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Surface behavior of jojoba oil alone or in mixtures with soybean oil

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Abstract

In the present work, the behavior of jojoba oil (JO), soybean oil (SBO) and JO/SBO mixtures at the air–water interface was studied. Experiments were performed by applying the Langmuir balance method. Monomolecular layers were prepared on a water subphase, which were subjected to lateral compression in a rectangular trough, using a Wilhelmy plate as a surface pressure transducer. The results showed that JO form stable and reproducible monomolecular layers at the air–water interface. The surface pressure–area isotherms showed an extremely low collapse pressure (π_c) of 2.3 mN/m, a mean molecular area of 210 Å^2/molecule and a compressional modulus at π_c of 23 mN/m, characteristic of liquid expanded monolayers. The compression–expansion cycle exhibited an unusual hysteresis, leading to π values higher in the expansion isotherm compared to those in the compression isotherm at the same mean molecular area. This behavior was interpreted as an increase in the hydration level of the polar groups during the lateral compression, which forced it to be immersed in the subphase. This excess hydration free energy, released to the environment during the compression process, was equivalent to $\Delta\Delta G = -94$ J/molecule. SBO and JO formed non-ideal mixtures, stabilized by attractive interactions at all proportions. The values of surface tension calculated for the water/monolayer interface ($\gamma_{\mathrm{w/m}} = 60$–$70$ mN/m for JO content between 0 and 100%) as well as the bending energy of this interface (700 kT units for micro-emulsion particles of 20 nm radii) were extremely high compared with those needed to obtain spontaneous emulsification (0.01 mN/m). This indicated that SBO/JO/water micro-emulsion require the addition of surfactants to become thermodynamically stable.

Keywords: Jojoba wax; Soybean oil; Monomolecular layers; Oil–wax mixtures

1. Introduction

Long-chain common wax esters have a wide application in industry as lubricants, plasticizers, cosmetics, and pharmaceuticals. The wax obtained from jojoba (*Simmondsia chinensis*) seeds, commonly known as jojoba oil (JO), is a mixture of straight-chain esters of monounsaturated, long-chain fatty acids and long-chain primary fatty alcohols, mainly two ester molecules containing 40 and 42 carbon atoms representing the 80% of the oil [1]. Interest in JO stems from its unusual properties which differ from all other known seed oils. It exhibits extraordinary high thermal and oxidative stabilities [2].

Soybean oil (SBO) is a natural complex mixture of triglycerides, sterified at the glycerol backbone mainly with polyunsaturated fatty acids [3 and Refs. therein], a characteristic that turns SBO very susceptible to peroxidation with molecular oxygen. Therefore, researches are starting to consider non-conventional natural lipid sources, as well as more simple processes such as mixing, in order to obtain pre-designed fat products with the desired physical, chemical, and nutritional characteristics. In that respect, the JO was shown to increase significantly the oxidative stability of SBO, when they were mixed, even in low proportions of JO (Maestri, DM, unpublished).

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Lipids from vegetal or dairy origin have gained a renewed interest as excipients in pharmaceutical formulations for the oral administration of hydrophobic drugs. This is due to their ability to enhance the oral bio-availability and to decrease the variability in the plasmatic concentrations [4]. The lipidic structures commonly used for the entrapment of hydrophobic molecules as well as hydrophilic substances such as enzymes and DNA are liposomes (uni or multilamellar vesicles). They are composed of lipids with cylindrical molecular geometries (critical packing parameter $P > 0.5$) that allow them to self-assemble in bilayers [5]. Other lipidic formulations used for the entrapment of hydrophobic molecules are pure liquids (triglycerides). The emulsions (oil plus surfactant) are also used which will be liquid or solid depending on the lipid transition temperature. At present, the use of liquid crystalline cubic phases (e.g. monoolein/water systems) as matrices to study immobilized enzymes and small molecules are also gaining a growing interest [6–9].

