Binary Mixture of Monostearin-Distearin Monolayers at the Air—Water Interface

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The study of mixed films has become of considerable interest both from theoretical and practical points of view. The π-A isotherms of monostearin-distearin (about 50% 1,3- and 50% 1,2-isomers) mixed films spread on water as a function of emulsifier ratio and temperature were studied in an automated Langmuir-type film balance. When molecules of both emulsifiers are spread on the air–water interface they are packed more closely together than when either emulsifier is present alone, and they enter into some form of association. This association can be demonstrated by surface pressure-area isotherms and by thermodynamic studies. The characteristics of the mixed films, their elasticity and miscibility, which are of interest in emulsion or foam stability, are discussed. A molecular model established can explain the interactions between film and subphase molecules and their relationships with variables of the process (pressure and temperature). This model fits the calculated thermodynamic parameters.

Introduction

Many real food systems are complex dispersions such as foams and emulsions. These dispersions are inherently unstable systems because of their large interfacial area. Stability is one of the most important properties of such dispersions. Two types of molecules add stability to the system due to a strong tendency to accumulate at the oil–water and air–water interfaces: protein and low-molecular-weight emulsifiers (Cavallo et al., 1990; Dickinson, 1989; Dickinson and Stainsby, 1987; Halling, 1981; Krog et al., 1985), which are essentially mono- and diglycerides (Als and Krog, 1991; Charalambous and Doxastakis, 1989; Larsson and Friberg, 1990; Leadbetter, 1990). Emulsifier-based foods such as margarine, spreads, ice cream, imitative dairy products, and cereal-based foods—such as bread, cakes, and other bakery products—either as traditional foods (Charalambous and Doxastakis, 1989; Krog et al., 1985; Leadbetter, 1990) or low-fat products and instant foods (Dickinson, 1993; Dickinson and Stainsby, 1987) are some examples of food systems in which mono- and diglycerides are added as emulsifiers.

In the study of model food systems the characteristics of the emulsifier monolayers at the air–water interface are of great interest. The use of the monolayer as a food model presents several advantages. On one hand, relationships be-

tween structural characteristics of the emulsifier film on the air–water interface and emulsion and foam stability have been established (Krog et al., 1985; Larsson, 1973, 1978), as well as between condensed film formation and emulsifier association in the bulk phase (Albrecht et al., 1978; Krog et al., 1985; Lundquist, 1978). On the other hand, intermolecular interactions at the interface lead to alterations in surface properties which have measurable rheological consequences (Buhaenko et al., 1988; Chen et al., 1993; Djabbarah and Wasan, 1982, 1985; German et al., 1985; Kim and Kinsella, 1985). So, for a fundamental understanding of the role of emulsifiers in the stabilization of food dispersions it is essential to obtain information on their packing at the interfaces. These are the reasons why the study of mixed films has become of considerable interest both from the theoretical and practical points of view.

Several workers have reported that a mixture of two or more emulsifiers will produce a more stable emulsion than will any of the single-component emulsifiers (Kako and Kondo, 1979). This stability is improved still further by incorporating protein in both mono- and diglycerides (Doxastakis and Sherman, 1983, 1984; Rahman and Sherman, 1982; Reeve and Sherman, 1988). Interactions between proteins and lipids have been reported for model food systems in solutions or in emulsions (Coke et al., 1990; Dickinson, 1992; Dickinson et al., 1989; Wilde and Clark, 1993), but little is known about

about the film characteristics (structure and stability). Understanding how the different components of colloidal systems interact and how they behave under differing environmental conditions is of scientific and technical interest (Kinsella and Whitehead, 1989; McClements et al., 1993). This type of information is crucial for the development of new colloidal foods and the improvement of the existing products. Consequently, a substantial amount of basic research has been carried out to identify the various factors that influence the physicochemical properties of dispersed systems.

The aim of this work was to obtain information on the nature of the interactions at the air–water interface between molecules of mono- and diglycerides as a function of the emulsifier ratio, temperature, and surface pressure. Interactions and film structural characteristics were determined by spreading the emulsifier mixture—to obtain a monolayer—on water, using a film balance. The thermodynamic parameters of the mixed monolayers confirm the existence of these interactions.

Mixed Monolayer Interactions

Miscibility and stability of a mixed monolayer

The interactions between monolayer components in a mixed monolayer can be studied from two points of view: miscibility and stability. The study of $\pi - A$ isotherms allows one to establish both characteristics. The linear plot of the mean molecular area as a function of the molar ratio in mixed monolayers adhered to the additivity rule, indicating that ideal mixing of the two components takes place. If there are not significant variations between the mean molecular area and the values predicted by the ideal mixtures, it can be considered that only small perturbations in molecular parameters of film-forming components occur. Such ideal behavior results either from a homogeneous surface mixture of noninteracting molecules or from an interface formed by immiscible components (Gaines, 1966).

It should be possible to distinguish between these events (Figure 1) by analyzing the $\pi - A$ isotherms at high surface pressures on the basis of the surface phase rule (Defay, 1966). When two film-forming components are immiscible, the mixed monolayers collapse at the same surface pressure, regardless of composition. The component of the mixed film that has a

lower equilibrium pressure is squeezed out of the monolayer at a surface pressure that corresponds to its pure monolayer pressure (Gaines, 1966). A relationship between the collapse pressure and the molecular interactions in a mixed monolayer has been suggested, a higher collapse pressure being taken to indicate stronger interactions than an ideal mixture.

