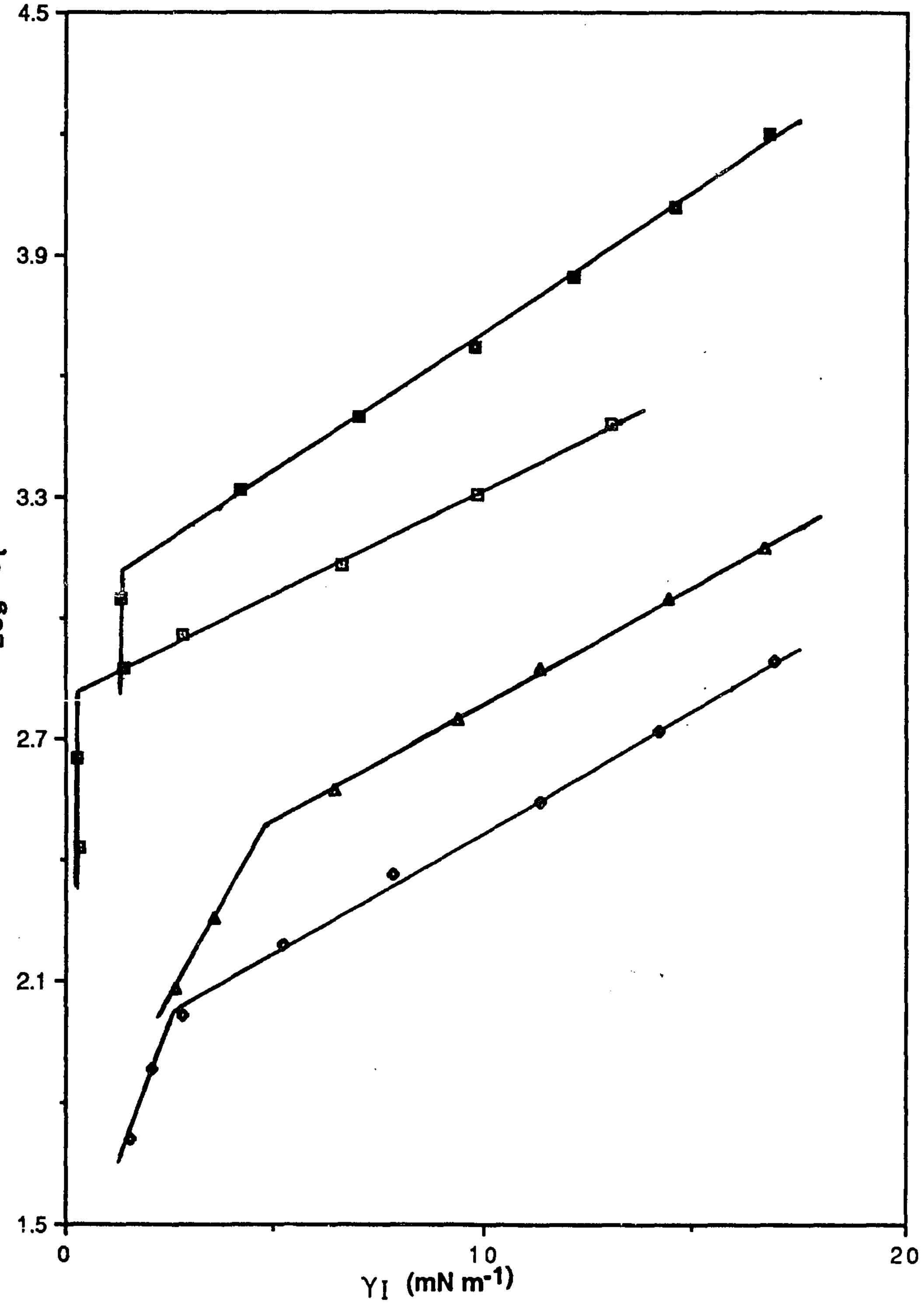

Figure B4. Nonionic surfactants in hexadecane/aqueous systems at 25.0°C. Surfactant/aqueous phase: $C_{12}P/H_2O$ (◆), $C_{12}EO_3/H_2O$ (□), $C_{12}EO_2/H_2O$ (▲), and $C_{16}HGEO_5OH/0.1M$ NaCl (■).

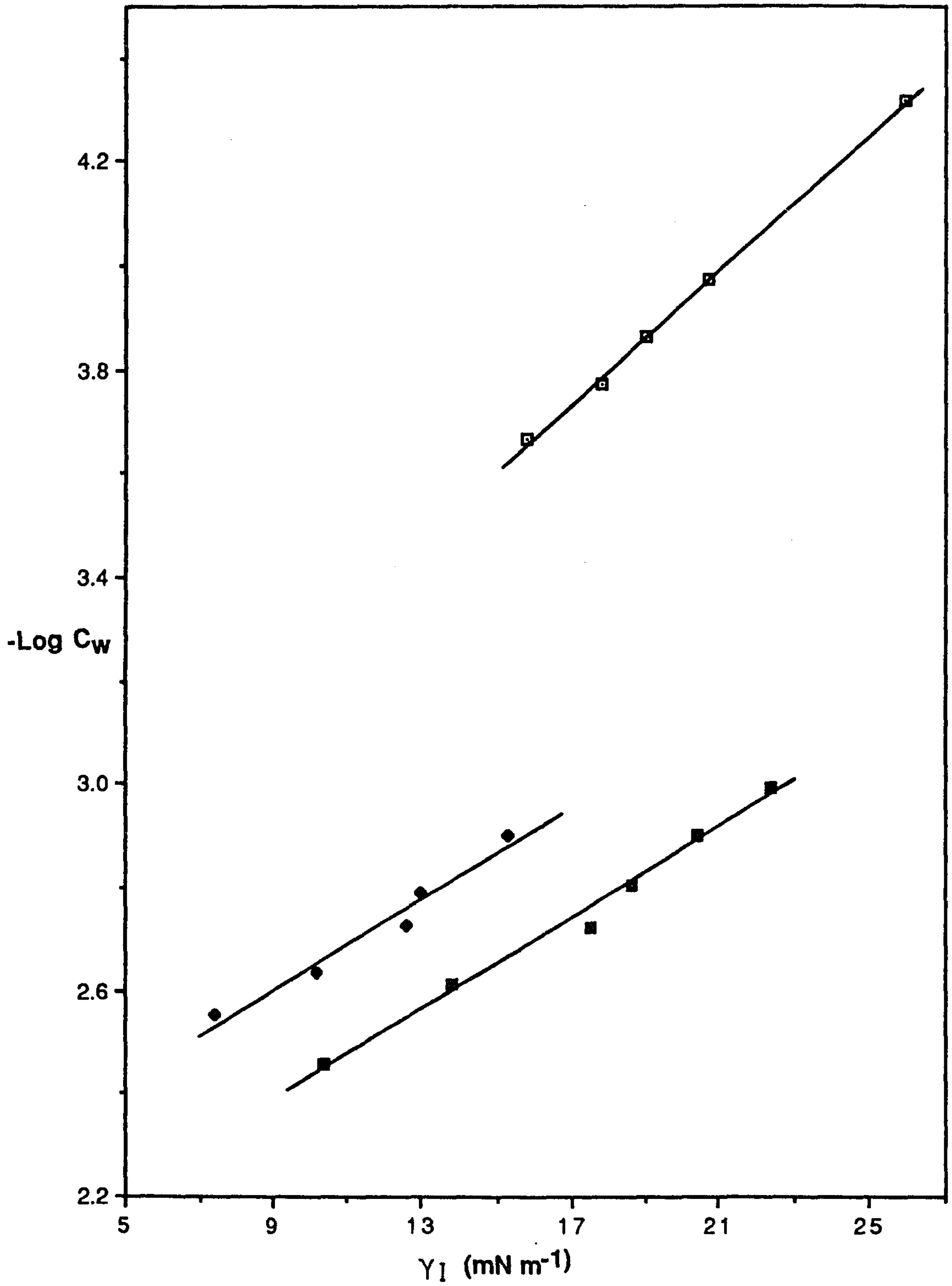

Figure B5. Nonionic surfactants in hexadecane/aqueous systems at 25.0°C. Surfactant/aqueous phase: C_8P/H_2O (◆), C_8P/0.1M NaCl (■), and $C_{10}P$/0.1M NaCl (□).

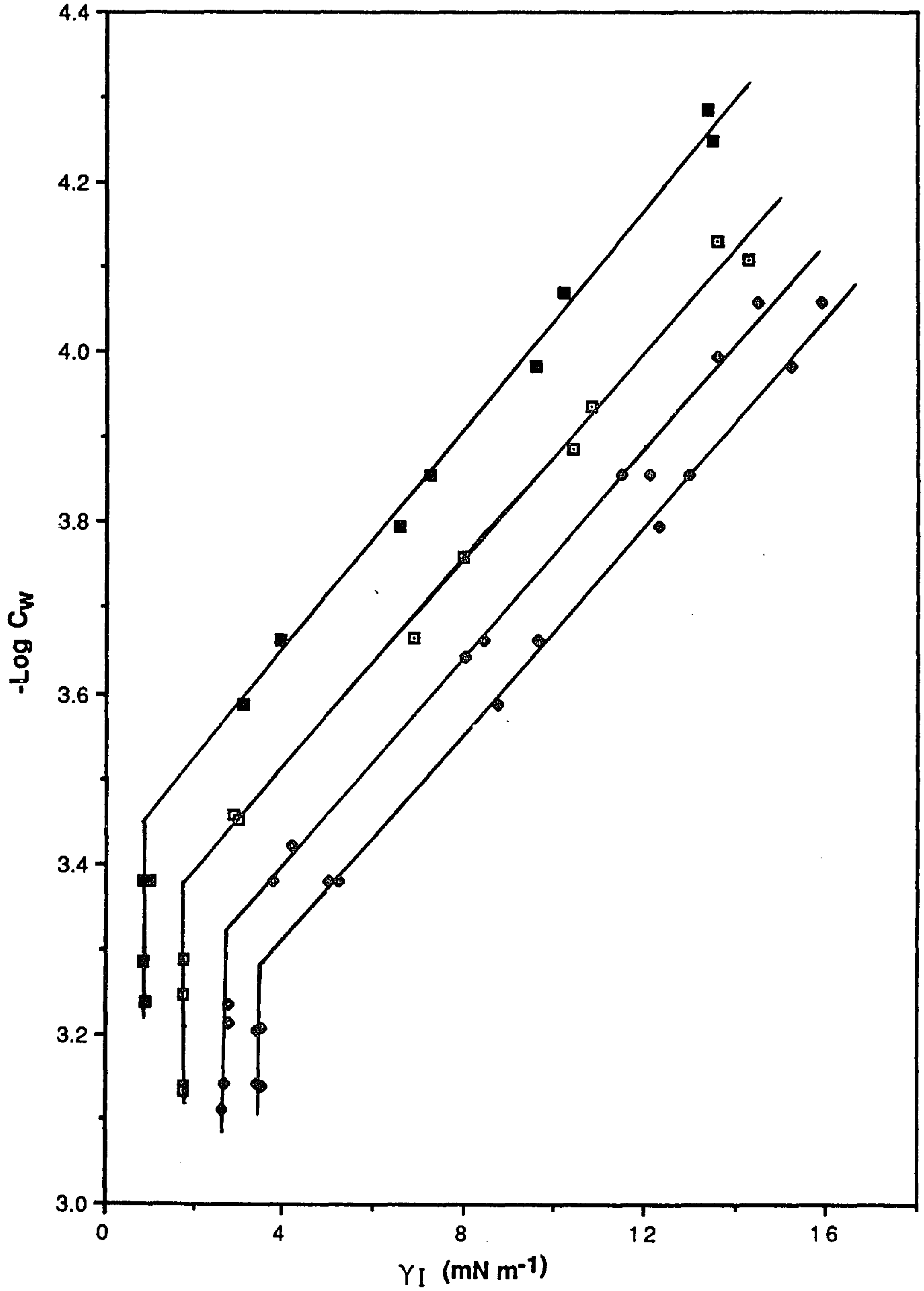

Figure B6. C_{12}BMG in hydrocarbon/H_2O systems at 25.0°C. Hydrocarbon phase: hexadecane (◆), dodecane (◇), heptane (▣), and cyclohexane (■).

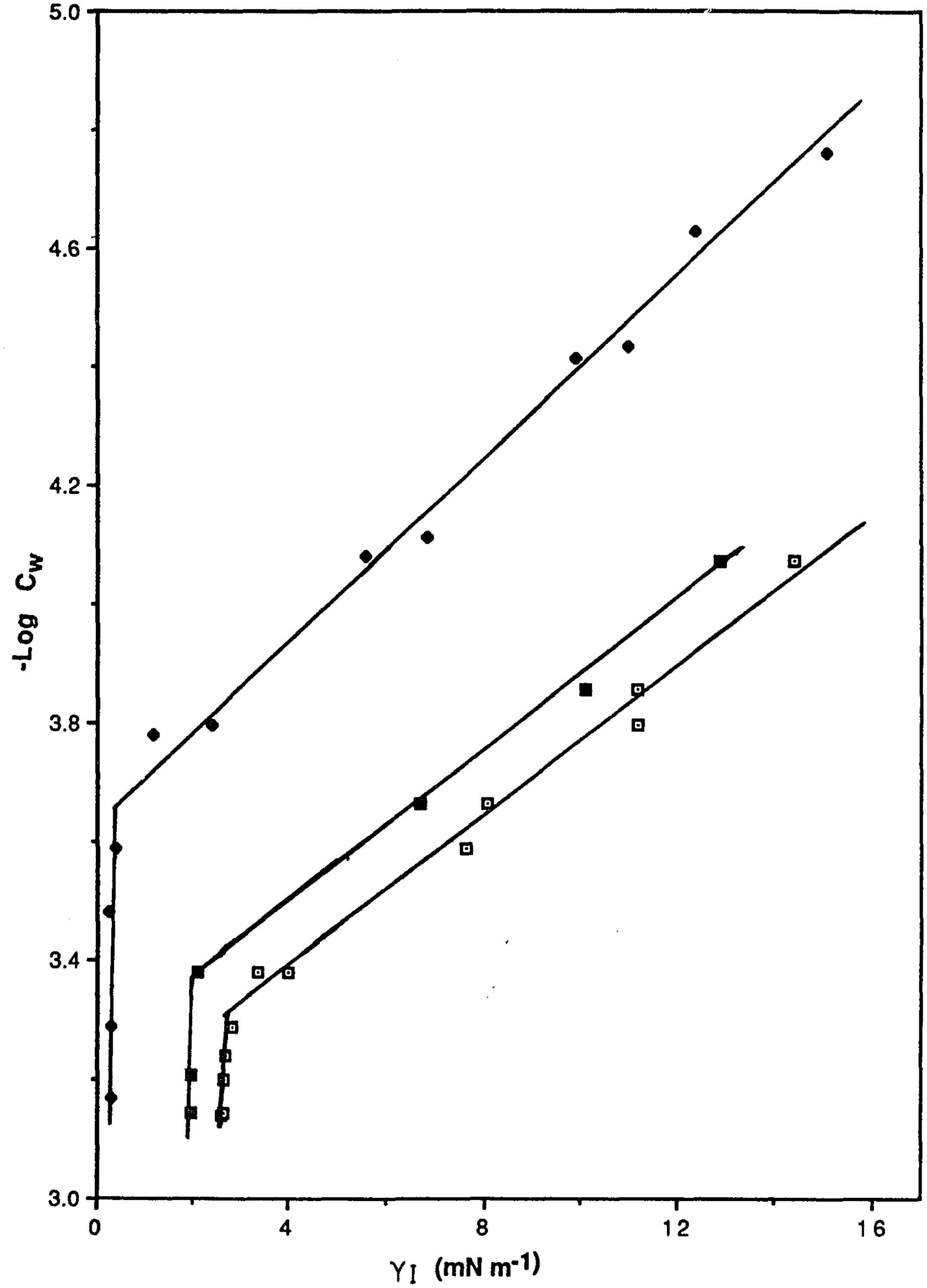

Figure B7. C_{12}BMG in hydrocarbon/H_2O systems at 25.0°C. Hydrocarbon phase: isooctane (■), heptamethylnonane (▣), and toluene (◆).