In the search for hydrophobic-drug delivery systems, we considered that SBO/JO mixtures would be convenient carriers, due to the low cost and accessibility of SBO and the stability of its blends with JO. Compounds of the type present in SBO and JO are amphipathic and, as such, they will tend to organize at interfaces. The knowledge of the properties and dynamics of the intermolecular interactions established between one another would help to predict their ability to self-assemble as well as the type and stability of the structures in which they would form.

In the present work we described the behavior of JO and SBO/JO mixtures at the air–water interface.

2. Materials and methods

2.1. Materials

Refined, bleached and deodorized soybean oil (SBO) was provided by Aceitera General Deheza (Córdoba, Argentina), and it was stored under N_2 at $-10\,^{\circ}C$ until used. Jojoba seeds were collected from commercial plantations at Aimogasta, La Rioja, Argentina. The oil was extracted using a manually operated pilot-plant hydraulic press as described previously [1]. The jojoba oil (JO) obtained was filtered through Whatman No. 1 paper and stored at $-10\,^{\circ}C$, without further treatment.

2.2. Oil analyses

Fatty acids and alcohols from JO and SBO were analyzed by gas chromatography (GC). Briefly, oils were subjected to alkaline saponification (1N potassium hydroxide in methanol) and unsaponifiable matter extracted with *n*-hexane. The fatty acid methyl esters were obtained using 1N sulphuric acid in methanol and analyzed by GC according to Maestri et al. [3]. Unsaponifiable material from JO was fractionated on preparative TLC (silica gel 60 G, 0.5 mm), developed with *n*-hexane: diethyl ether (50:50, v/v). After developing, the alcohol fraction was extracted from the plate with chloroform and then purified further by repeated preparative silica gel TLC for subsequent GC analysis. The identification of fatty acids and alcohols was carried out by GC–mass spectrometry [10,11], and by comparison of the retention times with those of reference compounds.

2.3. Monomolecular layers at the air–water interface

Monomolecular layers were prepared and monitored essentially as described previously [12,13]. The equipment used was a Minitrough II (KSV Instruments Ltd., Finland). Between 5 and 30 μl of a chloroformic solution of lipids was spread on an unbuffered aqueous surface; about 5 min were allowed for the evaporation of chloroform. Lateral surface pressure (π) was measured by the Wihelmy plate method. Reproducibility was within $\pm 0.001\,nm^2$ and ± 0.001 mN/m for molecular area and surface pressure, respectively.

2.4. Surface pressure (π) versus molecular area (A) isotherms

The surface behavior of SBO, JO and JO alcoholic fraction were studied. The SBO/JO mixtures at JO percentage composition between 0 and 100% were also investigated. Dipalmitoyl phosphatidylcholine (dpPC) π–area isotherm was also run as a reference molecule. For these experiments we used a rectangular trough fitted with two barriers that were moved synchronously by electronic switching. The signal corresponding to the surface area (automatically determined by the Minitrough according to the relative position of the two compression barriers) and the output from the surface pressure transducer (measured automatically by the Minitrough with a platinized Pt foil 5 mm wide × 20 mm long × 0.025 mm thick) were fed into a personal computer through a serial interface using a specific software. Before each experiment the trough was rinsed and wiped with 70% ethanol and several times with bidistilled water. The absence of surface-active compounds in the pure solvents and in the subphase solution (bidistilled water) was checked before each run by reducing the available surface area to less than 10% of its original value after enough time was allowed for the adsorption of possible impurities that might have been present in trace amounts. The monolayer was compressed at a constant low rate of $20\,mm^2/s$ at $28 \pm 0.5\,^{\circ}C$. A lower compression rate ($12\,mm^2/s$) was tested, and identical results were obtained. The JO, SBO as well as the alcohol fraction from JO, consisted of mixtures of molecules with different chain lengths. The composition of each sample was determined as indicated previously. This information was used to calculate the weighted mean molecular masses (MMM) required for determining the mean molecular areas.