When the components are completely miscible, the collapse pressure of the mixed monolayer follows Eq. 1 (Joos, 1969):

$$1 = x_1\gamma_1\exp\left(\frac{\pi_c^M - \pi_c^1}{kT}A_c^1\right) + x_2\gamma_2\exp\left(\frac{\pi_c^M - \pi_c^2}{kT}A_c^2\right), \quad (1)$$

where x_i is the molar fraction of each component in the mixed monolayer, A_c^i and π_c^i are the molecular area and the collapse pressure at the collapse point of reach component, π_c^M is the collapse pressure of the mixed monolayer, k is the Boltzmann constant, and γ_i is the coefficient of surface activity in the collapse point. If there is no interaction between components, $\gamma_1 = \gamma_2 = 1$ and calculated π_c^M correspond to the collapse pressure of the mixed monolayer without interactions.

If the collapse pressures of the pure components are close, Eq. 1 can be expressed by Eq. 2 (Joos and Demel, 1969):

$$\pi_c^M = x_1 \cdot \pi_c^1 + x_2 \cdot \pi_c^2. \quad (2)$$

A comparison between the collapse pressure value of a mixed monolayer and those calculated by Eqs. 1 and 2 can give information about the interactions between film-forming components. So, if the collapse pressure of a mixed film is higher than that of the pure components, a strong interaction between those components exists.

On the other hand, a plot of mean molecular area against the molar ratio of a component in the mixed monolayer that is not linear overall, but does contain a linear segment (Figure 1), can be an indication that the components are only partially miscible (Phillips et al., 1975).

The area of a two-component monolayer (A_M) can be compared to that of the unmixed components at the same surface pressure and temperature to give the excess area of mixing (A_{exc}), Eq. 3:

$$A_{exc} = A_M - (x_1 \cdot A_1 + x_2 \cdot A_2). \quad (3)$$

If the surface solution is ideal, or if the two components are immiscible, the excess area will be zero. Deviation from this value indicates miscibility and nonideality, or, at least, that the film-forming components are partially miscible (Bacon and Barnes, 1978). Positive deviations indicate that one or both components occupy a larger area per molecule than that on its pure component film, while negative deviations are indicative of reduced area or condensation (Cadenhead and Müller-Landau, 1980), both effects being due to a geometric factor or hydrophobic interactions.

Thermodynamics of a mixed monolayer

An alternative approach to characterizing the interactions that occur in mixed monolayers is derived from the equation
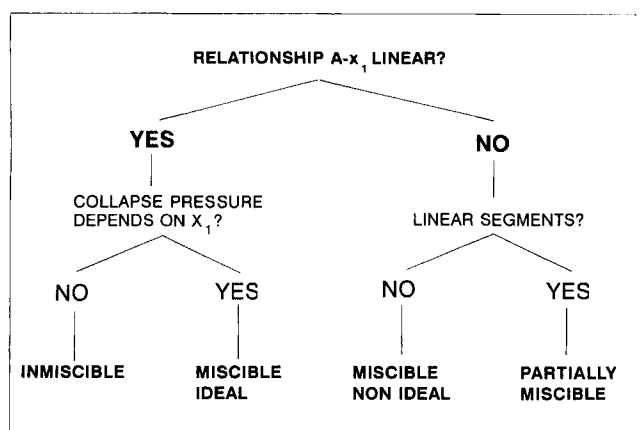

Figure 1. Miscibility of mixed monolayers.

developed by Goodrich (1956) and Pagano and Gershfeld (1972). The excess free energy of mixing can be evaluated and treated as an indication of interactions. The thermodynamic properties of the mixtures can be treated quite simply by the method suggested by Goodrich (1956). The application of the method assumes that no chemical reaction takes place in the process. So, at low surface pressures the free energy of mixing can be calculated by a statistical expression, independently of the nature and structural characteristics of the components.

For a process of mixing, the value of the free energy of mixing (ΔG_M^π) is the sum of the excess free energy (ΔG^{exc}) and the ideal free energy (ΔG^{id}) (Eq. 4), where the expression of each is determined by Eqs. 5 and 6:

$$\Delta G_M^\pi = \Delta G^{exc} + \Delta G^{id} \tag{4}$$

$$\Delta G^{exc} = \int_{\pi \to 0}^{\pi} A_{exc} d\pi \tag{5}$$

$$\Delta G^{id} = RT(x_1 \ln x_1 + x_2 \ln x_2). \tag{6}$$

Goodrich applied his method to the gaseous state of the monolayer. Later Gershfeld (1974) demonstrated that differences exist between the values obtained in the condensed state and those from applying Goodrich's method. However, information about the behavior of the mixed monolayers is obtained by applying the Goodrich assumption independently of the physical state of the monolayer, as shown in most of the works listed in the bibliography. These results give information about miscibility and interactions between monolayer components (Kulkarni and Katti, 1982).