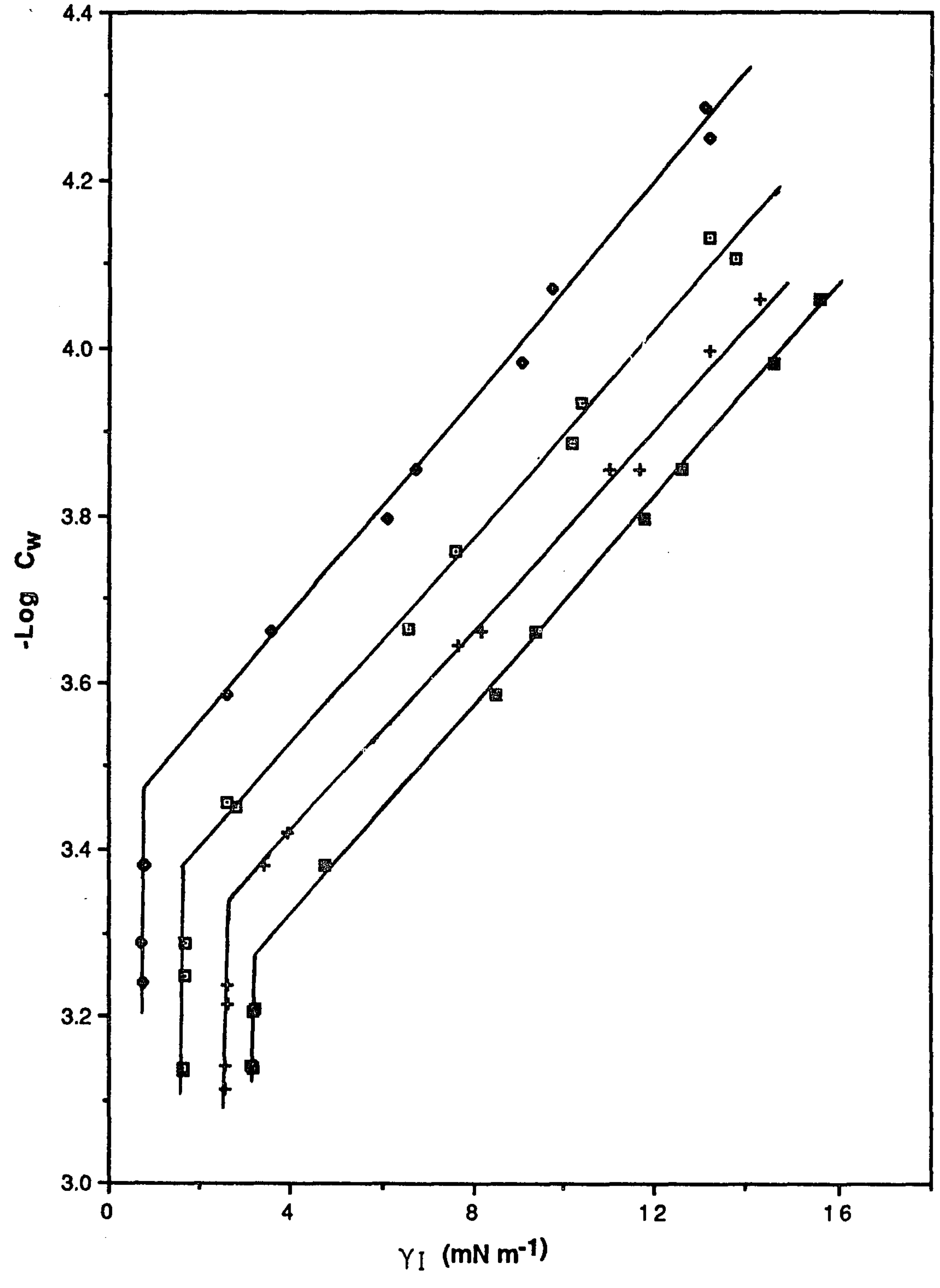

Figure B8. C_{12}BMG in hydrocarbon/H_2O systems at 35.0°C. Hydrocarbon phase: hexadecane (■), dodecane (+), heptane (⊡), and cyclohexane (◆).

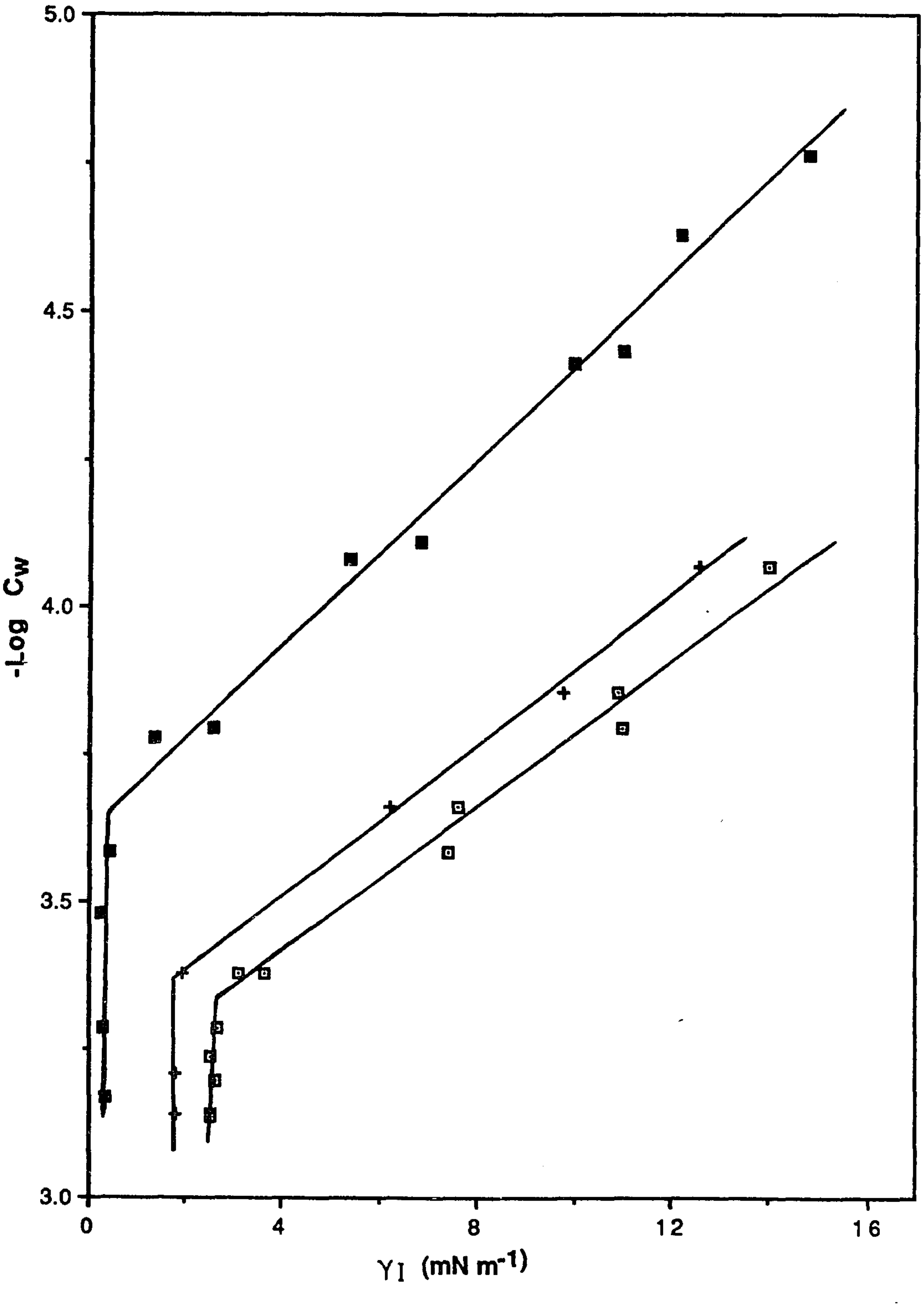

Figure B9. C_{12}BMG in hydrocarbon/H_2O systems at 35.0°C. Hydrocarbon phase: isooctane (+), heptamethylnonane (⊡), and toluene (■).

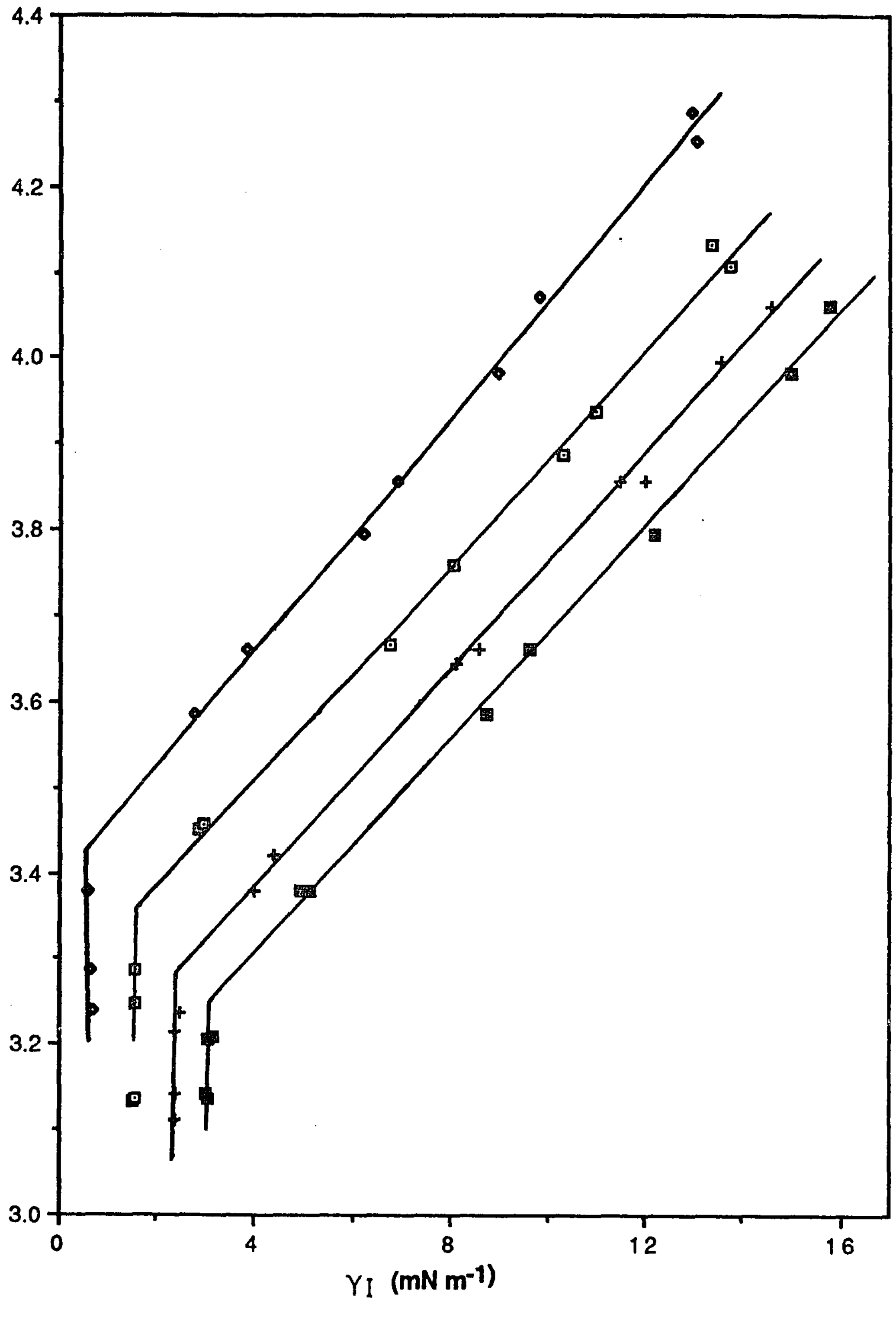

Figure B10. $C_{12}BMG$ in hydrocarbon/H_2O systems at 45.0°C. Hydrocarbon phase: hexadecane (■), dodecane (+), heptane (▣), and cyclohexane (◆).

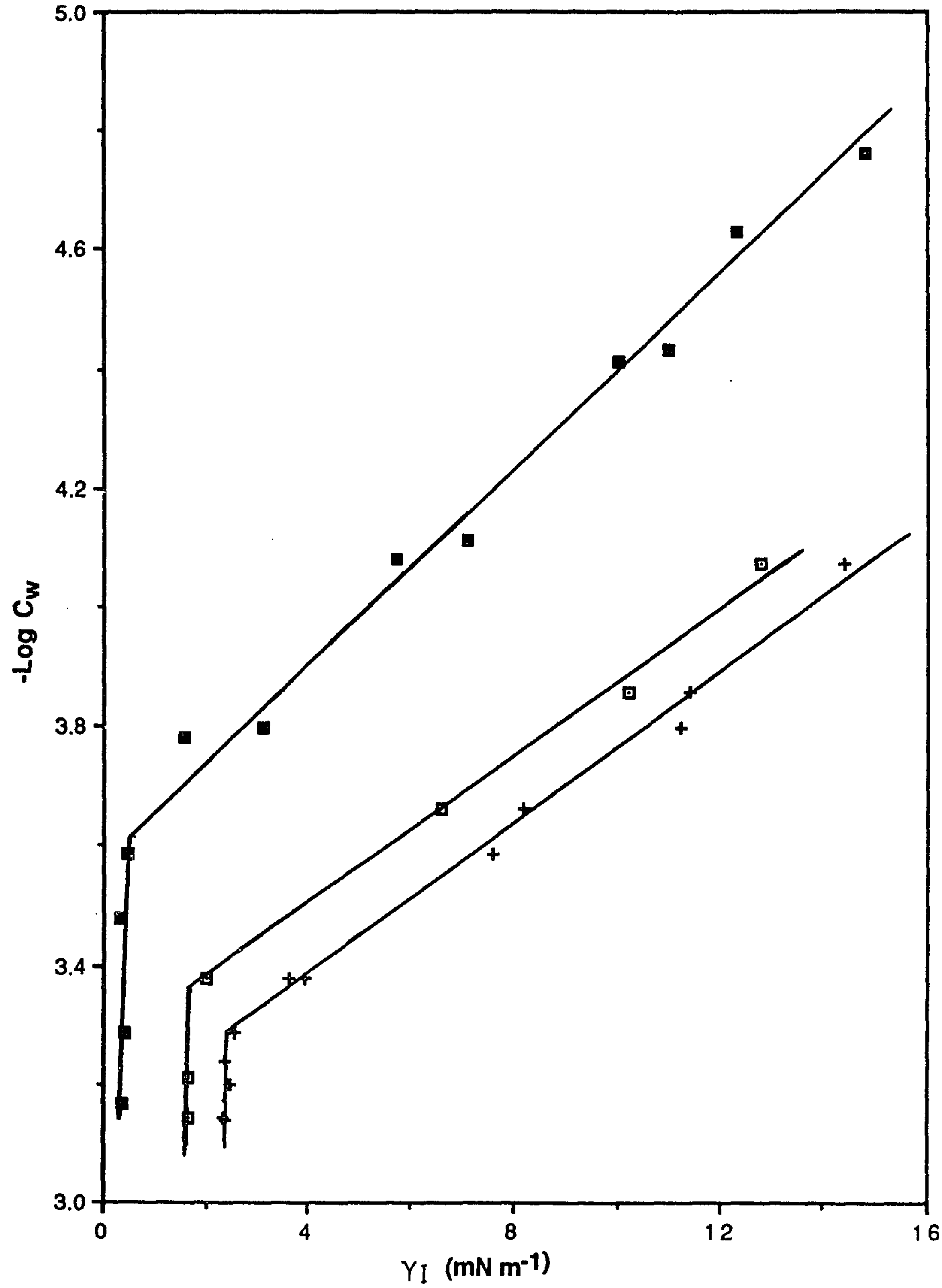

Figure B11. $C_{12}BMG$ in hydrocarbon/H_2O systems at 45.0°C. Hydrocarbon phase: isooctane (▣), heptamethylnonane (+), and toluene (■).