MMM values were calculated as follows: $\mathrm{MMM} = [\sum(\%\mathrm{MW})]/100$, where% is the percent composition of the sample taken from Table 1 and MW is the molecular weight of the individual component. Hence, the

Table 1
Chemical composition of soybean oil (SBO) and jojoba oil (JO)

Component (%)	SBO	JO
Fatty acids		
Hexadecanoic (C16:0)	10.9	1.08
Octadecanoic (C18:0)	4.21	Tr
cis 9-Octadecenoic (C18:1)	20.6	10.1
cis 9, *cis* 12-Octadecadienoic (C18:2)	55.7	Nd
cis 9, *cis* 12, *cis* 15-Octadecatrienoic (C18:3)	7.84	Nd
cis 11-Eicosenoic (C20:1)	0.38	72.5
cis 13-Docosenoic (C22:1)	0.37	14.8
cis 15-Tetracosenoic (C24:1)	Nd	1.42
SFA	15.11	1.08
MUFA	21.35	98.82
PUFA	63.54	Nd
Fatty alcohols		
cis-9-Octadecenol		0.7
cis-11-Eicosenol		42
cis-13-Docosenol		48
cis-15-Tetracosenol		9
Hexadecanol		Tr
Octadecanol		Tr
Eicosanol		Tr
Docosanol		Tr

SFA: saturated fatty acids, MUFA: monounsaturated fatty acids, PUFA: polyunsaturated fatty acids. Tr, trace (<0.3%). Nd, not detected. MMM: mean molecular mass (calculated as described in Section 2.4).

MMM used for SBO, JO and JO alcohol fraction samples were 848, 608 and 313, respectively.

2.5. Thermodynamic calculations

The excess mean area of mixture, A_{ex}, at constant film pressure (π) can be express as:

$$A_{ex} = A_{12} - A_{id} = A_{12} - (X_1 A_1 + X_2 A_2) \tag{1}$$

where A_1, A_2, X_1 and X_2 are the molecular areas and mole fractions of single components 1 and 2, respectively, and A_{id} and A_{12} are mean molecular areas of the ideal and real mixtures of compounds 1 and 2, respectively. An $A_{ex} = 0$ means either immiscibility or ideal mixture of the components and $A_{ex} \neq 0$ represent a non-ideal mixture involving either attractive ($A_{ex} < 0$) or repulsive ($A_{ex} > 0$) interactions. The free energy involved in this interaction is the ΔG_{ex}, which can be calculated from the area under the curve of A_{ex} within a meaningful π interval (see Eq. (2), where N_0 is the Avogradro's number).

$$\Delta G_{ex} = N_0 \int_0^{\pi} [A_{12} - (X_1 A_1 + X_2 A_2)]\, d\pi \tag{2}$$

Even in ideal conditions, due to entropic contributions, any mixture of substances will involve a change in free energy identified as the ΔG_{id}:

$$\Delta G_{id} = RT(X_1 \ln X_1 + X_2 \ln X_2) \tag{3}$$

Hence, the total free energy change will be the sum of ideal and non-ideal contributions:

$$\Delta G_{mix} = \Delta G_{ex} + \Delta G_{id} \tag{4}$$

3. Results and discussion

3.1. Chemical composition of oils

Table 1 presents the fatty acid composition of SBO and JO used in this study. Linoleic (C18:2) acid was the predominant fatty acid in SBO, followed by oleic (C18:1), palmitic (C16:0) and linolenic (C18:3) acids in a decreasing order. Jojoba oil was exceptionally rich in *cis*-11-eicosenoic acid. Besides this fatty acid, oleic and *cis*-13-docosenoic acids were detected in similar amounts. As expected, SBO was characterized by a high proportion of polyunsaturated fatty acids (PUFAs), whereas monounsaturated fatty acids were almost 99% of the fatty acids present in JO. Eight fatty alcohols were found in JO: *cis*-11-eicosenol, *cis*-13-docosenol and *cis*-15-tetracosenol were the major components; *cis*-9-octadecenol, hexadecanol, octadecanol, eicosanol and docosanol were found in small proportions (Table 1). The combination between acids and alcohols in JO leaded to esters of 38, 40, 42, 44 and 46 total number of carbon atoms representing 4.4, 24.1, 55.1, 13.1 and 2.0% of the wax esters, respectively. These results are consistent with those reported by Busson-Breysse et al. [14].

