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ISOTERMAS DE ADSORCIÓN DE LANGMUIR PARA DIFERENTES SOLUCIONES ORGÁNICAS DE COLESTEROL

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Abstract

In this work, the surfactant properties of cholesterol in organic solvents are studied. Hexane, *iso*-octane, *iso*-dodecane and toluene were used as the hydrophobic phase, and bidistilled water was used as the water phase. The captive bubbles were supported on a quartz surface and the axisymmetric drop shape analysis (ADSA) routine was performed to obtain contact angles (θ) and surface tension values (γ). Cholesterol was effective in reducing the interfacial tension of the oil/water system in all organic solvents. The appearance of turbidity associated with cholesterol crystallization is observed to be below concentration limits in all samples, because the liquid-liquid interface reduces the energy barrier required for nucleation. Experimental values of γ were adjusted with theoretical values obtained by applying Szyszkowski-Langmuir isotherm, showing good correlation between data. Finally, Szyszkowski-Langmuir constant (K_L) and Gibbs energy of absorption were calculated for the binary systems.

Keywords: cholesterol, ADSA, surface tension, captive bubble, Szyszkowski-Langmuir equation.

Resumen

En este trabajo se estudian las propiedades del colesterol como surfactante en soluciones orgánicas. Se utilizaron hexano, *iso*-octano, *iso*-dodecano y tolueno como fase hidrofóbica y agua bi-destilada como fase acuosa. Las burbujas cautivas se apoyan sobre una superficie de cuarzo y la rutina ADSA (Axisymmetric Drop Shape Analysis) se realizó para obtener los ángulos de contacto (θ) y los valores de tensión superficial (γ). El colesterol fue eficaz en la reducción de la tensión interfacial del sistema de aceite/agua en todos los disolventes orgánicos. En todas las muestras se observó una turbidez asociada a la cristalización del colesterol, por abajo de los límites de concentración, debido a la interfaz líquido-líquido que reduce la barrera de energía necesaria para la nucleación. Los valores experimentales de γ se ajustaron con los teóricos obtenidos aplicando la isoterma de Szyszkowski-Langmuir, mostrando una buena correlación. Por último, para los diferentes sistemas binarios se calcularon la constante de Szyszkowski-Langmuir (K_L) y la energía de adsorción de Gibbs.

Palabras clave: colesterol, ADSA, tensión superficial, burbujas cautivas, ecuación de Szyszkowski-Langmuir.

1 Introduction

Cholesterol (5α-cholesten-3β-ol, Figure 1) is the most familiar steroid and is widely distributed in animals. Its chemical and physical properties are important in the metabolism of lipids and in the fluidity of membranes (Heimburg, 2007).

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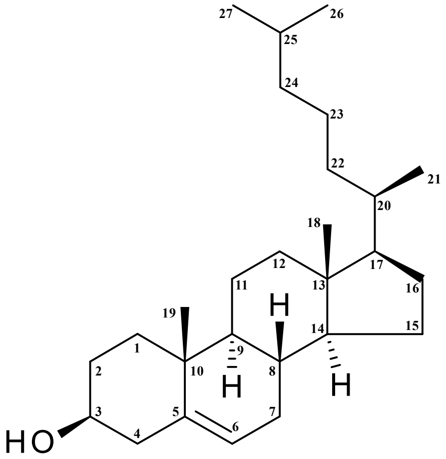

Fig. 1. Molecular structure of cholesterol.

The thermodynamic behavior associated with amphiphilic character of the cholesterol molecule is fundamental in the formation of excessive deposits on the flow-paths of some body fluids, causing problematic health issues that range from gallstone formation (Xie *et al.*, 2005) to intestinal lumen deposits and atherosclerotic plaques (Weinberg *et al.*, 2000; Wang, 2001). These phenomena are principally due to unbalanced relationships between cholesterol intake and deposition rate with the rate of its solubilization through the action of micellar, vesicular, and bilayer cleansing agents in bile and specific lipoprotein complexes in blood (Uskokovic, 2007). Thereupon, because of the potential development of reversible control, investigation of thermodynamic properties of cholesterol presents a task with large significance for both biomedicine and pharmacology.

Cholesterol acts as a natural surfactant in liquid-liquid interfaces. Ogino *et al.* (1981) studied the interfacial action of cholesterol, among others, in oil/water systems, observing turbidity associated with the formation of crystal nuclei near the saturation; however, their work is not focused on determining thermodynamic parameters, such as the surface tension (γ) of the system, which plays an important role in both scientific and technological areas, such as biomedical engineering, food science, biology and pharmacobiology, polymer science (Adamson *et al.*, 1997; Fahti-Azarbayjani *et al.*, 2009). Surface tension is often associated with wettability, obtained quantitatively through the measurement of the contact angle (θ) formed when a drop of liquid is placed on a surface. The tangent point of contact between the interfaces solid-liquid, liquid-vapor and solid-vapor sets the angle of contact, and when the liquid used is water, the surface can be classified as hydrophilic ($\theta < 90°$) or hydrophobic ($\theta > 90°$).