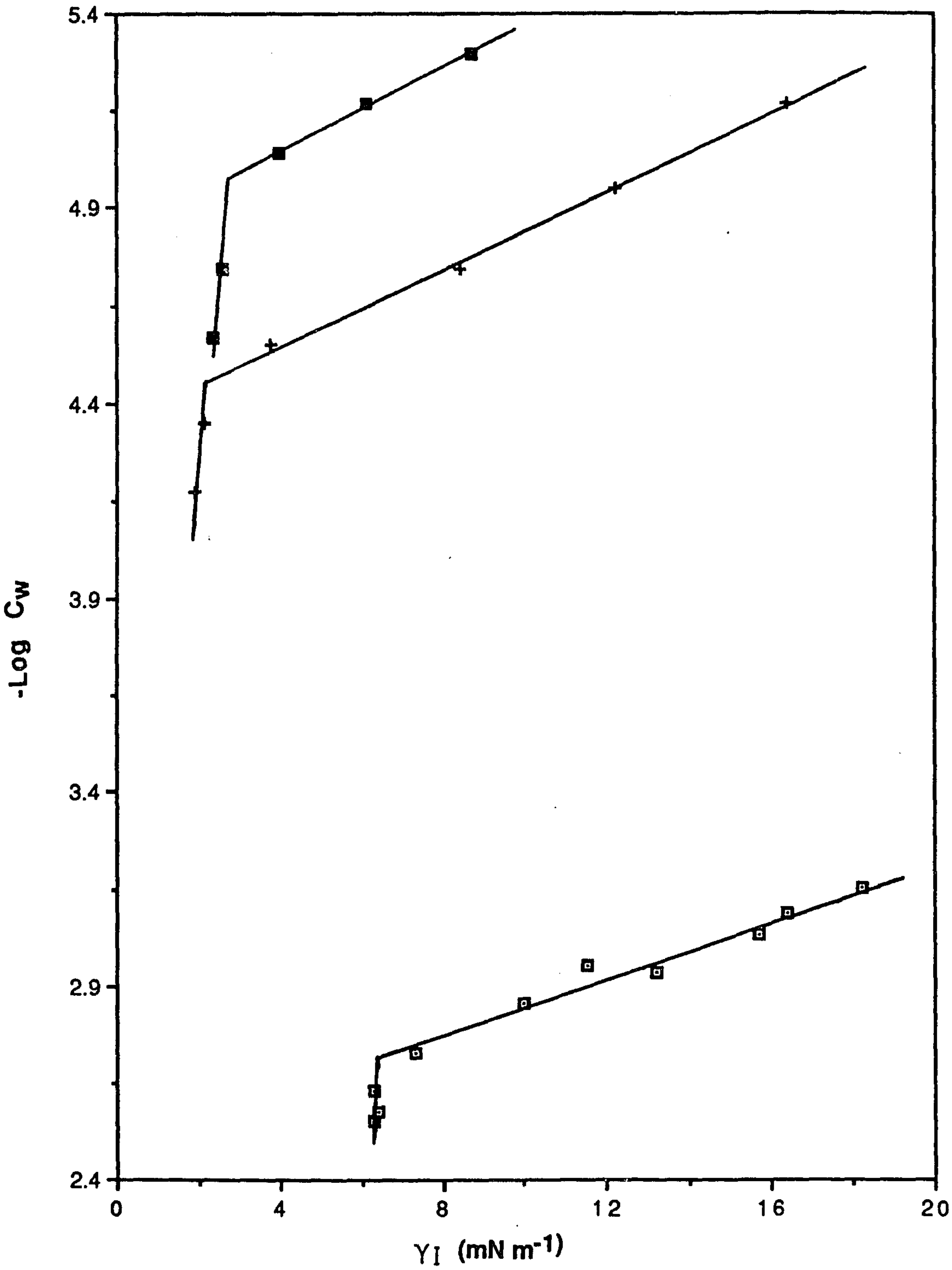

Figure B12. Anionic surfactants in hexadecane/0.1M NaCl aqueous solution systems at 25.0°C. Surfactant: $C_{16}HGEO_5S$ (■), $C_{16}EGEO_5S$ (+), and $C_{12}S$ (□).

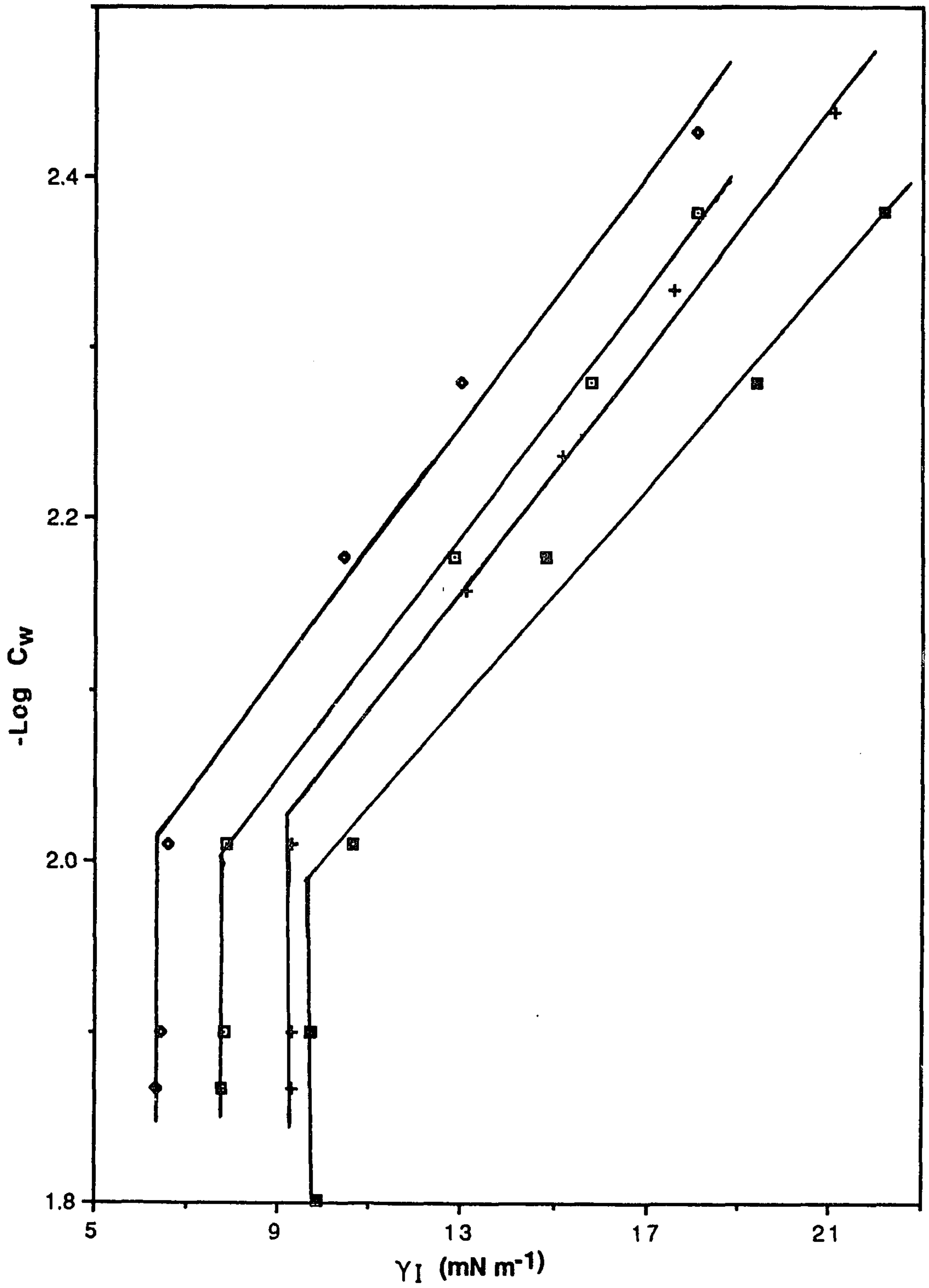

Figure B13. $C_{12}S$ in hydrocarbon/H_2O systems at 25.0°C. Hydrocarbon phase: hexadecane (▣), dodecane (+), heptane (⊡), and cyclohexane (◈).

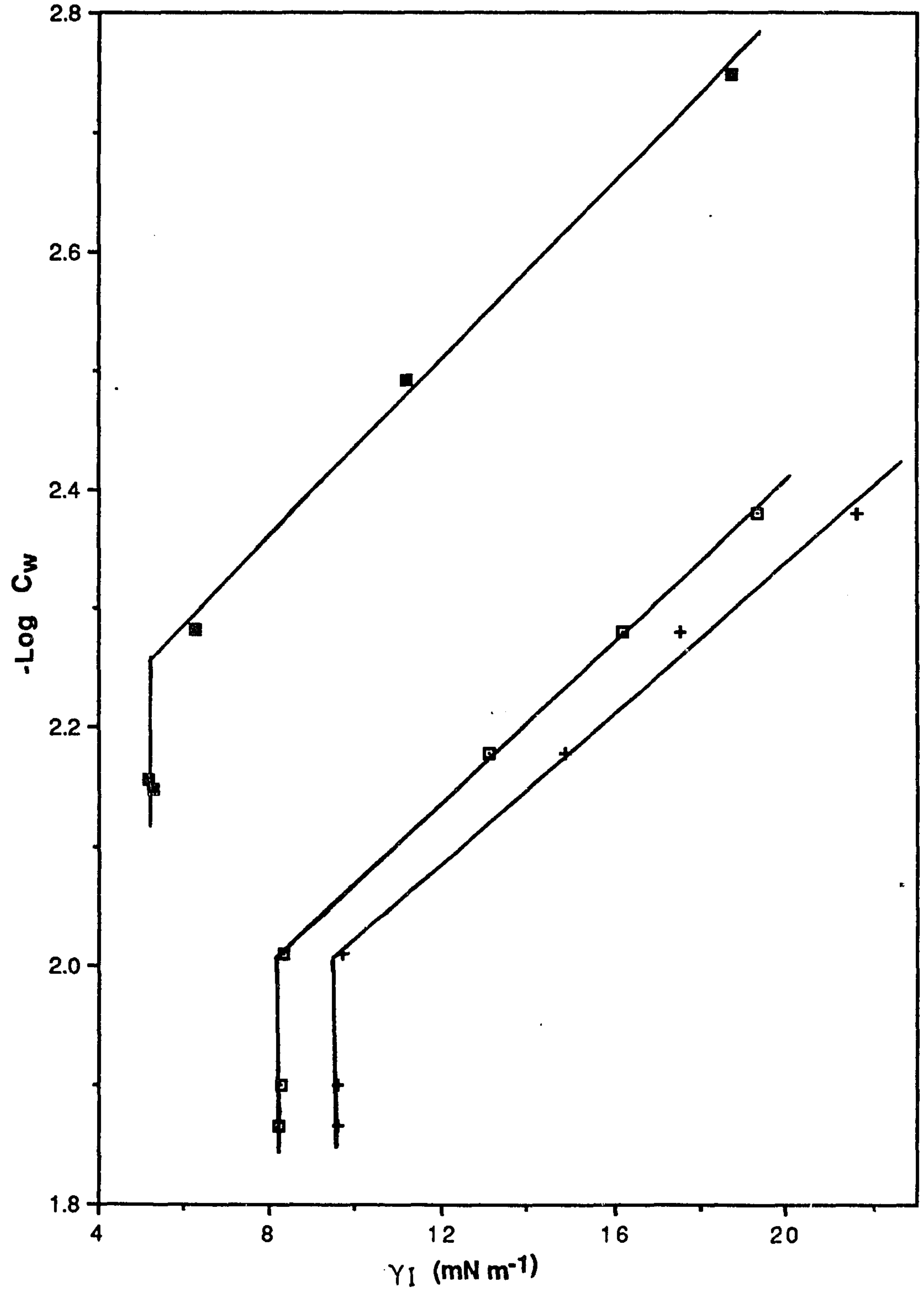

Figure B14. $C_{12}BMG$ in hydrocarbon/H_2O systems at 25.0°C. Hydrocarbon phase: isooctane (□), heptamethylnonane (+), and toluene (■).

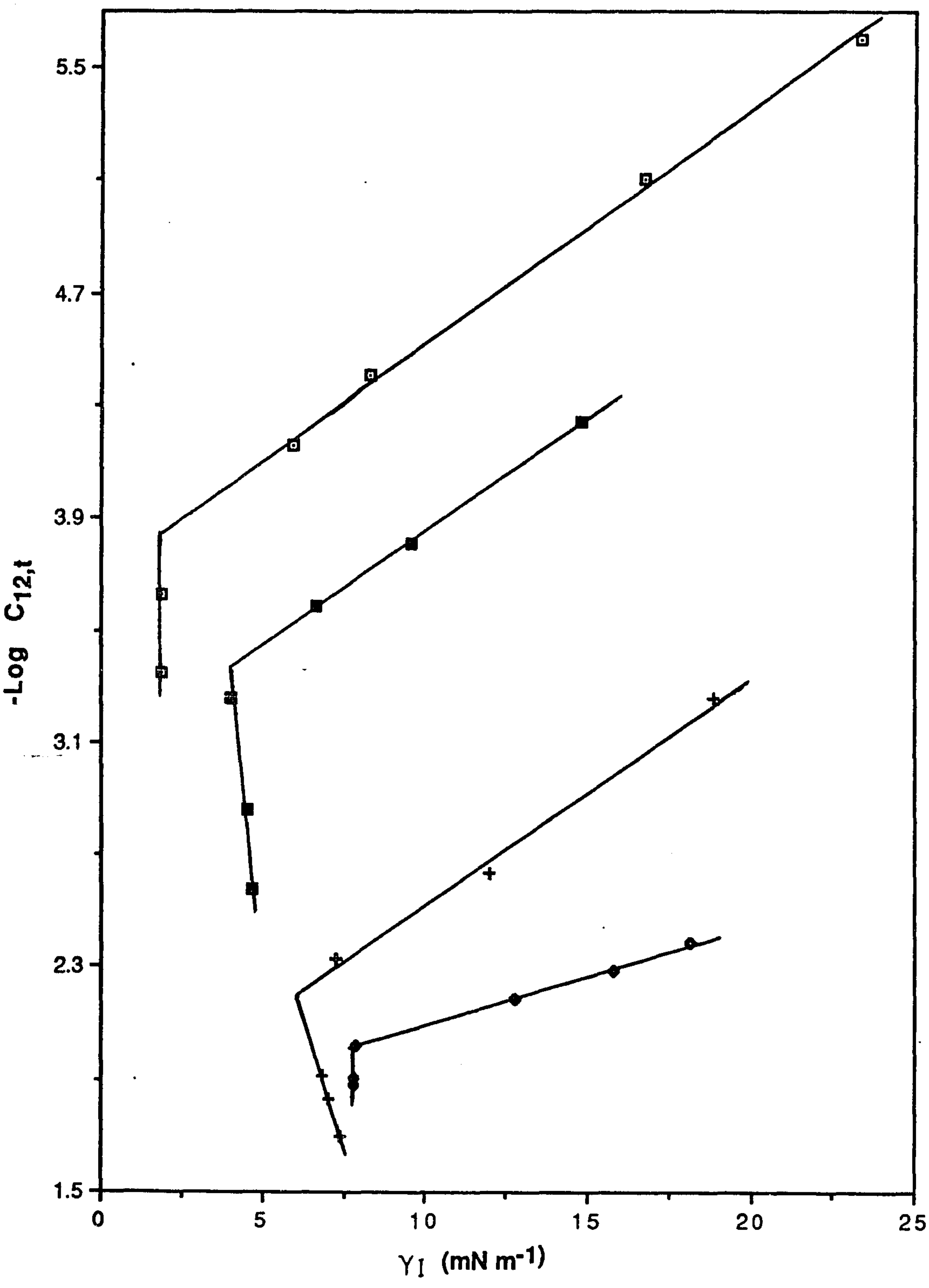

Figure B15. $C_{12}EO_7$, $C_{12}S$, and their mixtures in heptane/H_2O systems at 25.0°C. α_{C12EO7}: (◆), 0; (+), $3.7_5 \times 10^{-3}$; (■), 0.24_9; (□), 1.