3.2. Surface pressure–mean molecular area isotherms

3.2.1. dpPC

The reference isotherm of dpPC (Fig. 1a, central curve) showed the typical bidimensional phase transition at 8.2 mN/m and 72 Å^2/molecule, a collapse pressure at 55 mN/m and a minimal mean molecular area of 40 Å^2/molecule. These values were an indication of the good quality of the measuring system.

3.2.2. Jojoba oil

The JO monolayer (Fig. 1a, curve at the right hand side) showed a liquid expanded isotherm with a reproducible and strikingly low collapse pressure ($\pi_c = 2.3$ mN/m) and a minimal mean molecular area of 210 Å^2/molecule. In spite of the very low collapse pressure, the JO monolayer remained at the air–water interface, even after several compression–expansion cycles (Fig. 1b). The mean molecular area of the two hydrocarbon-chain components of JO was even higher than that of SBO (mostly composed of three hydrocarbon-chain triglycerides). This may be related with molecular packing problems. The combination of alcohol/acid chains lengths in JO, which is quite symmetric (20/18 (5.4%), 20/20 (24.3%), 22/18 (3.6), 22/20 (37.0%), 22/22 (2.1) and 24/20 (7%) [14]), would contribute favorably to the intermolecular interaction if a significant packing

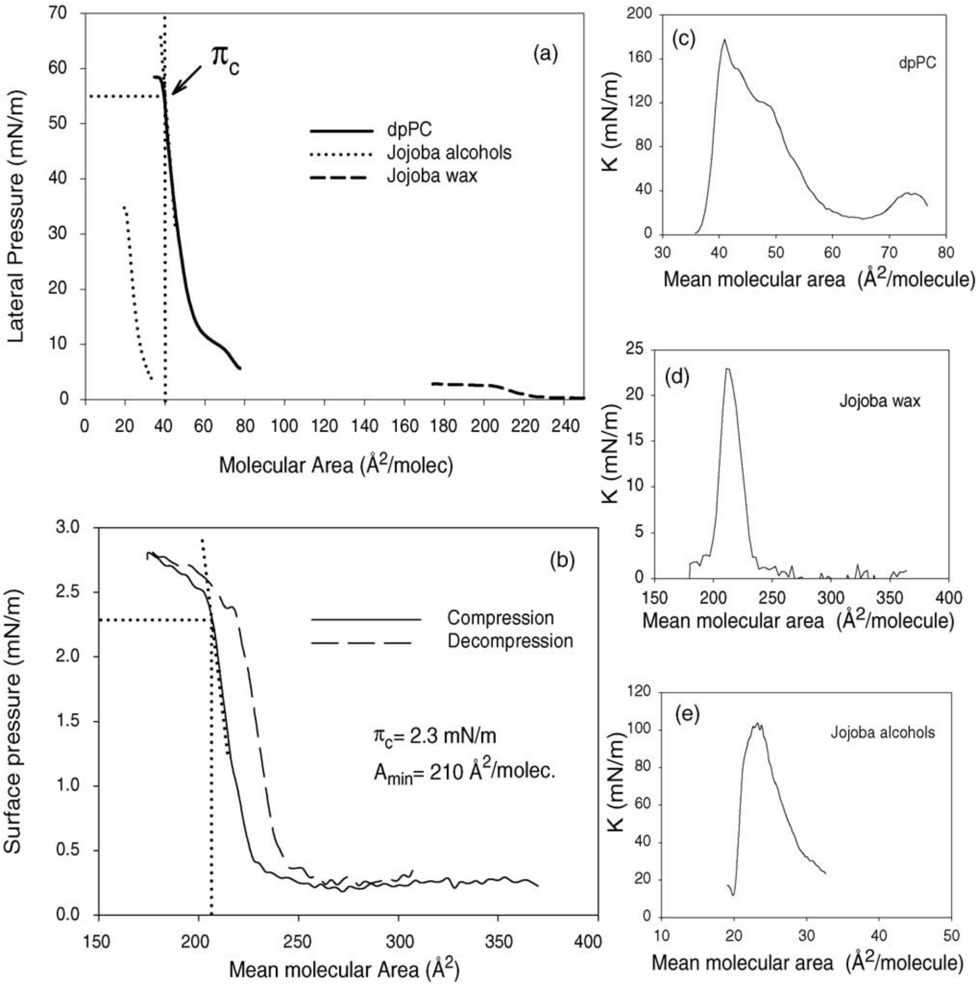

Fig. 1. Surface pressure–area isotherms of pure compounds. (a) Dipalmitoylphosphatidylcholine (dpPC), jojoba oil (JO) and long-chain unsaturated alcohols hydrolyzed from JO. The straight dotted lines indicate how to determine the collapse point (π_c) coordinates. (b) JO π–area compression and expansion isotherms showing an unusual hysteresis. (c–e) Compressional modulus of dpPC, JO and JO hydrolyzed alcohols calculated form the isotherms shown in (a). For the calculation of mean molecular areas, the weighted averages of the molecular masses of individual components of each sample were used.