Among the most commonly used methods for evaluation of surface tension and contact angle, the drop shape method has many advantages, including small sample quantity and the possibility of being applied to vapor-liquid, solid-liquid and liquid-liquid interfaces (Neumann *et al.*, 2010). The determination of interface properties using the drop shape method is based on a complex numerical analysis (Adamson *et al.*, 1997). Different numerical methods have been proposed (Adamson *et al.*, 1997); however, the ADSA (Axisymmetric Drop Shape Analysis) is versatile, powerful, and extensively used for measuring the interfacial tension and contact angle in sessile and pendant drop (Hoorfar *et al.*, 2004), as well as captive bubbles.

The aim of this study is to determine the interfacial tension and contact angle in captive bubbles of different cholesterol solutions in an aqueous environment, using a digital tensiometer and ADSA routine. The results will be correlated using the Szyszkowski-Langmuir (Adamson *et al.*, 1997).

2 Materials and methods

2.1 *Digital tensiometer*

Cholesterol (purity ≥ 99%), hexane and toluene (analytical grade, purity ≥ 95%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). *iso*-octane (analytical grade, purity ≥ 95%) was purchased from Merck (Darmstadt, Germany). Bidistilled H_2O was used in the experiments.

Surface tension was measured by a digital tensiometer, as described in Figure 1. Initially, the system was designed to catch sessile drops of $\emptyset = 1-2$ mm or eventually 1-5 μL of the sample.

A digital camera (Hitachi KB-D20B, Hitachi Ltd., Tokyo, Japan) located outside the chamber and in line with the magnifier was employed to digitally take an image (640 × 480 pixels). The camera had the following characteristics: $1/2'$ IT CCD, sensible area of 768×494 pixels, ≈ 15 μm of resolution. The camera was implemented with a zoom VZM 450 video lens, with a field of view from 8.8 mm to 1.4 mm and a video sensor of format 1/8", which allows observation of the drops with an appropriate resolution. The lighting system was diffused light.

For our work, a test cell for captive bubbles was implemented (Fig. 2) using a quartz cell

(Sigma-Aldrich, St. Louis, MO, USA) attached to an aluminum support, especially designed and manufactured for this purpose. A septum similar to those used in gas chromatography (Thermolite® Septa, Restek Co., Bellefonte, PA, USA) allows injection through a 50 μL syringe (Hamilton® Syringe, Sigma-Aldrich, St. Louis, MO, USA). LabVIEW NI Vision Development Mode module (version 8.5, National Instruments, Austin, TX, USA) was used to acquire the images. Volume of injected sample was 5 μL. Cholesterol was dissolved in hexane, *iso*-octane, *iso*-dodecane and toluene with increasing concentration up to saturation concentration. Temperature and humidity were kept constant, at 27 ± 0.5 ° C and 45%, respectively.

2.2 Axisymmetric Drop Shape Analysis (ADSA) procedure

The ADSA technique to measure interfacial tension consists of the detection of the profile of a sessile (or pendant) drop by use of a video camera or other suitable instrumentation. In our experiments, ADSA routine was performed in order to obtain interfacial tension and contact angle values, as described by Neumann's group (2010). They introduced the reasonable assumptions that external forces, other than gravity, are absent, and that sessile/pendant drop is axisymmetric. Under these assumptions, the meridian curve of a sessile/pendant drop can be represented by arc length s measured from the apex, as $x = x(s)$ and $z = z(s)$; these obey the following differential equations:

$$\frac{dx}{ds} = \cos\theta \tag{1}$$

$$\frac{dz}{ds} = \sin\theta \tag{2}$$

$$\frac{d\theta}{ds} = 2b + \frac{(\Delta\rho g)R_0^2}{\gamma}z - \frac{\sin\theta}{\mathrm{x}} \tag{3}$$

Here, $\Delta\rho$ is the density difference between the drop; the surrounding fluid, R_0 is the radius of curvature at the apex, γ is interfacial tension, g is gravity acceleration, and θ is the turning angle measured between the tangent to the interface at the point $(x; z)$ and the datum plane. It should be noted that the above equations represent both pendant and sessile drops, depending on axis arrangement and the choice of plus and minus values of $\Delta\rho$.

Solution methods for the differential equations and optimization method used in this research are explained in detail by Neumann (2010).

2.3 Fitting data to the Langmuir-Szyszkowski equation

A nonlinear least square regression method (Marquardt-Levenberg algorithm) was performed, and convergence was usually reached within less than 100 iterations, with termination tolerance on x of 10^{-6}. The curves were fitted using MATLAB^{TM} curve fitting tool (v. 7.11.0.584, The Mathworks Inc., USA).

3 Theoretical background

Surface tension (γ) is considered as a particular mechanical stress that develops along a separation surface (interface) between a fluid and another material (liquid, solid or gaseous). Thermodynamically, it can be defined as the work necessary to increase the surface of a liquid from a unit amount (Adamson, 1997). The work necessary to create a unit area is called surface-free energy. It can be expressed as a Gibbs adsorption equation:

$$\left(\frac{\partial\gamma}{\partial\ln(a_i)}\right)_{T,P} = -RT\Gamma_i \tag{4}$$

where a_i and γ_i are the activity, and the interfacial concentration of component i , and R, T, and P, respectively, have their usual meaning. The Gibbs adsorption equation is the mathematic expression that can explain how the surface tension is related to the concentration of a species in bulk phase and in the surface.