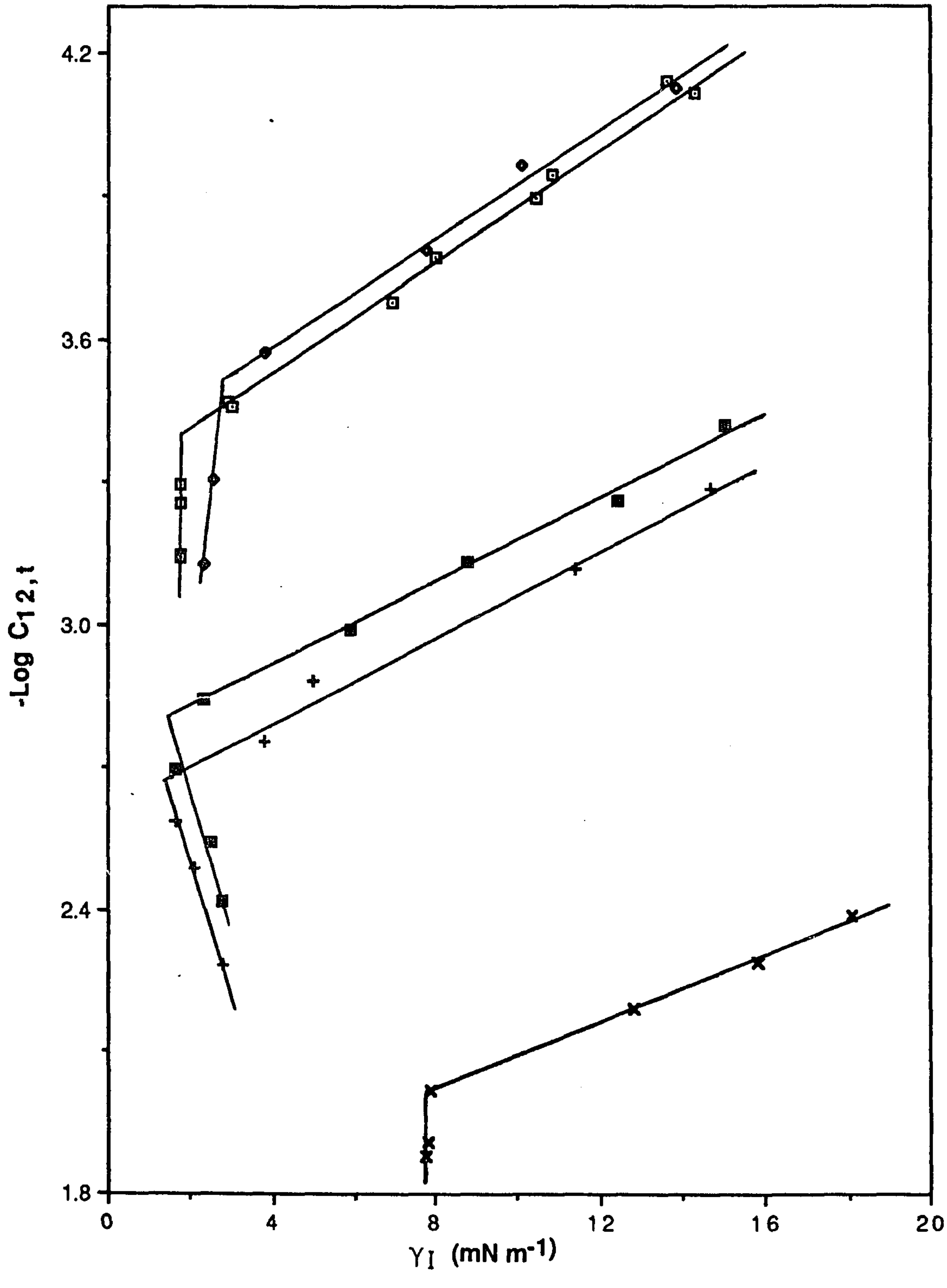

Figure B16. $C_{12}BMG$, $C_{12}S$, and their mixtures in heptane/H_2O systems at 25.0°C. α_{C12BMG}: (X), 0; (+), 0.027_7; (■), 0.051_3; (◆), 0.94; (□),1.

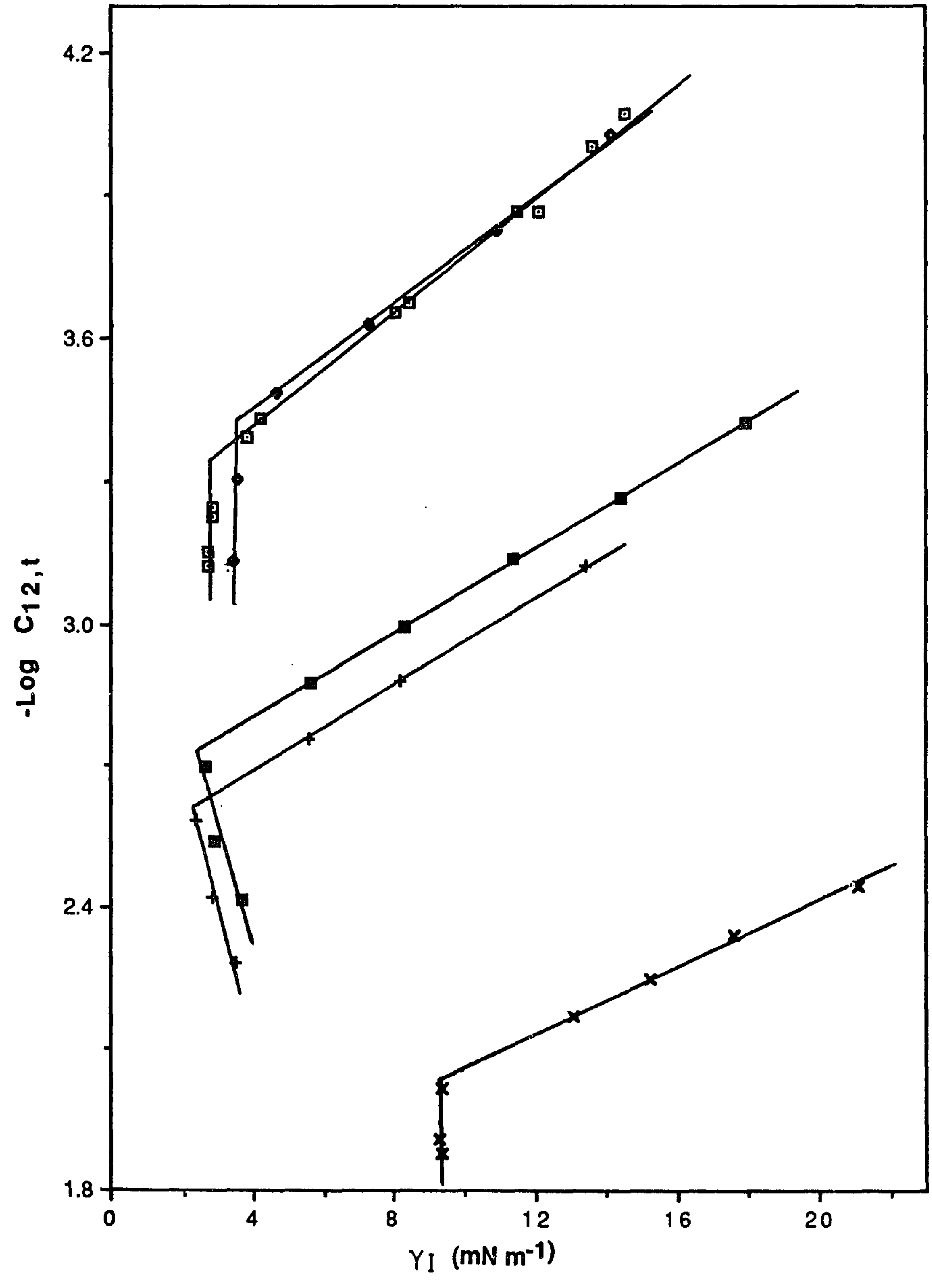

Figure B17. $C_{12}BMG$, $C_{12}S$, and their mixtures in dodecane/H_2O systems at 25.0°C. α_{C12BMG}: (X), 0; (+), 0.027$_7$; (■), 0.051$_6$; (◆), 0.94; (▣),1.

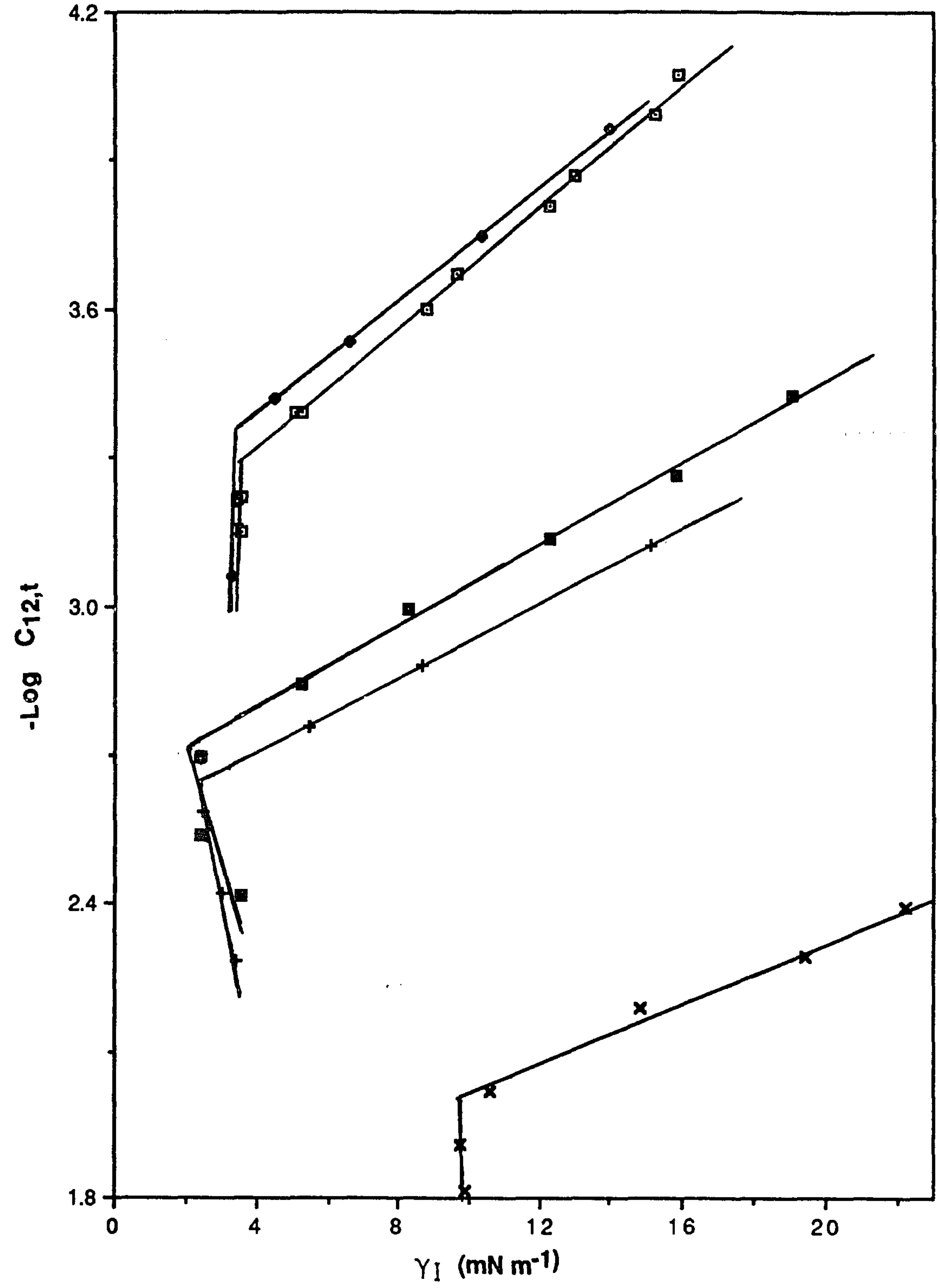

Figure B18. C_{12}BMG, C_{12}S, and their mixtures in hexadecane/H_2O systems at 25.0°C. α_{C12BMG}: (✕), 0; (+), 0.027$_7$; (■), 0.051$_6$; (◆), 0.94; (□),1.

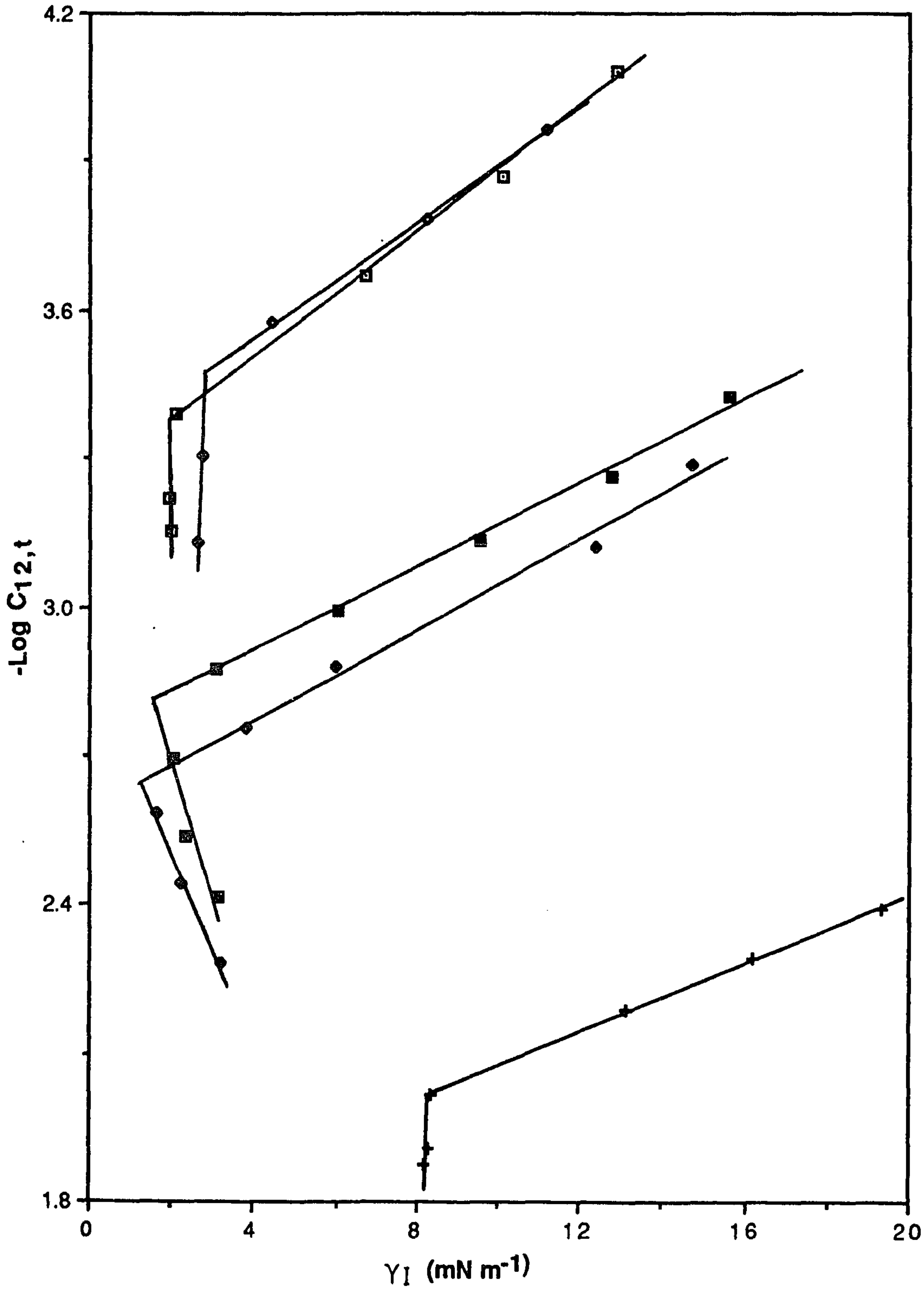

Figure B19. $C_{12}BMG$, $C_{12}S$, and their mixtures in isooctane/H_2O systems at 25.0°C. α_{C12BMG}: (+), 0; (◆), 0.027_7; (■), 0.051_6; (◇), 0.94; (□),1.