level could be reached. However, the presence of a polar head group, which is too small compared with the volume occupied by the bulky long and unsaturated hydrocarbon-chains leads to a low hydrophilic/hydrophobic balance in these molecules [5,12]. This would explain the collapse of the monolayer at a low surface pressure and at a very high minimal mean molecular area. In addition, the geometry of the monoester polar group might difficult the orientation of the two hydrocarbon chains parallel between one another and in the perpendicular direction with respect to the monolayer surface. On the contrary, in triglycerides the glycerol backbone facilitates this orientation of the hydrocarbon chains.

The compression–expansion cycle showed an unusual hysteresis [15]. The expansion isotherm deviated to higher surface pressures within the whole area range of the isotherm. The difference between the areas under the compression and expansion curves, from $\pi = 0$ to π_c, represented the free energy values of the corresponding process. From a ΔG compression = +866 J/mol and a ΔG expansion = −960 J/mol, we calculated a value of $\Delta\Delta G = -15.6$ mN/m Å²/molecule or −94 J/mol. This negative $\Delta\Delta G$ value represented and excess free energy released to the environment during the compression process. A differential hydration level of the ester groups of JO components at the interface may explain this result. The ester–water dipole interaction might be enhanced by lateral compression, obliging the carbon bearing at the ester group to rotate down and the alcoholic oxygen to immerse in the subphase. During expansion, this hydrated oxygen atom in addition to the carboxylic oxygen, might behave like a bulky polar group, increasing the surface pressure.

3.2.3. *Jojoba alcohol fraction*

The alcohols obtained from JO hydrolysis showed a liquid condensed monolayer which, taking into account the higher collapse pressure (33 mN/m), was much more stable than that of the oil they came from. The value of 21 Å²/molecule for their mean area at the collapse pressure was characteristic of close-packed one hydrocarbon-chain molecules [16]. This result suggest that the low collapse pressure of JO is not due to the unsaturation of the hydrocarbon chains of the esterified alcohols but to steric restrictions that hindered the proper packing of the ester molecules.