Negative values of ΔG_M^π indicate that the mixed monolayer is more stable than the pure components alone. The negative sign of ΔG^{exc} is considered as a criterium of stability (Alsina et al., 1991; Levy et al., 1991; Tomoaia-Cotisel and Chifu, 1983). However, positive values of ΔG^{exc} could suggest the possibility of a phase separation in the monolayers. The total free energy of mixing (ΔG_M^π) has to be calculated in order to examine this question following Eq. 4, and to obtain data about mixed monolayer stability. If the total energy is negative, this means that the two-dimensional state is more stable, thermodynamically, than the corresponding unmixed state (Costin and Barnes, 1975).

From the values of ΔG^{exc} the value of the interaction parameter [$\alpha(\pi)$] can be calculated following Eq. 7, corresponding to different surface pressures, and the interaction energy (Δh) by Eq. 8 (Joos and Demel, 1969; Mestres et al., 1992):

$$\alpha = \frac{\Delta G^{exc}}{RT(x_1 x_2^2 + x_2 x_1^2)} \tag{7}$$

$$\Delta h = \frac{RT\alpha}{Z}, \tag{8}$$

where Z is the coordination number, which can be obtained following the Quikendem and Tan model (Quikendem and Tan, 1974).

Materials and Method

Film balance

The compression isotherms (film pressure, π, vs. average area per molecule, A) were established on a fully automated Langmuir-type film balance (Lauda). The sensitivity of the film pressure is ± 0.1 mN·m^{-1} and the sensitivity of the area measurement is ± 0.005 nm^2·molecule^{-1}. The temperature of the system formed by the spread film and the subphase (adjacent bulk water) was maintained constant within $\pm 0.03°$C by a Lauda K2R electronic thermostat. Other specifications of the film balance have been described elsewhere (Rodríguez Patino et al., 1992, 1993).

Chemicals

Monostearin (1-monooctadecanoyl-rac-glycerol) and distearin (dioctadecanoylglycerol, approximately 50% 1,3- and 50% 1,2-isomers) of purity greater than 99% were acquired from Sigma. Analytical grade ethanol and hexane were acquired from Merck and used without further purification. The water used as subphase was purified by means of a Millipore filtration device (Milli-Q). The absence of surface-active contaminants in water and in the hexane–ethanol mixture (9:1, v/v) used as the spreading solvent was verified.

Procedure

Monostearin and distearin were dissolved in the spreading solvent. Mixtures of particular molar ratios—ranging between 0 and 1, expressed as the molar fraction of monostearin in the mixture, x_M—were prepared from these stock solutions. Before each measurement, the film balance was calibrated at 20°C. The lipid solutions were spread on the aqueous substrate over the maximum available area by means of a micrometric syringe and allowed to evaporate for 15 min before being compressed at a constant rate of 6.2·10^{-2} nm^2·molecule^{-1}·min^{-1}. This value was such that the isotherms obtained from previous experiments with monoglyceride–water systems are practically coincident (Rodríguez Patino et al., 1992; Rodríguez Patino and Ruíz Domínguez, 1993). The experiments were carried out at temperatures ranging between 5 and 40°C. All isotherms were recorded and then analyzed off-line. Each isotherm consisted of data records of surface pressure (mN·m^{-1}) and barrier position, automatically corrected for the number of spread molecules using a built-in analog correcting device of the Lauda filmbalance (nm^2·molecule^{-1}).

Results

Monolayer structural characteristics

Monolayer structural characteristics can be obtained from $\pi - A$ isotherms by a procedure following Gaines (1966). The $\pi - A$ isotherms for monostearin and distearin mixtures ranging between 0 and 1 in molar fraction, at 20 and 30°C are shown in Figures 2 and 3, respectively. It can be seen that the monolayer states are limited to two different structures, liquid-condensed and liquid-expanded, no matter what the temperature is. The existence of a plateau—corresponding to the transition between both structures— is more evident in pure distearin monolayers. At 20 and 30°C the transition between
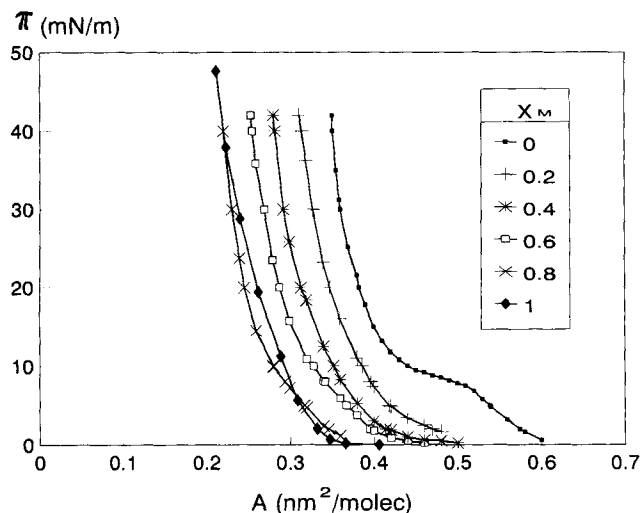
Figure 2. Surface pressure–area isotherms (compression curves) of monostearin and distearin and their mixtures on a pure water subphase at 20°C.

both structures starts at values of surface pressure of 8 and 6 mN·m⁻¹, respectively. We note, however, that the phase change does not occur at constant surface pressure. The π – A isotherms in the region of liquid-condensed to liquid-expanded transition has a small, finite slope that increases markedly at the highest temperature. This is in contrast to the behavior of a first-order phase change that occurs at constant pressure. The change of phases degenerates when the amount of monostearin in the mixture increases. So, when the content of monostearin in the mixture is more than 0.2, the plateau corresponding to the transition between liquid-condensed and liquid-expanded structures is not observed.