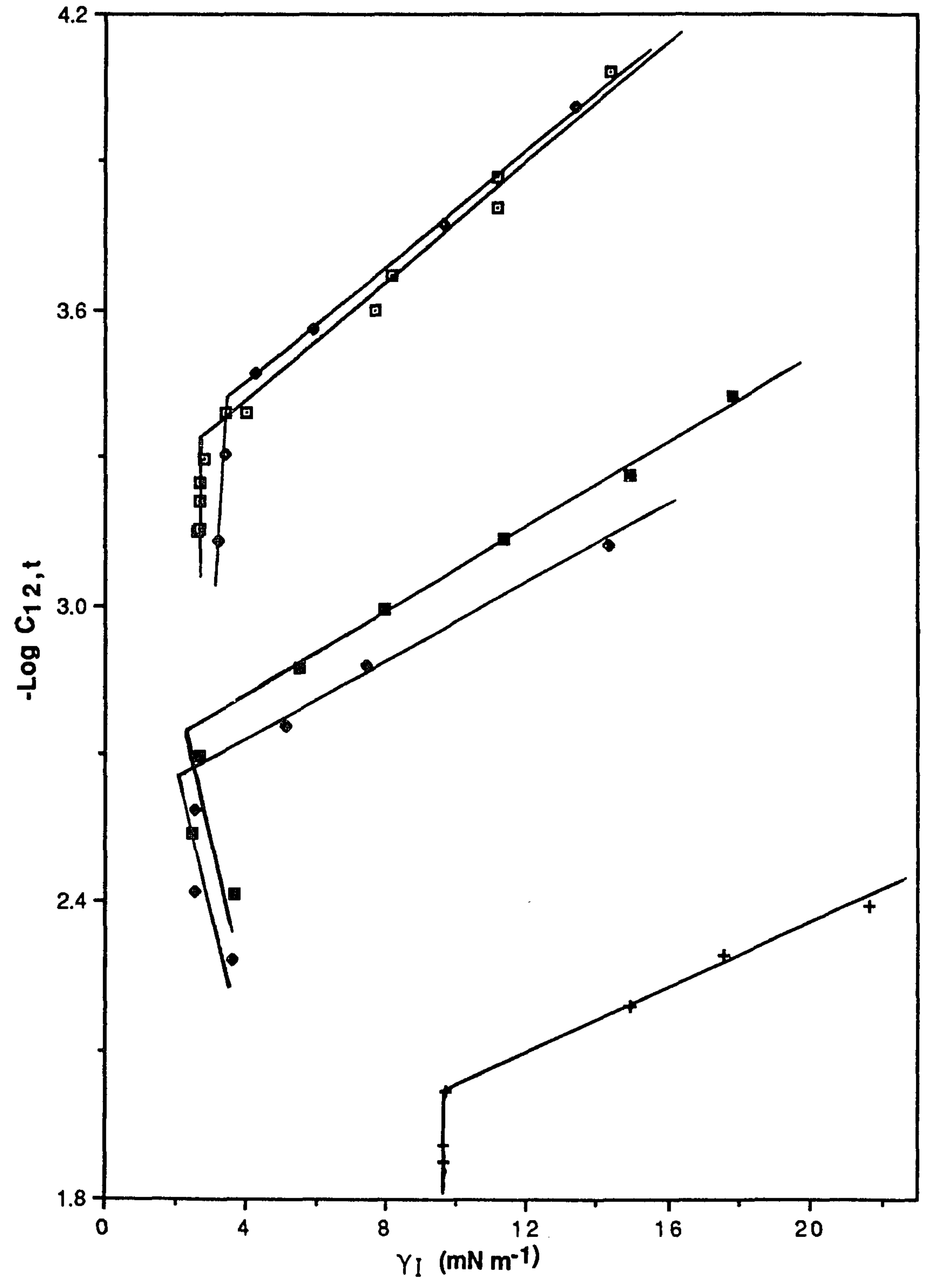

Figure B20. $C_{12}BMG$, $C_{12}S$, and their mixtures in heptamethylnonane/H_2O systems at 25.0°C. α_{C12BMG}: (+), 0; (◆), 0.027_7; (■), 0.051_6; (◇), 0.94; (□),1.

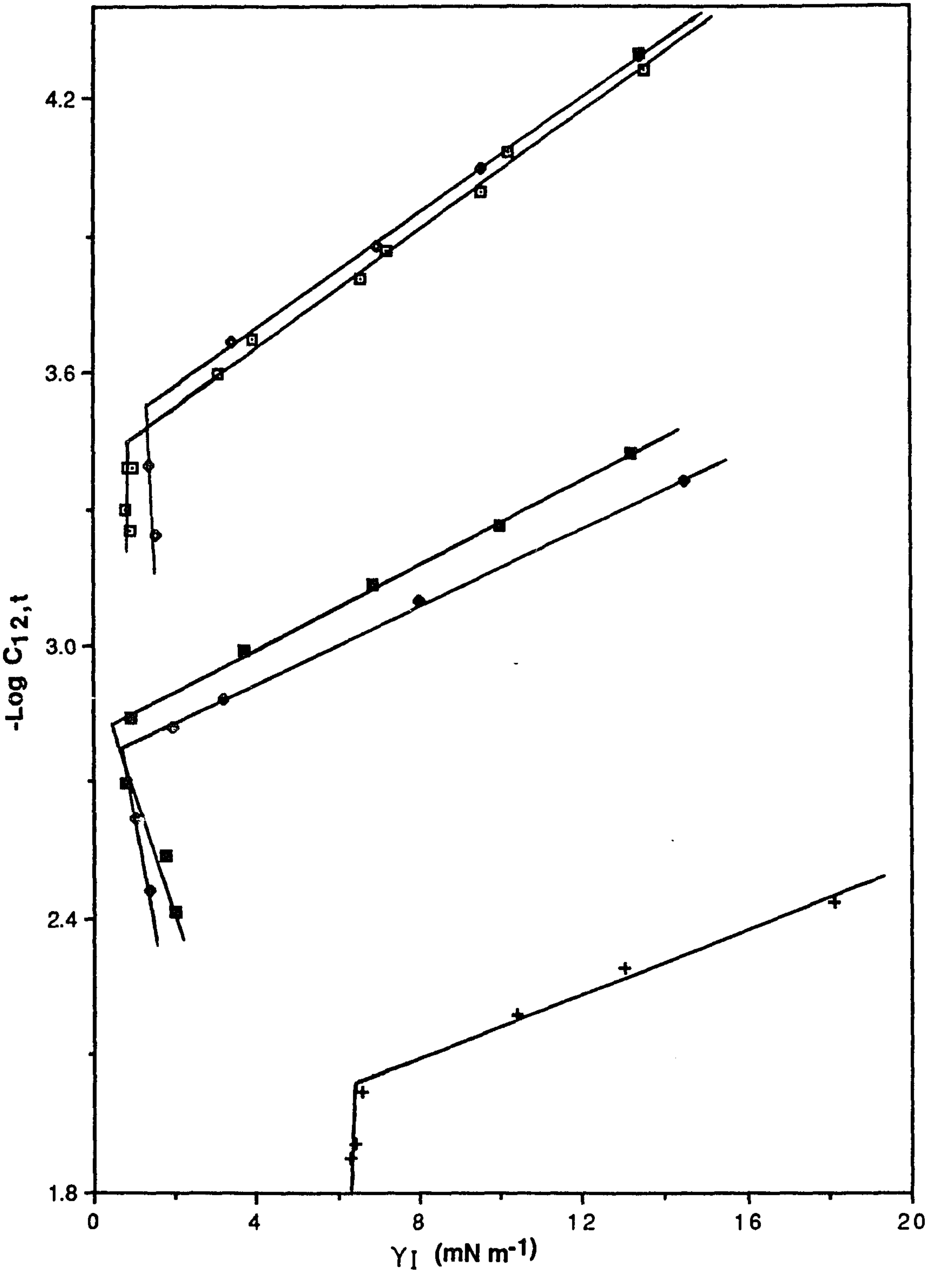

Figure B21. $C_{12}BMG$, $C_{12}S$, and their mixtures in cyclohexane/H_2O systems at 25.0°C. α_{C12BMG}: (+), 0; (♦), 0.027_7; (■), 0.051_6; (◇), 0.94; (◻),1.

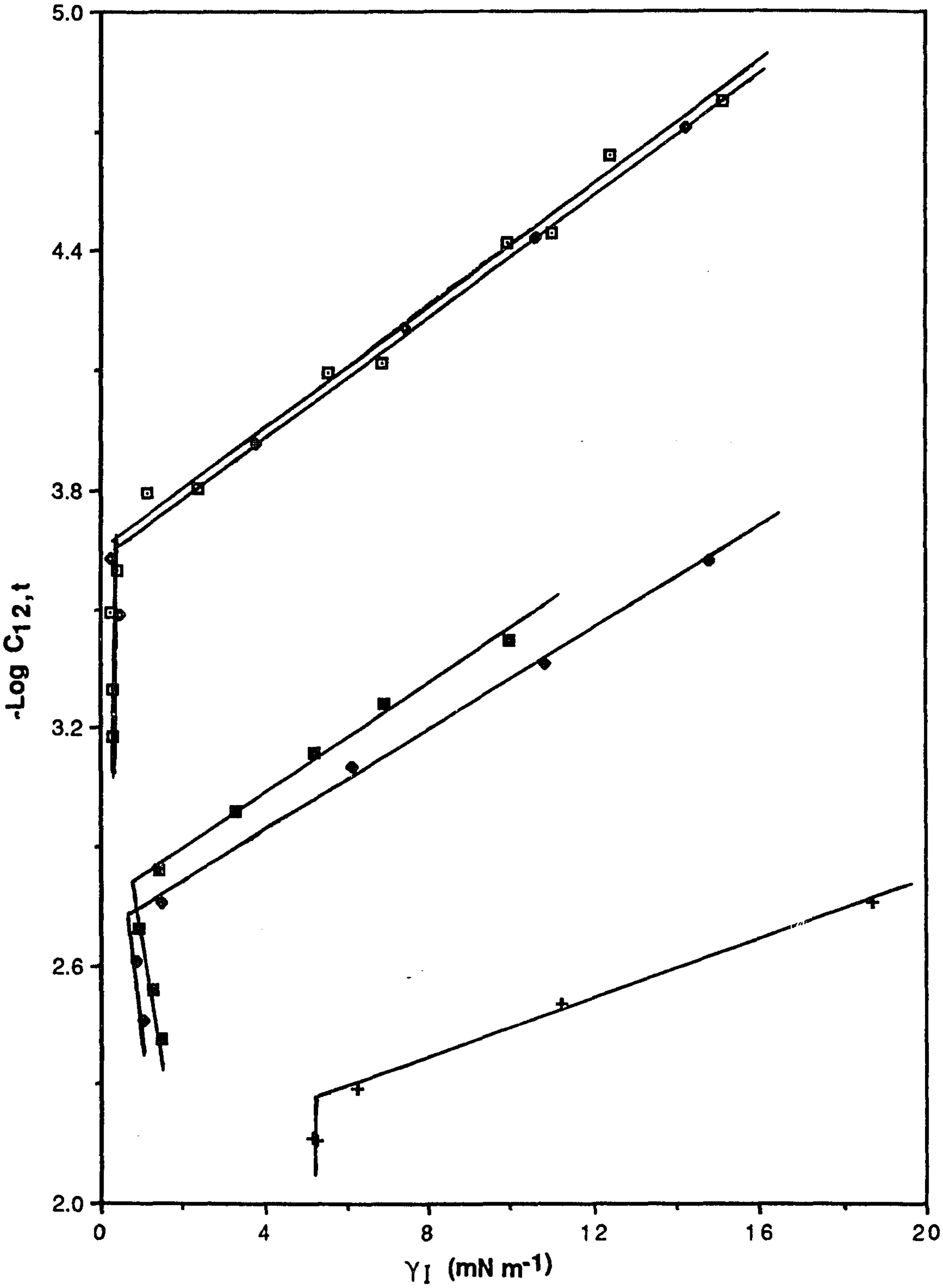

Figure B22. $C_{12}BMG$, $C_{12}S$, and their mixtures in toluene/H_2O systems at 25.0°C. α_{C12BMG}: (+), 0; (◆), 0.027$_7$; (■), 0.051$_6$; (◇), 0.94; (▣),1.

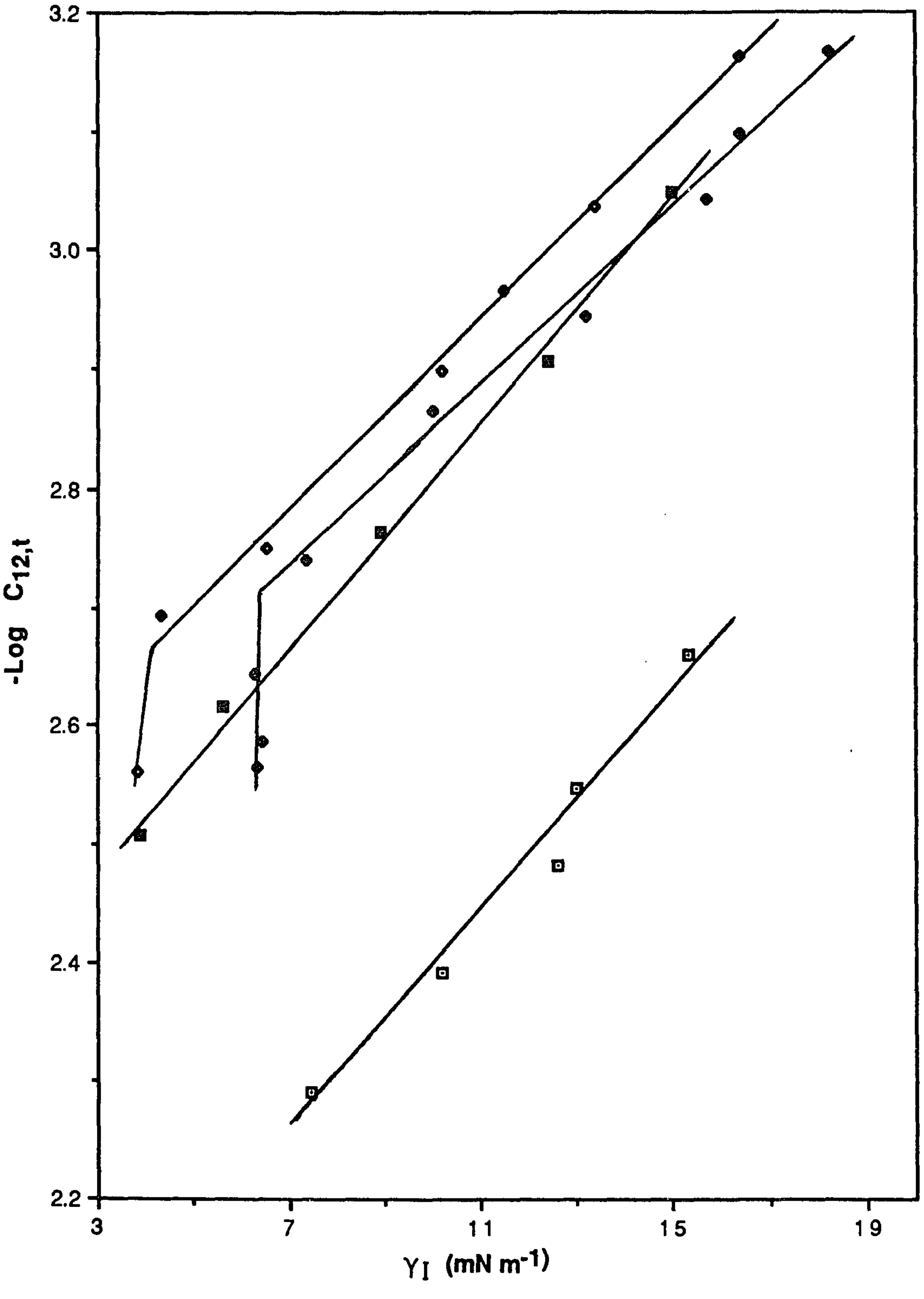

Figure B23. $C_{12}S$, C_8P and their mixtures in hexadecane/0.1M NaCl aqueous solution systems at 25.0°C. α_{C12S}: (▣), 0; (■), 0.27$_5$; (◇), 0.77$_1$; (◆),1.