3.3. Compressibility modulus

Phase transition points and collapse points were better identified by determining the values of compressibility modulus (K) as a function of molecular areas (Fig. 1(c)–(e)), from the π–area isotherms data (Fig. 1a) using Eq. (5) [5]:

$$K = -(A_\pi)\left(\frac{\partial \pi}{\partial A}\right)_\pi \qquad (5)$$

where A_π is the molecular area at the indicated surface pressure. Because the molecular areas were mean values, this parameter reflected qualitatively the physical state and the bidimensional phase transition of the monolayer. Higher values of K values corresponded to lower values of interfacial elasticity. From a systematic analysis of π–A isotherms [17,18], it was concluded that the compressional modulus of solid condensed states are characterized by values from 1000 to 2000 mN/m, varying between 100 and 250 mN/m for liquid condensed films, while liquid expanded states showed values between 12.5 and 50 mN/m. This clearly allows concluding that the JO was in a liquid expanded state.

3.4. Jojoba wax–soybean oil mixtures

The JO/SBO mixtures exhibited isotherms with only one collapse point, reached at surface pressures that increased as a function of the proportion of SBO components (Fig. 2a). The latter contained the molecules with the highest collapse pressure in the mixture (see Fig. 2(a) and (c)). This behavior was a good indication that SBO and JO were laterally mixed. The area–composition diagram, not only at collapse pressure (Fig. 2b) but also at 2 mN/m (Fig. 3b), showed a negative deviation from the ideal behavior at all proportions (represented by the straight dotted line). This reflected attractive interactions between both types of components. The π–composition graph showed also a deviation from ideality, and stressed the concept that the monolayer stability increased with the proportion of SBO in the mixture (Fig. 2c). A similar behavior was observed upon analyzing the π–area isotherms at a constant $\pi = 2$ mN/m (Fig. 3).

A detailed thermodynamic analysis of the surface mixing properties of JO and SBO is shown in Table 2. Within the whole range of JO mole fraction, the negative values of A_{ex} at $\pi = 2$ mN/m in the mixture of JO and SOB, leaded to an excess Gibbs free energy (ΔG_{ex}). This indicated that intermolecular attractive forces in the mixed monolayers took place in the stabilization of the films. However, if the values of ΔG_{ex} and the Gibbs free energy of mixtures in ideal conditions (ΔG_{id}) were compared, it became clear that the contribution of attractive forces to the whole thermodynamic stability of the films were low.

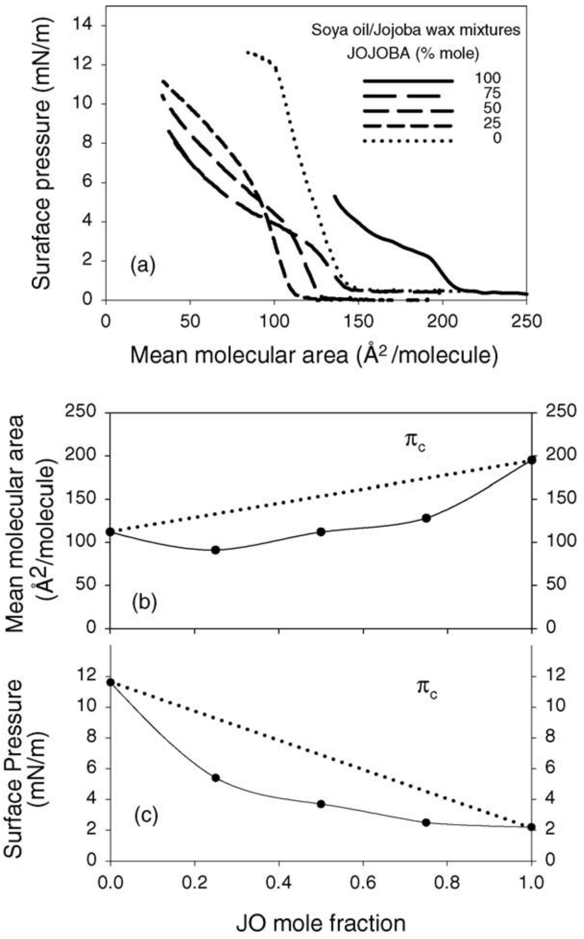

Fig. 2. Surface behavior of SBO/JO mixtures. (a) π–Area isotherms of SBO/JO mixtures. (b) Mean molecular area at collapse pressure. (c) Collapse pressures as a function of JO composition in mole fraction units. Points are experimental data and the dotted lines represent the theoretical ideal behavior.