It can be observed that, independent of the molecular structure in the monolayer, when the temperature increases,
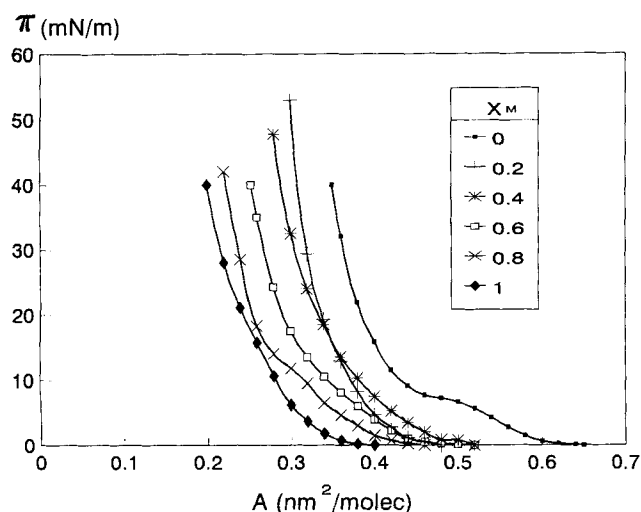

Figure 3. Surface pressure–area isotherms (compression curves) of monostearin and distearin and their mixtures on a pure water subphase at 30°C.
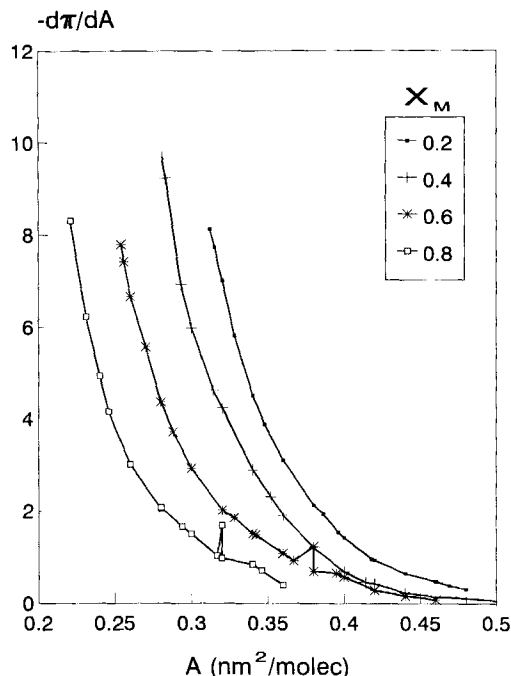

Figure 4. Elasticity modulus vs. area of monostearin-distearin mixed monolayers on a pure subphase at 20°C.

the monolayer is expanded. However, the amount of monostearin in the monolayer composition produces the opposite effect. There is a contraction of the isotherms—the isotherms are displaced toward the pressure axis—when the monostearin content in the mixture increases. Moreover, the magnitude of the displacement is not a linear function of the film composition. These results may be due to interactions between monostearin and distearin molecules at interface. This point will be discussed later.

The rheological properties of the film give a complementary description of the monolayer characteristics. The most relevant factors for film and bubble stability are the elasticity ($-A \cdot d\pi/dA$) and the dynamic dilatational modulus or elasticity modulus ($-d\pi/dA$) (German et al., 1985, 1990; Graham and Phillips, 1980; Kim and Kinsella, 1985; McRitchie, 1986). These are measured as the change in surface pressure as a function of change in surface area. A relationship between elasticity modulus of the film and its structure can be calculated directly from the slope of the $\pi - A$ isotherms in Figures 2 and 3. Figure 4 shows elasticity modulus vs. area for monostearin-distearin mixtures on water at 20°C. It can be seen that with the same structure, and at the same area, the monolayers with a higher content of monostearin are less rigid—have a lower value of the elasticity modulus. This behavior is due to a displacement of the isotherms toward the π-axis when the monostearin content in the mixture increases. That is, the molecular packing at the interface is more compact in the monostearin-rich zone. So, the development of intermolecular associations at the interface leads to alterations in surface properties that have measurable rheological consequences, as can be seen from the values of the elasticity modulus. The binary mixtures of monostearin and distearin
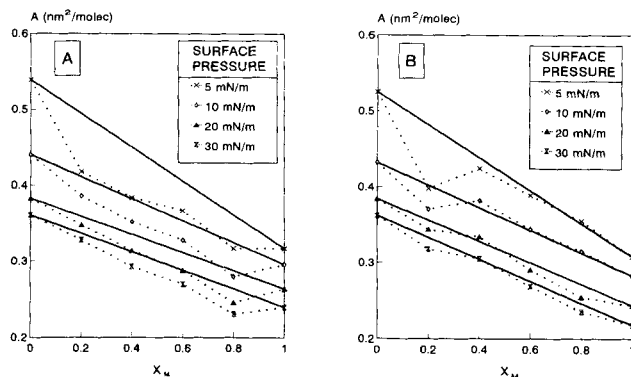
Figure 5. Area additivity relationships showing deviation from the ideal with varying monolayer composition and surface pressure for monostearin–distearin mixed films on pure water subphase at 20°C (A) and at 30°C (B).