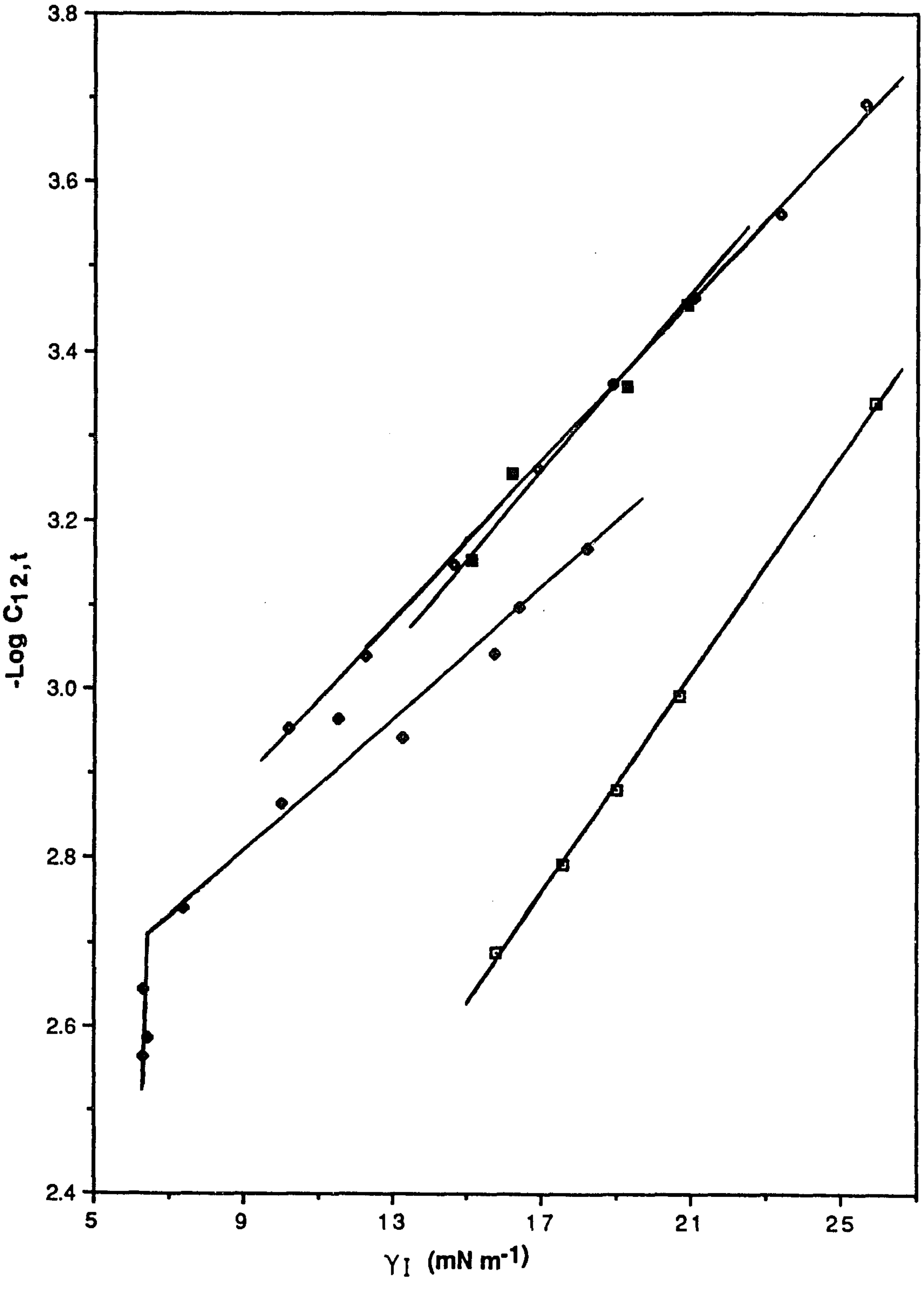

Figure B24. $C_{12}S$, $C_{10}P$ and their mixtures in hexadecane/0.1M NaCl aqueous solution systems at 25.0°C. α_{C12S}: (□), 0; (■), 0.41_6; (◈), 0.74_8; (◆),1.

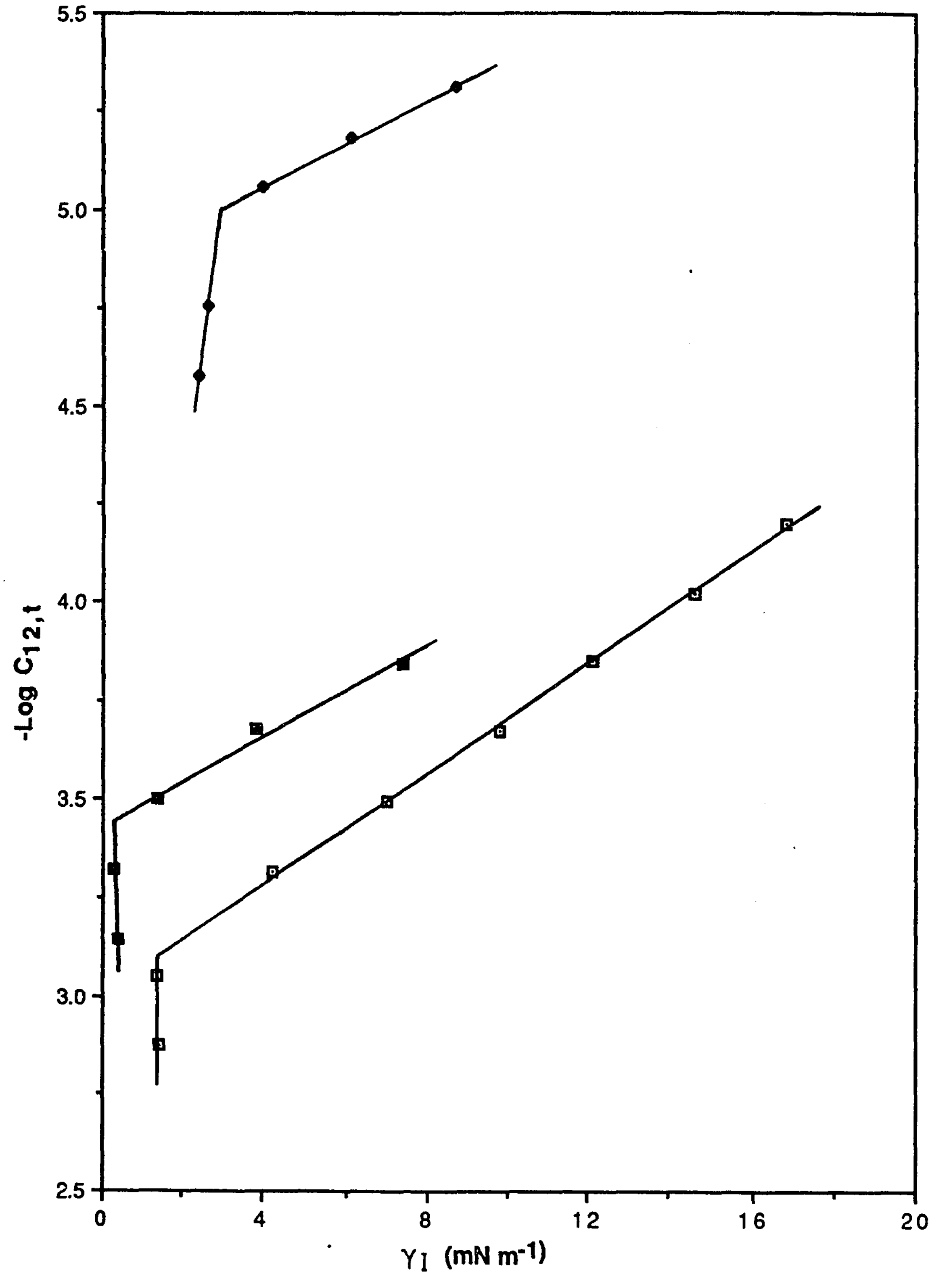

Figure B25. $C_{16}HGEO_5S$, $C_{16}HGEO_5S$, and a mixture of theirs in hexadecane/0.1M NaCl aqueous solution systems at 25.0°C. α C16HGEO5S: (□), 0; (■), 0.013_8; (◆),1.

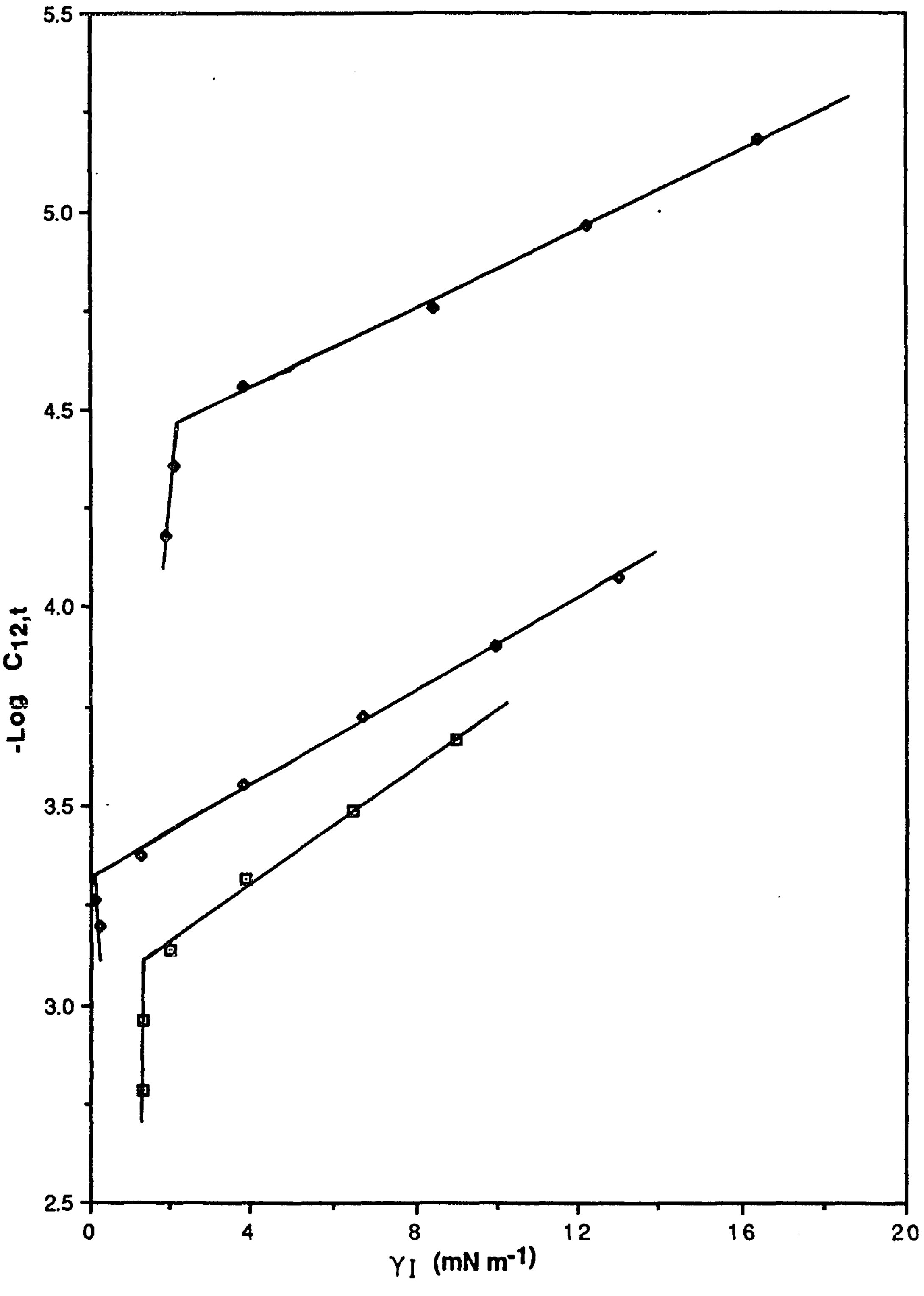

Figure B26. $C_{16}EGEO_5S$, $C_{16}EGEO_5S$, and a mixture of theirs in hexadecane/0.1M NaCl aqueous solution systems at 25.0°C. α C16EGEO5S: (◘), 0; (◈), 0.012g; (◆),1.

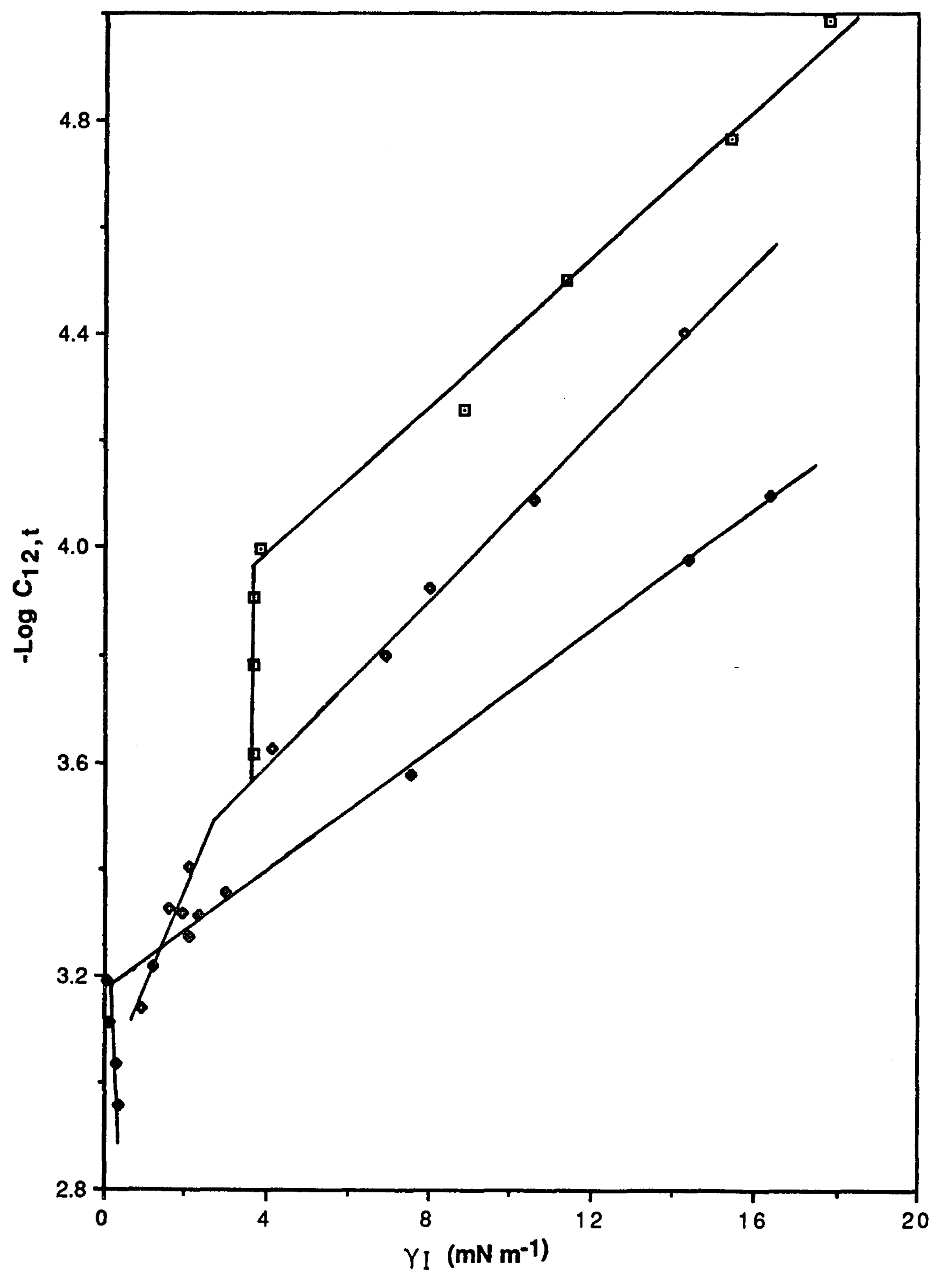

Figure B27. $C_{12}EO_8$, $C_{12}EO_4$, and a mixture of theirs in hexadecane/H_2O systems at 25.0°C. α C12EO8: (◆), 0; (◈), 0.25_5; (◘),1.