Compressional modulus of JO/SBO isotherms from JO mole fraction from 1 to 0 showed that JO and SBO always form liquid expanded films ($K < 40$ mN/m), with a compactness that increased with the SBO content (Fig. 4).

3.5. Stability of an eventual oil in water micro-emulsion of SBO/JO dispersion in water

It can be roughly assumed that the interfacial tension between air and clean water ($\gamma_{\mathrm{a/w}}$) is the resultant of the two microscopic interfacial tensions between the air and the monolayer ($\gamma_{\mathrm{a/m}}$) and between the water and the monolayer ($\gamma_{\mathrm{w/m}}$) according to Eq. (6):

$$\gamma_{\mathrm{a/w}} = \gamma_{\mathrm{a/m}} + \gamma_{\mathrm{m/w}} \qquad (6)$$

However, this equation is not always valid. The difference between the two sides of the equation was defined by Langmuir as the spreading factor for oil films spreading over the clean air–water interface, which could have a positive, zero or negative value [19]. With this limitation in mind, taking

Table 2
Thermodynamic analysis of SBO/JO films at $\pi = 2$ mN/m

JO mole fraction	Mean molecular area (Å^2/molecule)	A_{ex} (Å^2/molecule)	ΔG_{id} (J/mol)	ΔG_{ex} (J/mol)	ΔG_{mix} (J/mol)
1	192.4	0	–	–	–
0.75	129.26	−48.86	−1374	−16.19	−1390
0.50	117.34	−46.5	−1694	−60	−1754
0.25	103.24	−46.32	−1974	−56.43	−1430
0	135.28	0	–	–	–

The mean molecular areas, were taken at $\pi = 2$ mN/m from the isotherms shown in Fig. 1(a). A_{ex}: areas excess; ΔG_{id}: ideal free energy of mixing; ΔG_{ex}: excess free energy of mixing; ΔG_{mix}: energetic tendency to form a mixture as compared to unmixed components in the monolayer. See text for details.

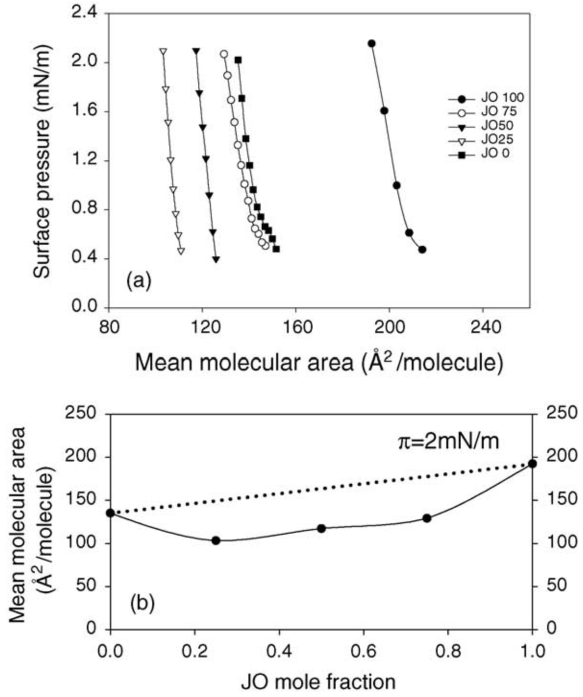

Fig. 3. Miscibility of SBO/JO mixtures at 2 mN/m. (a) Detail of the π–area isotherms shown in Fig. 1. (b) Deviation from the ideal behavior of SBO/JO mixtures at a constant lateral surface pressure of 2 mN/m.