Dashed lines represent the ideal area additivity case.

monolayers on water at 30°C behave in a similar way (data not shown).

Monolayer miscibility

The miscibility between the monolayer components can be studied by comparing the molecular area—at a fixed surface pressure—with the mean area. Figure 5 shows the molecular area as a function of the monostearin composition in the mixture at 20 and 30°C.

The deviations between molecular area and mean area—especially at 20°C and at the lower surface pressures—can be due to geometric factors (the molecules of one of the two components in the mixture must occupy the space between the other molecules) or to the existence of interactions between the monolayer components at interface. So, the monolayer miscibility will be not ideal (Cadenhead and Müller-Landau, 1980; Costin and Barnes, 1975; Gabrielli and Baglioni, 1980). These interactions could be of a hydrophobic character between monolayer molecules (Cadenhead and Müller-Landau, 1980; Tomoaia-Cotisel and Chifu, 1983).

At 30°C (Figure 5B), except when the molar ratio of monostearin in the mixture is 0.2, the molecular and mean area are practically the same. The fulfillment of the additivity rule indicates that either the components in the mixture are completely immiscible or ideally miscible (Figure 1). To distinguish between both of these behaviors and to study the existence and magnitude of interactions between monolayer components, it is useful to establish the dependence of the mixture composition on the collapse pressure.

Figure 6 shows the effect of the monolayer composition on experimental (points) and calculated—by Eq. 1 (discontinuous line and Eq. 2 (continuous line)—collapse pressures. Significant deviations can be observed between experimental and calculated data. These deviations can be due to the existence of two immiscible phases at interface. In this case, the collapse pressure of mixed monolayers must be similar to that of the component with lowest collapse pressure (Tomoaia-Cotisel et al., 1985), since the degree of freedom in the system is zero following the rule phase of Defay and Crisp (De-

fay et al., 1966). That is, the component with the lowest equilibrium surface pressure—in this study monostearin (Rodríguez Patino and Martín Martínez, 1994)—will be excluded from the monolayer at the collapse pressure (Gaines, 1966), which will coincide with the monolayer collapse pressure of the mixture.

The relative molecular area deviations (Figure 5) as well as the relationship between the collapse pressure (Figure 6) and the composition of the monolayer show that the monolayer components at the air–water interface are compatible. So, the condensation effect, which can be seen in $\pi - A$ isotherms (Figures 2 and 3) and in Figure 5, should be interpreted along the lines of either molecular packing or molecular interactions. Whatever the cause, one can conclude that no ideal miscibility between monolayer components exists, because of the intermolecular associations between the components at the interface, especially at 20°C. At 30°C and at the higher concentrations of monostearin in the mixture ($x_M \geq 0.4$), the monolayer components could be present as two immiscible phases. This behavior agrees with either the additivity rule (Figure 5) or with collapse pressure-mixture composition variation (Figure 6). A more definitive conclusion about the miscibility of the monolayer components can be drawn from the negative values of the change of the Gibbs free energy of mixing.

Thermodynamic parameters

The excess free energy of the mixing was calculated according to the Goodrich method (Goodrich, 1956), Eq. 5. For this calculation, the function $A_{exc} = f(\pi)$ was integrated analytically after a polynomial equation obtained for the $A_{exc} - \pi$ relationship (Eq. 9):

$$A_{exc} = a + b \cdot \pi + c \cdot \pi^2 + d \cdot \pi^3 + e \cdot \pi^4 \qquad (9)$$

where a, b, c, d, and e are the regression coefficients. The linear regression coefficient was better than 0.95 in all cases. The deviations between the experimental points—deduced from the $\pi - A$ isotherms (Figures 2 and 3)—and the values of the A_{exc} calculated by Eq. 9 (continuous line) is shown in Figure 7. From the data in the figure it can be deduced that
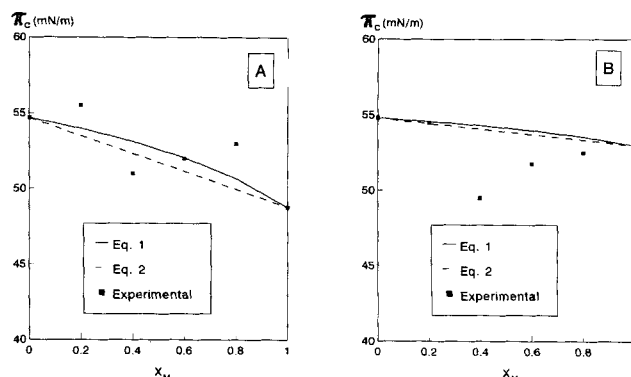