At low concentrations γ_i increases linearly with a_i, while at high concentrations γ_i reaches the limit value γ_∞. If the relationship between surface excess concentrations is known, this equation can be integrated to obtain the surface tension as a function of solute concentration. Considering that the free energy of adsorption is constant and the surface is in equilibrium with the layers below the surface, this relationship is defined by the Langmuir isotherm:

$$K_L C_i = \frac{\Gamma_i}{\Gamma_\infty - \Gamma_\mathrm{i}} \tag{5}$$

In this equation K_L is the adsorption constant at equilibrium. In Langmuir isotherm, localized adsorption and no-interactions between molecules are assumed.

Substituting this relationship in the preceding we obtain:

$$d\gamma = -\mathrm{RT}\sum_{\mathrm{i}}\Gamma_i\log(1 + \sum_j K_L C_i) \tag{6}$$

If we solve Eq. (6) for the excess surface and replace this expression in the Gibbs equation, we obtain the integrated Szyszkowski-Langmuir equation:

$$\gamma = \gamma_0 - \mathrm{RT}\Gamma_\infty \log\left(1 + \sum_j K_L C_i\right) \qquad (7)$$

where γ_0 is the surface tension of the solution in the absence of surfactant.

Finally, knowing K_L, we can calculate the Gibbs energy of adsorption by the van't Hoff equation:

$$\Delta G^o = -\mathrm{RTlnK_L} \qquad (8)$$

4 Results and discussion

4.1 Drop shape

The aim of this study is to evaluate the interfacial behavior of organic solutions of cholesterol. Due to volatile organic solvents, a captive bubble system was used, in which the two phases are practically immiscible with each other. The captive bubble system has proven to be a useful technique for monitoring low and ultralow interfacial tension, which is problematic to reveal with pending drop method. In fact, at low surface tensions, pendant (hanging) drops are difficult to manipulate because gravity overpowers surface tension and the drop falls from the support (Prokop *et al*., 1998).

We used bi-distilled water as an external phase, while hexane, *iso*-octane, *iso*-dodecane and toluene were used as solvents to obtain solutions at increasing concentrations. In the captive bubble tensiometer, the bubble is floated against the quartz wall and the interfacial tension is measured. The bubble is completely surrounded by water, and hence the molecule of cholesterol at the interface cannot escape (Fig. 2).

Figure 3 shows an image of droplets obtained. In alkanes, with increasing cholesterol concentration, there is a gradual flattening of the droplet, which loses its round shape. In toluene's solutions, changes in the shape of the drop are not perceptible, but only a progressive increase in the contact area was observed. These phenomena are related to the surfactant effect of cholesterol lowering the surface tension and improving adhesion between liquid/solid surfaces. It is well known that in captive bubbles a thin layer is trapped between the support and the drop (Crenmer *et al*., 1999), acting like a lubricant.

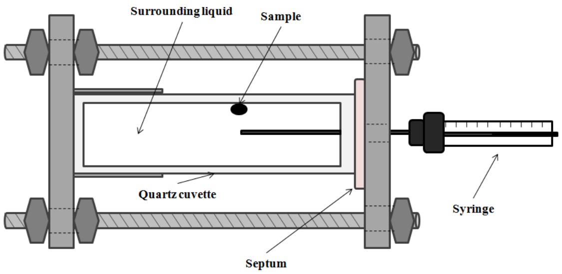

Fig. 2. Scheme of analysis cell used for evaluating contact angle and surface tension of cholesterol solutions (liquid 2) in water (liquid 1).

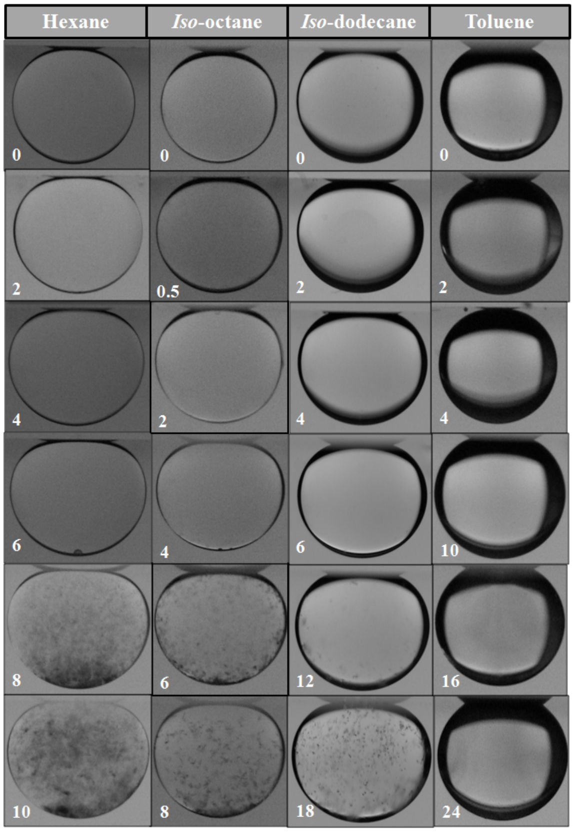

Fig. 3. Images of droplets of different solutions of increasing cholesterol concentration (mg/ml).