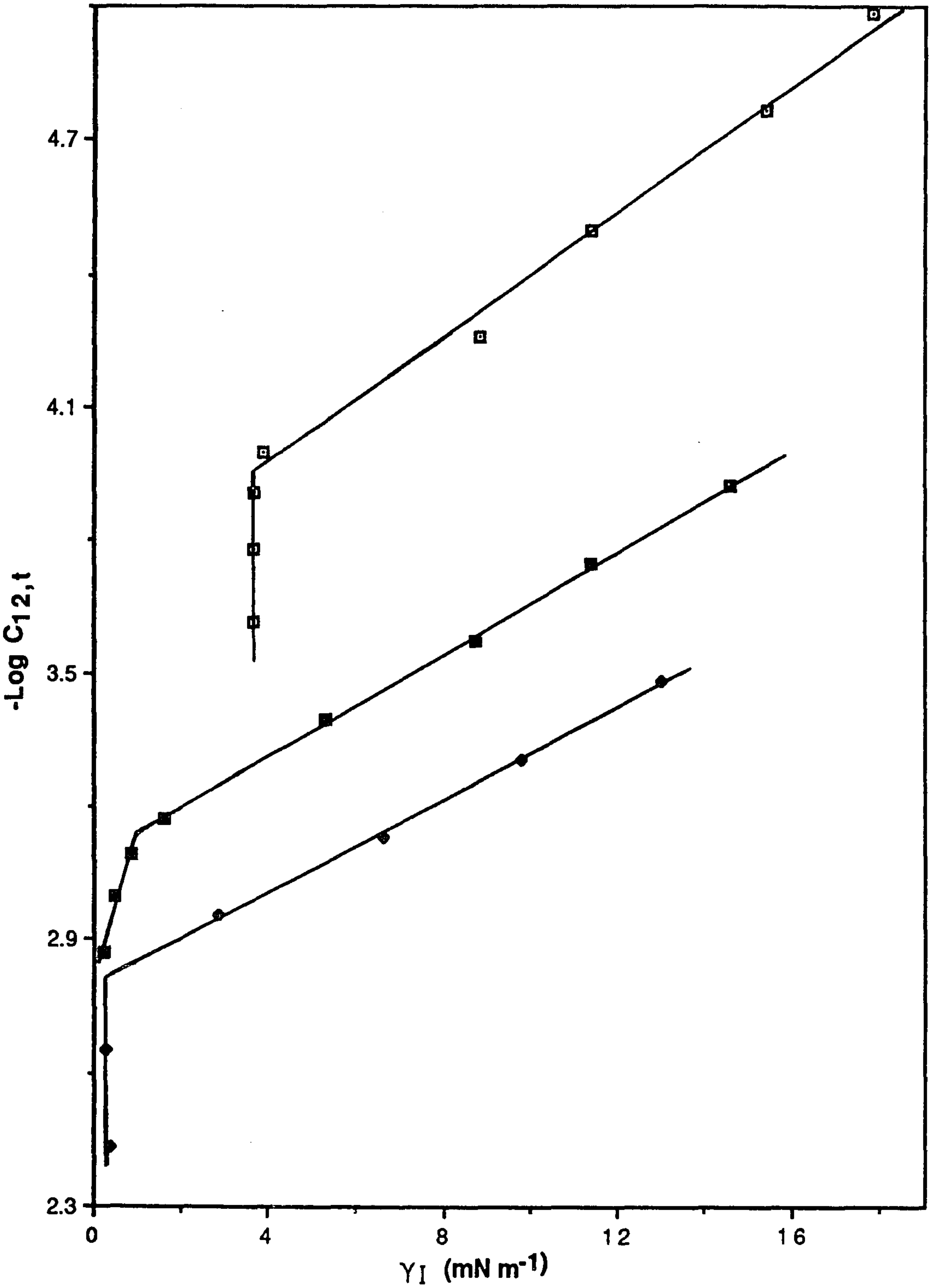

Figure B28. $C_{12}EO_8$, $C_{12}EO_3$, and a mixture of theirs in hexadecane/H_2O systems at 25.0°C. α $C_{12}EO_8$: (◆), 0; (■), 0.079_9; (▣),1.

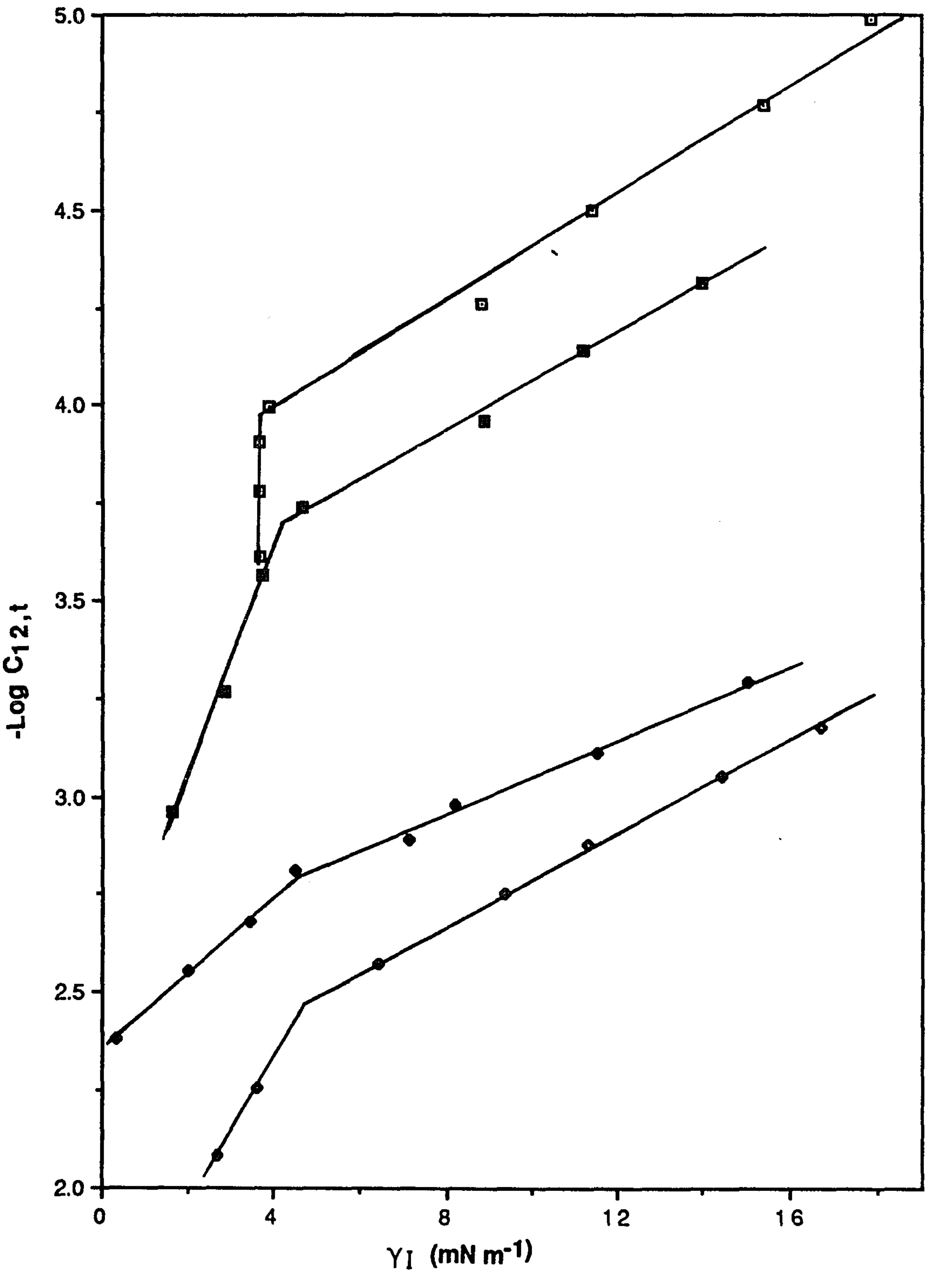

Figure B29. $C_{12}EO_8$, $C_{12}EO_2$, and their mixtures in hexadecane/H_2O systems at 25.0°C. α C12EO8: (◇), 0; (◆), $8.9_2 \times 10^{-3}$; (▣), 0.38_7; (◻),1.

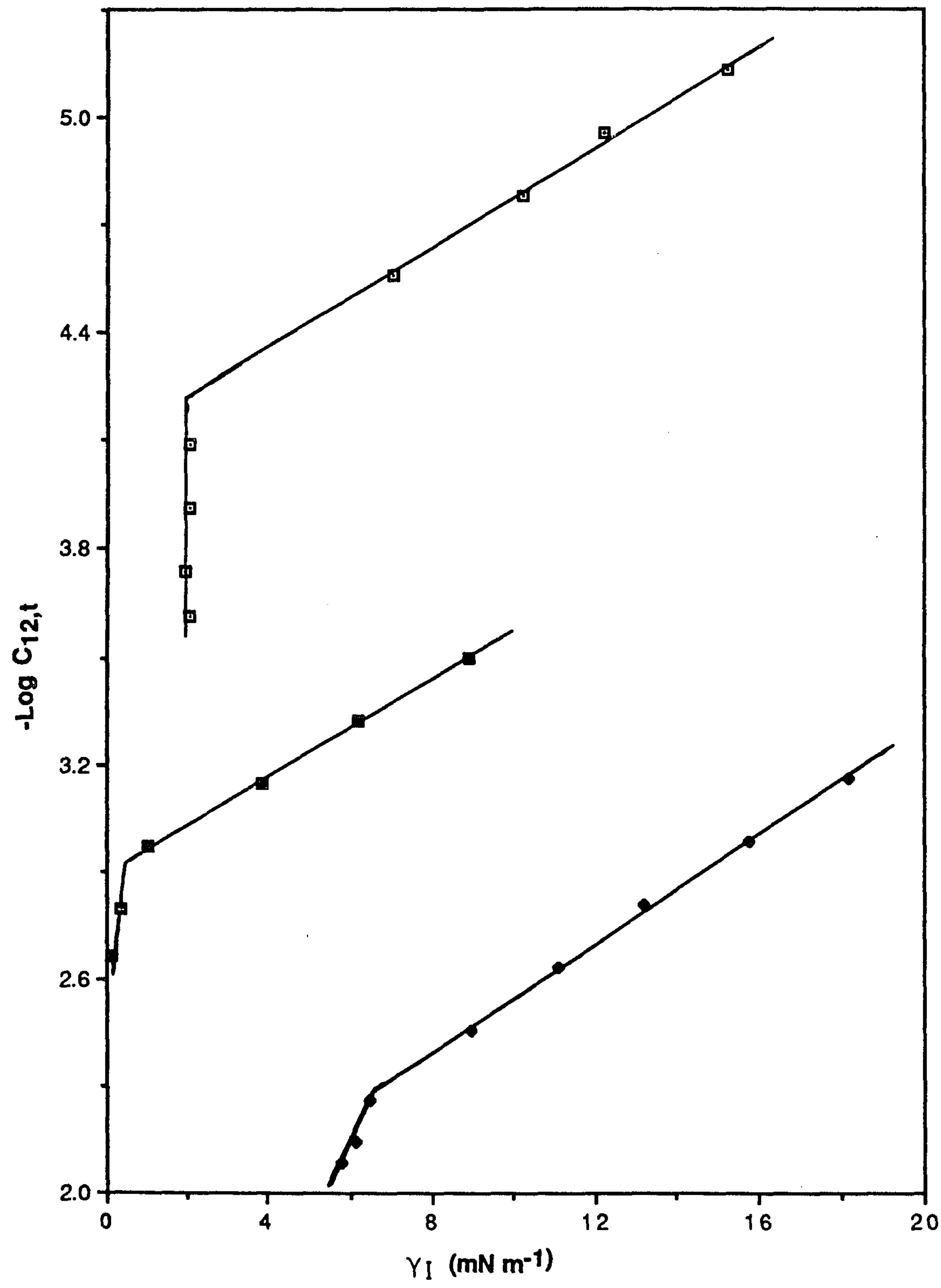

Figure B30. $C_{12}EO_8$, $C_{12}EO_2$, and a mixture of theirs in heptane/H_2O systems at 25.0°C. α C12EO8: (◆), 0; (▣), 0.046$_9$; (□),1.

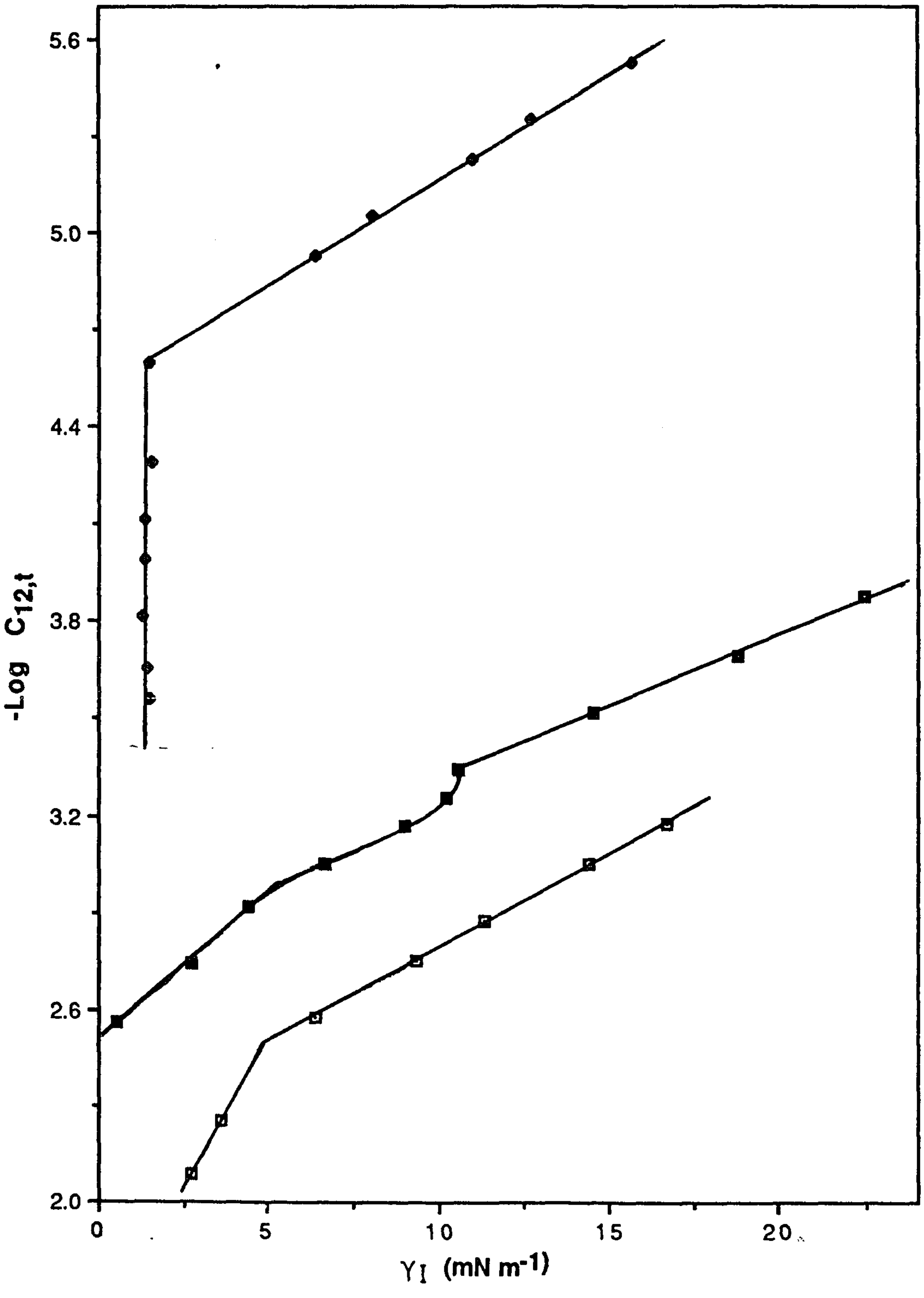

Figure B31. $C_{16}EO_8$, $C_{12}EO_2$, and a mixture of theirs in hexadecane/H_2O systems at 25.0°C. α C16EO8: (□), 0; (■), $6.5_8 \times 10^{-3}$; (◆),1.