Figure 6. Collapse pressure vs. surface composition for monostearin–distearin mixed monolayers on pure water subphase at 20°C (A) and at 30°C (B).
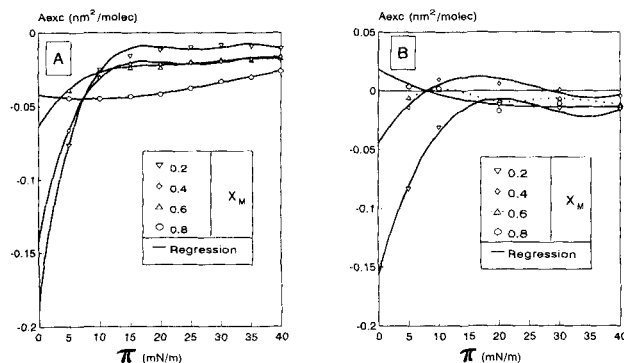
Aexc (nm²/molec)

A

▽ 0.2
◇ 0.4
△ 0.6
○ 0.8
— Regression

X_M

Aexc (nm²/molec)

B

▽ 0.2
◇ 0.4
△ 0.6
○ 0.8
— Regression

X_M

π (mN/m) π (mN/m)

Figure 7. Excess area vs. surface pressure for mono-stearin–distearin mixed films on pure water subphase at 20°C (A) and at 30°C (B).

the $\pi - A$ isotherms of the mixed films are practically parallel to that of an ideal mixture when there is a high content of monostearin in the mixture at high values of π. That is, interactions between molecules at interface do not cause monolayer structural changes, since A_{exc} does not depend on the surface pressure significantly (Alsina et al., 1991; Costin and Barnes, 1975). When the surface pressures are lower than 10 mN/m, especially at 20°C, and with a high content of distearin, the opposite effect is observed.

Figure 8 shows the excess free energy of mixing—calculated using Eq. 5—vs. monolayer composition, at surface pressures ranging between 5 and 30 mN/m, and at 20 and 30°C, respectively. It can be seen that the behavior of the mixed monolayer depends on the temperature. At 20°C (Figure 8A) the excess free energy of mixing is negative in all experimental conditions. Moreover, the absolute value of the excess free energy of mixing increases with the surface pressure. There are two minima in the $\Delta G^{exc} - x_M$ relationship which correspond to approximately the ratio of monostearin in the mixture of 0.2 and 0.8. Data in Figure 8A suggest that the mixed monolayer at the interface is more stable than the single-component monolayers (Alsina et al., 1991; Levy et al., 1991; Tomoaia-Cotisel and Chifu, 1983). The most stable monolayers appear in the zone rich in one of the two compo-
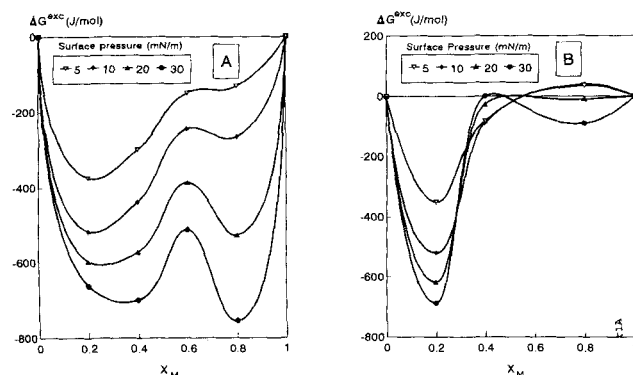
nents in the mixture, that is, at $x_M = 0.2$, and $x_M = 0.8$, no matter what the surface pressure is. The compositions are similar to those in which the minima in ΔG^{exc} appear.

At 30°C, except for a mixed monolayer in which $x_M = 0.2$, the $\Delta G^{exc} - x_M$ relationship is different from that observed at 20°C. It can be seen in Figure 8B that the values of ΔG^{exc} are either positive or negative, depending on the mixture composition. This behavior is due to the expansion of the monolayer structure at 30°C (Figures 2 and 3). The isotherms are displaced to higher surface areas with temperature, although no change in the monolayer structure can be seen. The displacement of the $\pi - A$ isotherms in the mixed monolayer is higher than that with pure components, in the same temperature range (Figures 2 and 3).

A change in excess free energy of mixing could also be due to relaxation processes such as molecular organization or monolayer molecular loss by desorption or collapse. These relaxation processes occur, in general, at surface pressures higher than the equilibrium surface pressure (Arnet et al., 1988). In this work the ΔG^{exc} was calculated (Table 1) at surface pressures lower than the equilibrium surface pressure of the pure components (Rodríguez Patino and Martín Martínez, 1994). So, collapse can be rejected as the cause of monolayer instability at surface pressures lower than 30 mN/m. Monolayer molecular loss by desorption was checked for by continuous compression–expansion cycles up to a surface pressure of 35 mN/m. No significant hysteresis was observed at the compression rates studied. The stability of monostearin monolayers on water has previously been reported (Fuente Feria and Rodríguez Patino, 1994a). For a full explanation of this phenomenon it is necessary to determine the stability of the mixed monolayer. This study, which is important from a theoretical and practical point of view, is under way at present, and confirms the stability of the mixed films (Fuente Feria and Rodríguez Patino, 1994b).