Near the saturation limit, there is a turbidity associated with the formation of crystal nuclei. Previously, formation of large crystals was observed only in triglycerides such as safflower oil and corn oil containing cholesterol (Ogino *et al*., 1981). In all of our samples, this event has been pointed out at concentrations below the saturation limit. Cholesterol has amphiphilic characteristics: a polar group corresponding to the C-3 hydroxyl and a principal nonpolar structure formed by the cyclopentaphenanthren nucleus and the aliphatic chain (Medina-Meza *et al.*, 2011; Figure 1). The molecular interaction at the interface is sensitively influenced by the stereochemical configuration and the kinds of polar groups of the two interacting molecules. So, the hydroxyl group interacts with external water by H-bonds, and the steroid nucleus is oriented towards the organic solvent.

We can explain spontaneous crystallization by considering a self-assembly of cholesterol molecules at the interface into an ordered multilayer film. The presence of liquid-liquid interface lowers the energy barrier required for nucleation. The molecules tend to migrate to the interface, causing a local saturation, resulting in the nucleation and growth of particles in the interfacial zone, but not in the bulk phase. The formation of nuclei occurs at interface, and then they progressively diffuse in the bulk.

Analogous phenomena have been studied by Kadota *et al.* (2007) during liquid-liquid crystallization of KCl and NaCl agua/1-butanediol systems. The authors obtained asymmetric particles with a narrow size distribution by utilizing the slight mutual diffusion between essentially immiscible solvents at the interface. In the liquid-liquid crystallization, elevation of supersaturation is confined to the mixing area at the liquid-liquid interface (Kitayama *et al.*, 2009). In the same manner, Ogino *et al.* (1981) discussed the spontaneous emulsification of natural surfactants in oil/water systems, more recently confirmed by Pautot *et al.* (2003).

4.2 Contact angles and surface tensions

Surface tension and contact angle measurements were obtained through the ADSA method, after a digital image acquisition. Figure 4 shows the pretreated image and the profiles obtained by ADSA algorithm. The general steps for measuring contact angles using ADSA include capturing a profile image of a captive bubble, processing the drop image to obtain the drop interface data and substrate surface data, and finding a solution to the set of first-order, nonlinear differential equations which produces a Laplacian curve which matches the drop interface (Neumann *et al.*, 2010). The solution is found by minimizing the distance between the Laplacian curve and the drop interface data at a point above the contact line. After a rotation of 180°, we digitalized the image with a MATLAB^{TM} built-in function, transforming it in a binary matrix.

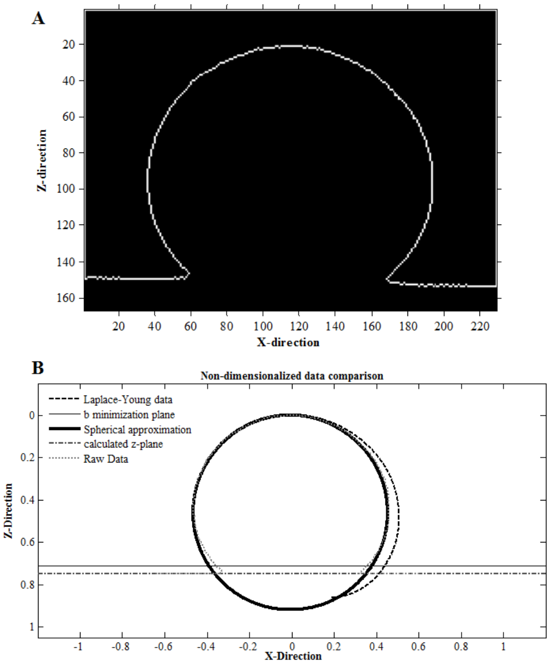

Fig. 4. Example of ADSA routine: (A) digitalized image; (B) optimization procedures showing raw data (dotted line) and spherical approximation (straight line).

Another function is performed in the binary image to extract the drop interface data (Fig. 4-A). Next, we can insert physical parameters of liquid phase, such as density, and gravimetric constant. Then, a numerical integration of Laplace equation of capillarity was performed using Runge-Kutta method with variable step side, as described by Neumann *et al.* (2010). The solution can be varied by changing the boundary conditions. In Fig. 4-B the image after the ADSA routine treatment is showed. The ADSA routine gives contact angles (θ) and surface tension (γ) as output values.