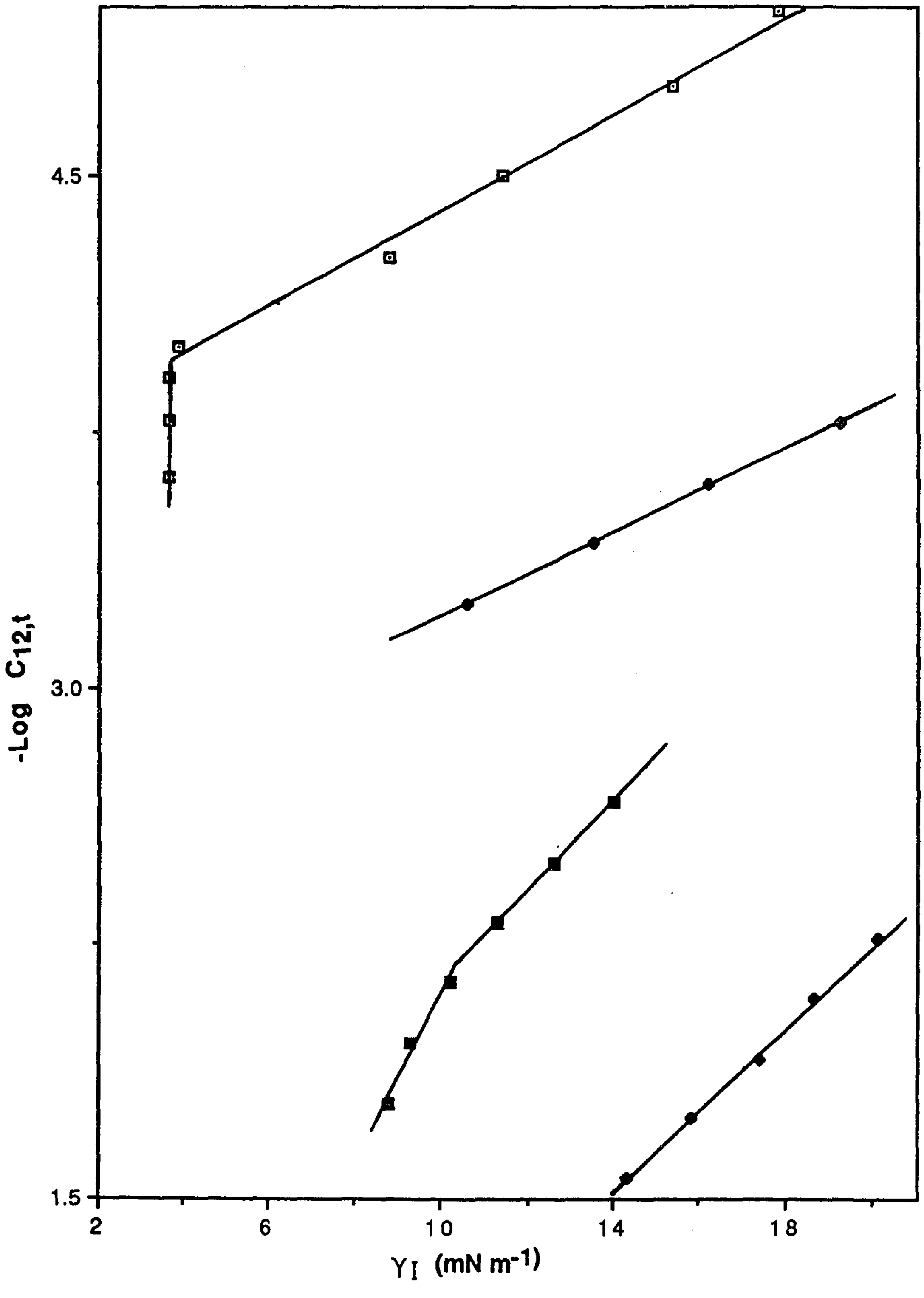

Figure B32. $C_{12}EO_8$, $C_{12}OH$, and their mixtures in hexadecane/H_2O systems at 25.0°C. α C12EO8: (◆), 0; (■), $2.0_2 \times 10^{-3}$; (◈), 0.035_3; (▣),1.

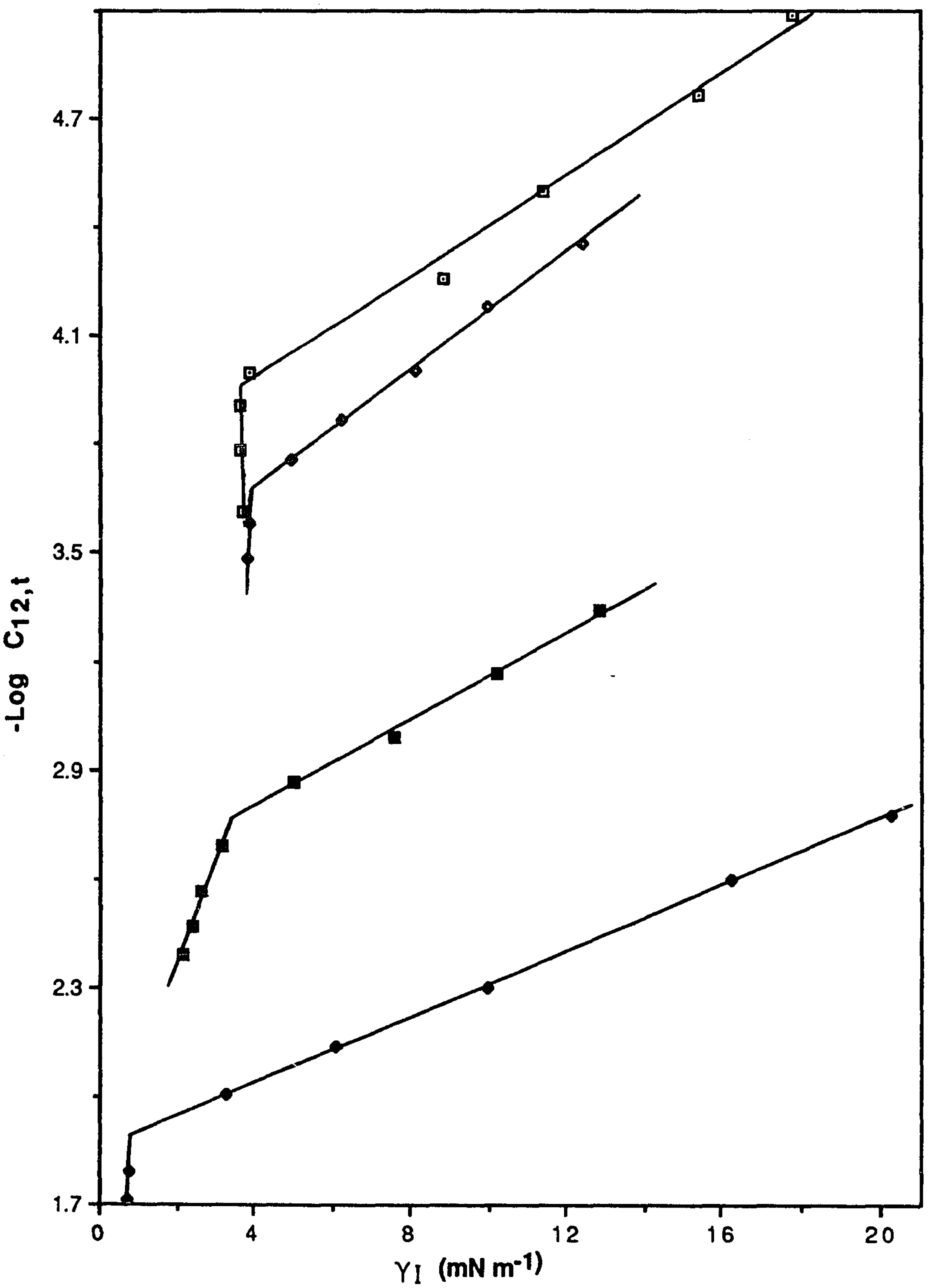

Figure B33. $C_{12}EO_8$, C_8P, and their mixtures in hexadecane/H_2O systems at 25.0°C. α C12EO8: (◆), 0; (■), 0.042_8; (◇), 0.52_3; (▣),1.

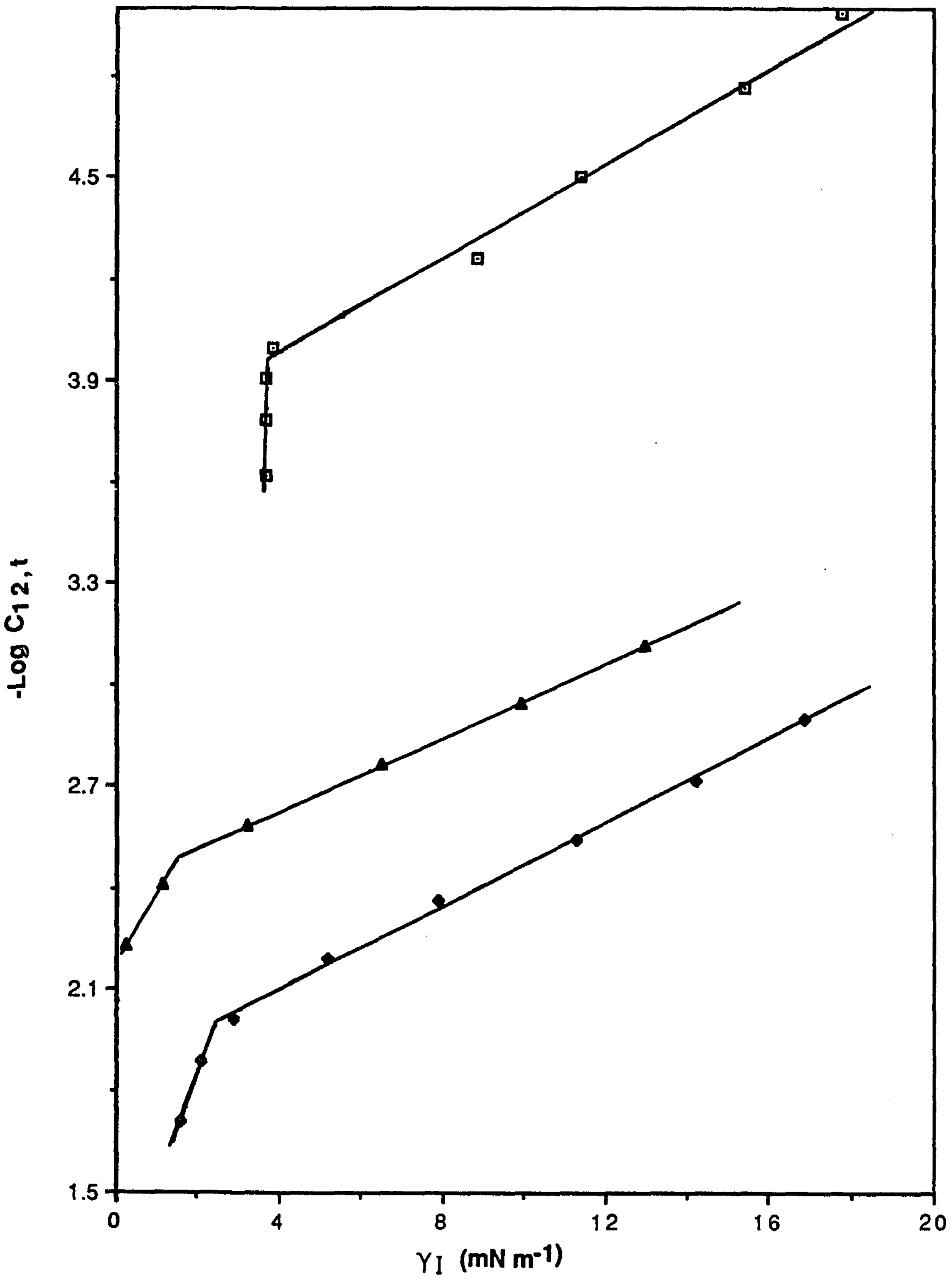

Figure B34. $C_{12}EO_8$, $C_{12}P$, and a mixture of theirs in hexadecane/H_2O systems at 25.0°C. α C12EO8: (◆), 0; (▲), 0.013_6; (▣),1.

APPENDIX C

SYMBOLS

A_{min}	minimum area per surfactant molecule at an interface;
α_1	mole fraction of surfactant 1 in the total surfactant in the entire system;
α^{*}_{1}	α_1 value at the minimum or maximum in the $C_{12,t}$ vs α_1 curve;
$\alpha^{*,M}_{1}$	α_1 value at the minimum or maximum in the $CMC_{12,t}$ vs α_1 curve;
$\alpha^{*,E}_{1}$	α_1 value at the minimum or maximum in the $\gamma_{CMC,12,t}$ vs α_1 curve;
$\beta^{\sigma}_{LL}, \beta^{M}_{LL}$	the molecular interaction parameters for mixed monolayer formation at the liquid-liquid interface, and in the mixed micelle, respectively;
C_W	molar concentration of surfactant in the aqueous phase;
C_t	molar concentration of surfactant in the entire system;
$C_{12,t}$	the total molar concentration of surfactant 1 and 2 combined, in the mixed surfactant system, at a given α_1 and interfacial tension;
$C^{0}_{1,t}, C^{0}_{2,t}$	the molar concentrations of individual surfactants 1, and 2, respectively, at the same interfacial tension as the mixture;

$C^{0,CMC}_{1,t}$, $C^{0,CMC}_{2,t}$	molar concentrations of individual surfactants 1 and 2, respectively, required to yield an interfacial tension equal to $\gamma_{CMC,12,t}$ of any mixture;
$C_{12,t,min}$	$C_{12,t}$ value at the minimum or maximum in the $C_{12,t}$ vs α_1 curve;
cmc_w	molar concentration of surfactant in the aqueous phase at the point of intersection of the two almost linear portions of the interfacial tension vs log aqueous phase concentration curve;
cmc_t	molar concentration of surfactant in the entire system at the point of intersection of the two almost linear portions of the interfacial tension vs log total (i.e., in the entire system) concentration curve;
$CMC_{12,t}$	the cmc_t value for surfactants 1 and 2 combined, in the mixed surfactant system, at a particular α_1 value;
$CMC^0_{1,t}$, $CMC^0_{2,t}$	cmc_t values of individual surfactants 1 and 2, respectively;
$CMC_{12,t,min}$	$CMC_{12,t}$ value at the minimum or maximum in the $CMC_{12,t}$ vs α_1 curve;
$CMC^*_{12,t}$	$CMC_{12,t}$ value corresponding to the α_1 value at the minimum or maximum in the $\gamma_{CMC,12,t}$ vs α_1 curve;
ΔG°_{ads}, ΔG°_{mic}	standard free energy of adsorption and micellization, respectively, for a given surfactant;
ΔH°_{ads}, ΔH°_{mic}	standard enthalpy of adsorption and micellization, respectively, for a given surfactant;
ΔS°_{ads}, ΔS°_{mic}	standard entropy of adsorption and micellization, respectively, for a given surfactant;

φ	ratio of the volume of the oil phase to the water phase in the mixed surfactant system;
φ^0_1, φ^0_2	φ values for systems containing individual surfactants 1 and 2, respectively;
Γ_{max}	maximum interfacial excess concentration attainable for a given surfactant;
γ_{min}	minimum interfacial tension attainable for a given surfactant;
$\gamma^0_{CMC,1,t}$, $\gamma^0_{CMC,2,t}$	interfacial tension values at their cmc$_t$'s of individual surfactants 1 and 2, respectively;
$\gamma_{CMC,12,t}$	interfacial tension of mixed surfactants 1 and 2, at a given α_1, at the cmc;
$\gamma^*_{CMC,12,t}$	$\gamma_{CMC,12,t}$ value at the minimum or maximum in the $\gamma_{CMC,12,t}$ vs α_1 curve;
K^0_1, K_1	partition coefficient (concentration in the oil phase/concentration in the aqueous phase) of individual surfactant 1, and of surfactant 1 in its mixture with surfactant 2 at a given α_1 value, respectively;
K^0_2, K_2	partition coefficient (concentration in the oil phase/concentration in the aqueous phase) of individual surfactant 2, and of surfactant 2 in its mixture with surfactant 1 at a given α_1 value, respectively;
Π_{max}	maximum interfacial pressure attainable for a given surfactant;
$pC_{30,W}$	- Log $C_{30,W}$, where $C_{30,W}$ is the molar concentration of a given surfactant necessary to produce $\Pi = 30$ mN m^{-1};
S_1, S_2	slopes of the γ vs ln C^0_t plots of individual surfactants 1 and 2, respectively;

X_1, X^M_1	mole fraction of surfactant 1 in the total surfactant at the liquid-liquid interface, and in the micelle, respectively;
X^*_1	mole fraction of surfactant 1 in the total surfactant at the liquid-liquid interface corresponding to the minimum or maximum in the $\gamma_{CMC,12,t}$ vs α_1 curve.

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