As the absolute values of ΔG^{exc} are both small and lower than that of ΔG^{id} in all cases, it is necessary to calculate the free energy of mixing (Table 1), according to Eq. 4, to determine the interactions between components in the mixture and the magnitude of those interactions (Bacon and Barnes, 1978; Petrov et al., 1992; Levy et al., 1991; Mestres et al., 1992; Grainger et al., 1992). Low values of ΔG^{exc} have been associated either with the existence of weak interactions between molecules in the monolayer, especially at lower surface pressures (Levy et al., 1991), or with the existence of a transition in the monolayer structure (Costin and Barnes, 1975). This

ΔG^exc (J/mol)

Surface pressure (mN/m)
▲ 5 ▲ 10 ▲ 20 ▲ 30

A

X_M

ΔG^exc (J/mol)

Surface Pressure (mN/m)
▲ 5 ▲ 10 ▲ 20 ▲ 30

B

X_M

Figure 8. Excess free energy of mixing as a function of varying film composition and surface pressure for monostearin–distearin mixed monolayers on pure water at 20°C (A) and at 30°C (B).

Table 1. Excess, Ideal, and Total Gibbs Free Energy for Mixed Monolayers of Mono- and Distearin on Deionizated Water (T:30°C)

ΔG (J/mol)	π (mN/m)	x_M:0.2	x_M:0.4	x_M:0.8
ΔG^{exc}	5	−350.0	−81.4	+35.6
	10	−520.1	−88.5	+39.3
	20	−617.3	−26.0	−10.1
	30	−686.8	+0.7	−90.0
ΔG^{id}	—	−1,258.5	−1,692.5	−1,258.5
ΔG^{π}_M	5	−1,608.5	−1,774.0	−1,222.8
	10	−1,778.6	−1,781.0	−1,219.2
	20	−1,875.8	−1,718.5	−1,268.6
	30	−1,945.3	−1,691.8	−1,348.5

phenomenon was previously deduced from the $A_{exc} - \pi$ relationships (Figure 7). From data in Table 1 it can be inferred that a phase separation in the monolayer does not exist. That is, the mixed monolayer is more stable from a thermodynamic point of view than the same monolayer with separation between its components. This assumption fits the negative values of the total free energy of mixing (Table 1).

Discussion

From the relationship between molecular area and monostearin content in the mixture at 20°C (Figure 5A) it can be deduced that a condensation in the monolayer structure takes place. This effect can be due to either molecular packing at the interface or molecular attractive interactions. The miscibility between both components at interface can be confirmed by the dependence of collapse pressure on monolayer composition (Figure 6). From these data it can also be inferred that interactions between components exist. The thermodynamic parameters (Figure 8a and Table 1) confirm the existence of interactions between both components at the interface. Moreover, as a consequence of attractive interactions between components at the interface, the mixed films are stable (Table 1), especially at compositions close to those in which minima in ΔG^{exc} appear (Figure 8A). At 30°C an anomalous behavior is observed, especially at higher monostearin content in the mixed monolayer. The interactions between components in the mixture, and consequently the nonideal behavior in the mixed monolayer, decrease when the temperature and monostearin content in the mixture increases. The drop in interaction is due to the expansion of the monolayer with temperature, as a consequence of the repulsion between the polar heads of the components in the mixture.

Figure 9 shows a scheme of the molecular structure of the film-forming components Since monostearin is more hydrophilic than diglycerides, we propose three models for the molecular association at air–water interface, as a function of monostearin content in the mixture (Figure 10).

With low monostearin content, the monostearin molecules can occupy the spaces between distearin molecules (Figure 10A). Distearin molecules, adsorbed on the interface push monostearin molecules toward the subsurface plane. Thus, the immersion of monostearin molecules in the mixed film is greater than when the monostearin molecules are alone in the monolayer. This effect could explain the condensation observed in the mixed film, especially at lower values of surface pressure (Figures 5 and 7).

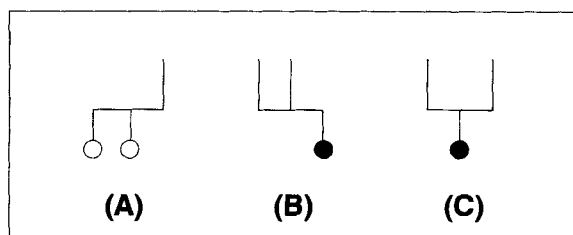In the intermediate range of composition (Figure 10B) the

Figure 9. Models for the molecules of monostearin (A), distearin 1,2-isomer (B), and 1,3-isomer (C).
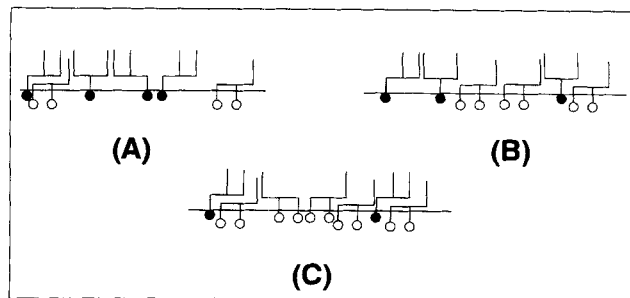
Figure 10. Models for monostearin–distearin arrangements at the interfacial region at rich-distearin zone (A), intermediate zone (B), and rich-monostearin zone (C) (for an explanation, see text).

existence of condensation in the monolayer structure is possible. However, since the number of molecules of each component is similar, the probability of one component occupying the free spaces between molecules of the other component decreases.