Figure 5 reports the θ for the four cholesterol solutions. In our experiments, the behavior is quite different in all samples. In hexane and *iso*-octane (Figs. 5A-B), the increase in cholesterol concentration gives a progressive decrease of contact angles. Oppositely, in *iso*-dodecane, a linear increase of contact angle was found (Fig. 5C), whereas in toluene, a marked increase is followed by a slight diminution in angle value (Fig. 5D). Contact angle is the angle between the solid-liquid interface and the tangent to the liquid-liquid interface at the three-phase line, measured in a plane normal to the solid-liquid and the liquid-liquid interfaces. In the case of hexane and *iso*-octane, the increase in contact angle corresponds

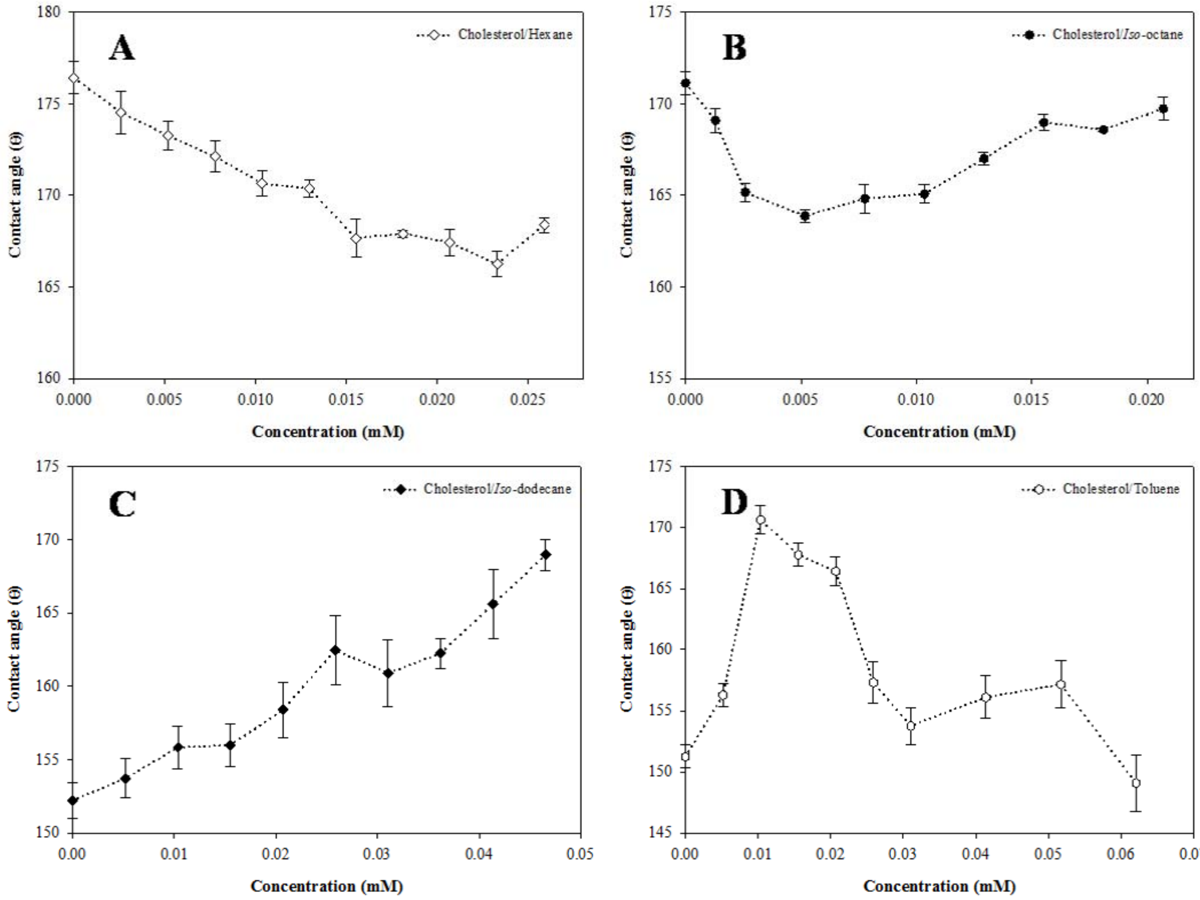

Fig. 5. Contact angles of cholesterol solutions at increasing concentrations.

to a greater surface wettability, as can be observed in Fig. 3. Quartz is a high-energy hydrophilic solid, and the surfactants molecules depend on their nature being able to interact with the quartz surface by van der Waals, acid-base and electrostatic forces (Zdziennicka *et al*., 2009). Amphipatic surfactant molecules are oriented with their polar heads towards the solid and their hydrophobic tails towards water. Adsorption in such a way occurs with ionic or polar solids when there are strong interactions between the hydrophilic groups in the surfactant and the ionic or polar sites on the solid. Such adsorption makes the surface of solids more nonpolar (Zdziennicka *et al*., 2010). In the case of *iso*-dodecane, our results are in contrast to Serrano-Saldaña *et al*. (2004), who pointed out that an increase of surfactant concentration causes a decrease in the *n*-dodecane/aqueous phase contact angles. Apparently, the contact angle value is related to drop shape and their progressive flattening, more than the wettability (Fig. 2).

At the center of contact angle research is the Young equation:

$$\gamma_{AB}\cos\theta_{SAB} = \gamma_{SB(A)} - \gamma_{SA(B)} = W_{SAB} \tag{9}$$

Here, θ_{SAB} denotes the angle, as measured in liquid A, and the phases in parentheses have saturated the immediately preceding phase. W_{SAB} is defined as adhesion tension. A strictly rigorous nomenclature would be yet more complicated; we simply assume that *A* and *B* are saturated by the solid and further take it for granted that the two phases at a particular interface are mutually saturated (Adamson *et al*., 1997). Molecular interactions between drop liquid and surface determine the primary surface/interfacial tensions; the surface/interfacial tensions then determine the contact angle. So, the perceived ‘surface tension components’ cannot be determined directly from contact angles through the Young equation.