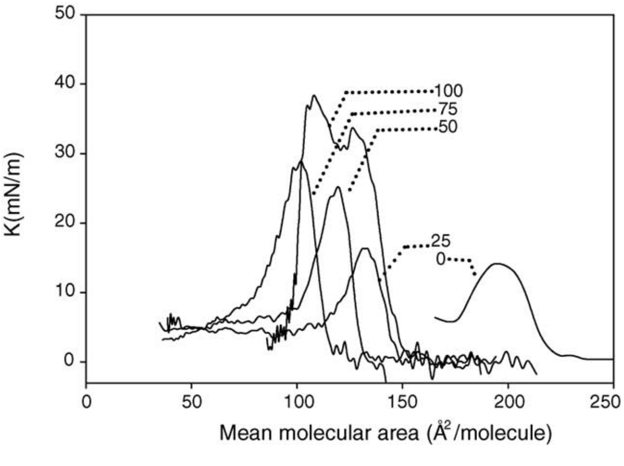

Fig. 4. Effect of JO content on the compressional modulus of JO/SBO mixed monolayers. Compressional moduli (K) were calculated from data shown in Fig. 2(a) according to Eq. (5). Numbers indicate the percent composition of SBO in the mixture.

$\gamma_{a/w} = 72$ mN/m and assuming that $\gamma_{a/m}$ in the vicinity of equilibrium has an approximately constant value equal to π_c, we calculated an approximate value of $\gamma_{w/m}$ for the SBO/JO mixtures which varied between 60 and 70 mN/m, with JO content ranging from 0 to 100%.

The Windsor II system is a two-phase system in which a micro-emulsion phase coexists with excess water phase. Moreover, at the critical micro-emulsion concentration (cμc), the emulsion is in equilibrium with a monolayer at the air–water interface [20]. The interfacial tension is related to the free energy difference of the interfacial film at the planar interface separating the bulk phases and at the curved interfaces of the micro-emulsion droplets. This difference contains contributions from the energy required to bend the monolayer and free energies associated with dispersing the droplets within the medium and inter-droplet interaction.

$$\gamma_{c\mu c} = \frac{2K + K'}{r^2} \tag{7}$$

where $\gamma_{c\mu c}$ is the $\gamma_{w/m}$ interfacial tension at the cμc, K the rigidity constant of the film monolayer and represents the energy required to bend a unit area of the film by a unit amount of curvature away from the spontaneous curvature and K' is the Gaussian curvature elastic modulus [5]; r the radius of the micro-emulsion particle. The high values of $\gamma_{w/m}$, calculated for JO/SBO blends as well as the bending energy of this interface (700 kT units for micro-emulsion particles of 20 nm radii) were extremely high compared with those needed to obtain spontaneous emulsification (0.01 mN/m) [21]. This indicated that SOB/JO/water micro-emulsions will require the addition of surfactants to become thermodynamically stable.

4. Conclusions

The liquid expanded monomolecular layers formed by JO at the air–water interface, in spite of its extremely low collapse pressure (π_c) of 2.3 mN/m, were stable in time and reproducible. The compression–expansion cycle exhibited an unusual hysteresis, leading to π values higher in the expansion isotherm, compared with those in the compression isotherm at the same mean molecular area. An increase in the hydration level of the polar groups during the lateral compression, may forced it to be immersed in the subphase, interact with water dipoles and behave as a bulky polar group, increasing the surface pressure. SBO and JO formed non-ideal mixtures, stabilized by attractive interactions at all proportions. The high values of surface tension calculated for the water/monolayer interface ($\gamma_{\mathrm{w/m}} = 60–70$ mN/m for JO content between 0 and 100%) and the consequent high bending energy of this interface (700 kT units for micro-emulsion particles of 20 nm radii) indicate that SOB/JO/water micro-emulsion will require the addition of surfactants to become thermodynamically stable.

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