With high monostearin content (Figure 10C), the situation is similar to that previously described with high distearin content in the mixture. In this case, the distearin molecules are dispersed in a monolayer formed mainly by monostearin. The distearin, which has a lower hydrophilic character, would be on the surface pushing the monostearin molecules toward the subphase. Thus, there would be a decrease between polar group interactions, and the monolayer would occupy less space. This behavior agrees with the displacement of the isotherms toward the pressure axis (Figures 2 and 3) with a monostearin molar fraction of 0.8.

With high distearin content in the mixed film (Figure 10A), the hydrophobic interactions between hydrocarbon chains prevail over the interactions between polar groups. In this case, the mixed films are more stable, which agrees with the minimum in ΔG^{exc} at $x_M = 0.2$ (Figure 8). With high monostearin content both repulsion between polar groups and hydrophobic interactions between hydrocarbon chains exist, because the molecules are very close together. The latter effect agrees with the minimum in ΔG^{exc}, especially at the higher surface pressures (Figure 8). That is, when the monolayer is more condensed and the hydrocarbon chains are close together. In the region of intermediate composition (Figure 10B) a compensation of both effects exists. Repulsions between polar heads are minimized. However, interactions between hydrocarbon chains are also important in this region, especially when the monolayer structure is more condensed. This agrees with the negative values of ΔG^{exc} at 20°C (Figure 8A).

When the temperature increases, the monolayer is more expanded. That is, the molecular area of the pure components increases (Rodríguez Patino et al., 1992). A similar phenomenon can be seen with the mixtures (Figures 2 and 3). Because the molecular separation increases, the interactions between monostearin and distearin decrease and the behavior approaches the ideal, with an excess area close to zero. This behavior can be seen at the region with an intermediate composition and with higher contents of monostearin in the mixture, especially at the lower surface pressures. This rea-
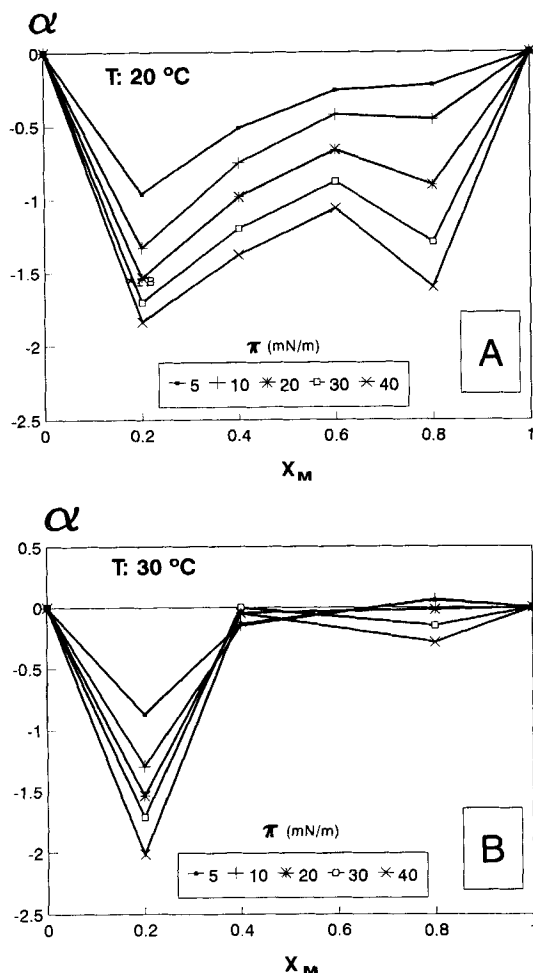
Figure 11. Interaction parameters vs. surface composition for monostearin–distearin mixed monolayers on pure water subphase at 20°C (A), and at 30°C (B).

soning agrees with the dependence of the mixture composition on ΔG^{exc} (Figure 8).

Finally, the interactions between film-forming components can be quantified by the interaction parameter $\alpha(\pi)$, calculated using Eq. 7. Figure 11 shows the variation of α vs. monolayer composition at 20 and 30°C. It can be observed that the variations of α are similar to those observed with ΔG^{exc} (Figure 8). At 20°C two minima appear that indicate an important interaction between film-forming components. These minima appear at high ($x_M = 0.8$) and low ($x_M = 0.2$) monostearin content in the mixture (Figure 11A). At 30°C the interactions between components are practically nil, except for a composition $x_M = 0.2$, which corresponds to the model in Figure 10C. Similar conclusions are derived from the interaction energy (Δh), calculated using Eq. 8 (data not shown).

Conclusions

In this work we studied the monostearin–distearin interactions from $\pi - A$ isotherms of films spread on water as a function of monostearin–distearin ratio and temperature.

Monolayer structures (restricted to the liquid-condensed and liquid-expanded structures in these systems) and the elasticity modulus depend on the surface composition and on the temperature. When molecules of both emulsifiers are spread on the air–water interface they may be packed more closely together than when either emulsifier is present alone, and they enter into different forms of association. This association can be tested by studies of surface pressure-area isotherms and of thermodynamics. Monostearin and distearin form homogeneous monolayers on the air–water interface. The degree of nonideality decreases with temperature.

Acknowledgment

Notation

R = constant of ideal gas, J/K·mol
T = temperature

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