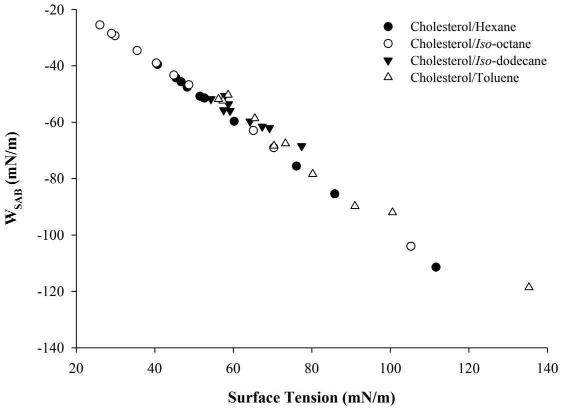

Fig. 6. Dependence between adhesional tension (W_{SAB}) and surface tension (γ) for organic solutions of cholesterol.

The dependence between $\cos\theta$ and surface tension of aqueous solution of nonionic, anionic surfactants are so complicated that it is difficult to find the critical surface tension of quartz wetting (γ_C) by extrapolation (Adamson *et al.*, 1997; Zdziennicka *et al.*, 2010). A rectilinear relation was established empirically between the cosine of the contact angle and the surface tension (Zisman, 1964; Zdziennicka *et al.*, 2010) for each homologous series of organic solutions (especially for hexane and *iso*-octane). However the low values of correlation does not allow an efficient determination of γ_C (data not shown).

Figure 6 shows the linear relationship between adhesion and surface tensions for cholesterol solutions. We found a good coefficient of determination for all tests ($R^2 > 0.99$). The work of adhesion between the solid and aqueous solution WSAB is composed of a constant contribution due to van der Waals interactions. A negative adhesion tension indicates that the denser phase (water) preferentially wets the solid surface. The negative slopes of the linear dependence between the adhesional and surface tension of solutions indicate that adsorption of the surface active solution at the quartz interface increase with the addition of cholesterol. In our case, the behavior is quite similar in all samples (Fig. 6), because it depends more on the surfactant than the solvent used, as described by Zdziennicka *et al.* (2010). These authors studied the wettability of quartz in the presence of a nonionic surfactant, finding that the slope of the curves is similar when using different alcohols. Finally, in Fig. 7, we plotted W_{SAB} vs. cholesterol concentration, observing a parabolic increase of adhesion tension.

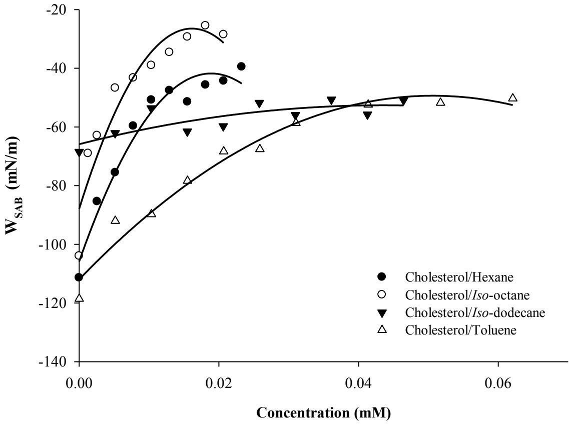

Fig. 7. Dependence between adhesional tension (W_{SAB}) and concentration for organic solutions of cholesterol.

The maximum point is found at concentrations that correspond to the appearance of spontaneous crystallization, a phenomenon which, as mentioned previously, is similar to the spontaneous emulsification observed in other systems (Ogino *et al.*, 1981; Pautot *et al.*, 2003). Clearly, the precipitation of cholesterol in crystalline form subtracts surfactant capacity to the system, causing a consequent decrease in the adhesion tension.

4.3 Application of Szyszkowski-Langmuir model

Figure 8 reports the graphs of experimental results as predicted by the Szyszkowski-Langmuir model. With the exception of the isotherm representing the cholesterol/*iso*-dodecane solution (Figure 5C), the Szyszkowski equation appears to fit the data points quite well, with $R^2 > 0.98$ for cholesterol/*iso*-octane and cholesterol/toluene mixture (Table 1). The Szyszkowski-Langmuir relation has been extensively and successfully used to describe the behavior of aqueous solutions of surface-active solutes, in which, ideally, whether for bulk or surface solutions, i.e., conformity to Raoult's law, where activity coefficients are equal to unity at all concentrations, would be considered extremely unlikely (Ross *et al.*, 1983). As can be seen in Fig. 8, the equation does not adjust well to high concentration values, corresponding to the spontaneous crystallization of cholesterol. For solutes of greater surface activity, Szyszkowski-Langmuir adsorption is not observed throughout the whole range of concentration below the critical micelle concentration (Ross *et al.*, 1983; Kolev *et al.*, 2002).

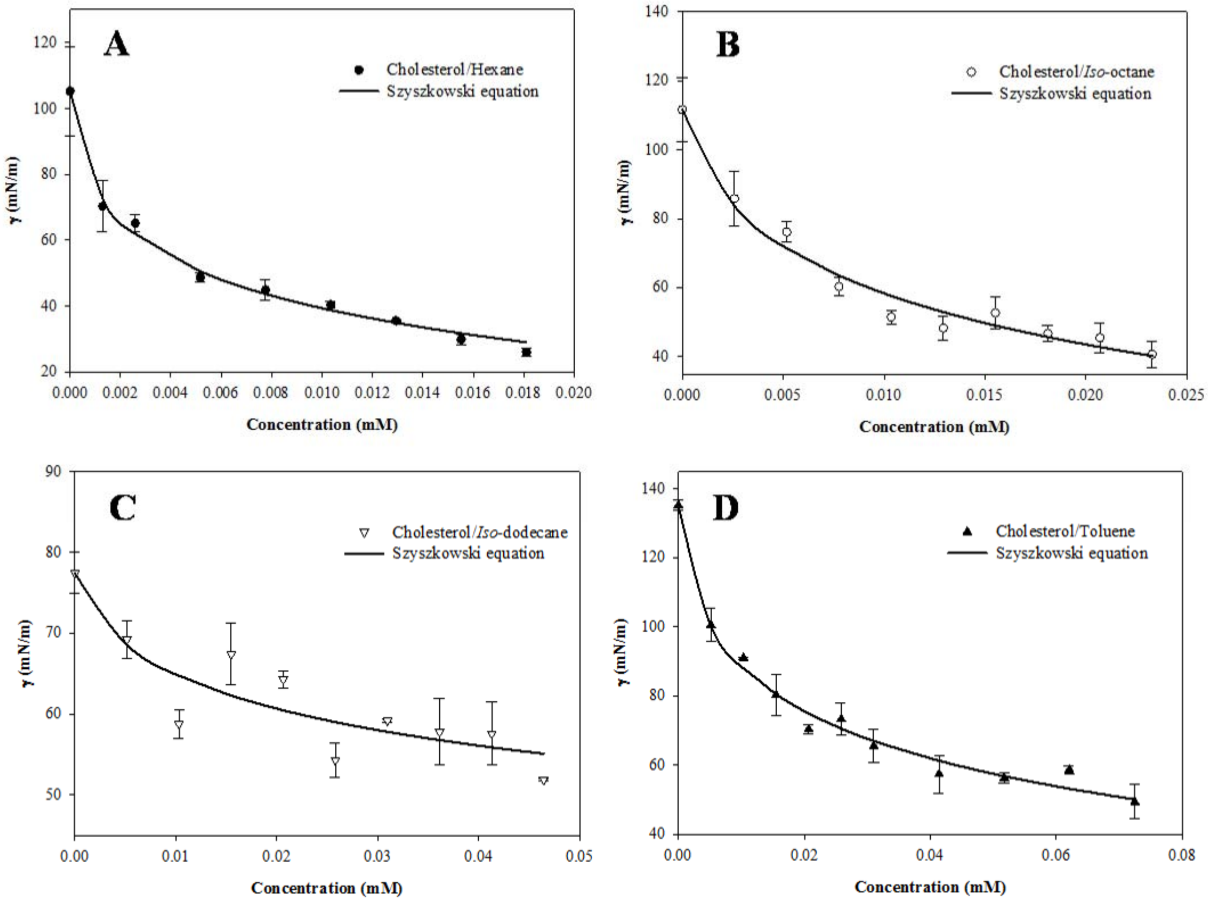

Fig. 8. Surface tension of cholesterol solutions at increasing concentrations. *Points*: experimental values, lines: values calculated by the Szyszkowski-Langmuir model.

The curves show a rapid decrease of γ, as a result of the surfactant activity of cholesterol at the interface, in contrast to what was affirmed by Ogino *et al.* (1981), who pointed out that cholesterol and oleic acid would be less influential in orienting interfacial molecules. It should be mentioned that Ogino *et al.* used soybean lecithin as a comparison, which has a very strong surfactant activity even at low concentrations. Furthermore, the results of these authors indicate that surfactant activity of cholesterol is higher where the organic phase is represented by nonpolar molecules (such as alkanes), whereas it is lower in fatty acids or triglycerides. The interaction between cholesterol and organic molecules greatly depends on the nature of the hydrocarbon chains, and it was suggested that this interaction was mainly due to London dispersion forces between the hydrophobic chain of alkanes and steroid nucleus of cholesterol. Table 1 shows the fitting parameters obtained from the application of Szyszkowski-Langmuir isotherm. The limit value of interfacial concentration (γ_∞) is very close in hexane and toluene solution, whereas it is smaller in *iso*-dodecane and *iso*-octane. In alkanes with larger side chains, cholesterol covers a smaller area at the interface, since a more ordered and compact structure is possible than in those with larger side chains. In the Szyszkowski-Langmuir model (nonlocalized adsorption), the γ_∞^{-1}) is defined as the area excluded by the molecule itself (Kolev, 2002). These last values are 45.05, 58.82, 353.35 and 50.76 Å2, for hexane, *iso*-octane, *iso*-dodecane and toluene, respectively. These results do not agree with Peltonen *et al.* (2001), who studied the effect of alkanes on the activity of sorbitan surfactants. They pointed out that as the chain lengths of the hydrocarbon at the oil phase increases, the molecular area decreases. However, sorbitans present hydrophobic tails that can positively interact with the hydrocarbon phase, whereas steroid nuclei in cholesterol molecules tend to pack together. Finally, we obtained Gibbs standard free energies of adsorption (ΔG^0). This value is similar to that of toluene and hexane, whereas it is minimal in the *iso*-octane/cholesterol system. As can be inferred from the negative values of the ΔG^0, in all cases the adsorption process occurs spontaneously. It is well known (Liu, 2009) that for diluted solutions the thermodynamic equilibrium constant of adsorption would be reasonably approximated by the Langmuir equilibrium constant (K_L), and thus the use of the Langmuir equilibrium constant for calculation of ΔG^0 is acceptable.

Conclusions

Our results confirm the role played by cholesterol as a surfactant in organic solvents at the oil/water interface. We observed a clear decrease of surface tension in all systems, accompanied by perceptible changes in drop shapes. Furthermore, the increase of interface concentration results in the formation of crystalline agglomerates below saturation. Contact angle behavior is different in all samples, suggesting a marked effect of drop shape. The application of Young's equation indicates that the denser phase (water) preferentially wets the quartz surface, giving a negative adhesion tension. The Szyszkowski-Langmuir model fits accurately with experimental data, but a higher cholesterol concentration (close to saturation) we speculate that interactions between molecules could be the cause of a deviation from the theoretical model.

References

Adamson, A.W., Gast, A.P. (1997). *Physical Chemistry of Surface*, 6th Ed., John Wiley & Sons, Inc.

Chen, P., Kwok, D.Y., Prokop, R.M., del Rio, O.I., Susnar, S.S., Neumann, A.W. (1998). Axisymmetric Drop Shape Analysis (ADSA) and its application. *Studies in Interface Science 6*, 61-138.

Chen, P., Lahooti, S., Policova, Z., Cabrerizo-Vilchez, M.A., Neumann, A.W. (1996). Concentration dipendence of the film pressure of human serum albumine at the water/decane interface. *Colloids Surface B 6*, 279-289.

Crenmer, P.S., Boxer, S.G. (1999). Formation and spreading of lipid bilayers on planar glass support. *Journal of Physical Chemistry B 103*, 2554-2559.

Demel, R.A., Joos, P. (1968). Interaction between lecithins and cholesterol at the air-water and oil-water interfaces. *Chemistry and Physics of Lipids 2*, 35-46.

Fahti-Azarbayjani, A., Jouyban, A., Chan, S.Y. (2009). Impact of surface tension in pharmaceutical studies. *Journal of Pharmaceutical Sciences 12*, 218-228.

Heimburg T. (2007). *Thermal Biophysics of Membrane*. Wiley-VCH, Weinheim.

Hoorfar, M., Neumann, A.W. (2004). Axisimmetric Drop Shape Analysis (ADSA) for the determination of surface tension and contact angle. *The Journal of Adhesion 80*, 727-743.

Kadota, K., Shirakawa, Y., Matsumoto, I., Shimosaka, A., Hidaka, J (2007). Formation and morphology of asymmetric NaCl particles precipitaded al liquid-liquid interface. *Advanced Powder Technology 18*, 775-785.

Kitayama, A., Yamanaka, S., Kadota, K., Shimosaka, A., Shirakawa, Y., Hidaka J (2009). Diffusion behavior in a liquid-liquid interfacial crystallization by molecular dynamics simulations. *Journal of Chemical Physics 131*, 174707.

Kolev, V.L., Danov, K.D., Kralchevsky, P.A., Broze, G., Mehreteab, A. (2002). Comparison of the van der Vaals and Frumkin adsorption isotherms for sodium dodecyl sulfate at various salt concentration. *Langmuir 18*, 9106-9109.

Liu, Y. (2009). Is the free energy change of adsorption correctly calculated? *Journal of Chemical & Engineering Data 54*, 1981-1985.

Medina-Meza, I.G., Rodriguez-Estrada, M.T., Lercker, G., García H.S. (2011). Unusual oxidative pattern in thermo-oxidation of dry films of cholesterol. *Revista Mexicana de Ingeniería Química 10*, 47-57.

Neumann, A.W., David, R., Zuo, Y. (2010). *Applied Surface Thermodynamics*, 2nd Ed., CRC Press.

Ogino, K., Onishi, M. (1981). Interfacial action of natural surfactants in oil/water system. *Journal of Colloid and Interface Science 83*, 18-25.

Pautot, S., Frisken, B.J., Cheng, J., Xie, X.S., Weitz, D.A. (2003). Spontaneous formation of lipid structures at oil/water/lipid interfaces. *Langmuir 19*, 10281-10287.

Peltonen, L., Hirvonen, J., Yliruusi, J. (2001). The behaviour of sorbitan surfactants at the water-oil interface: straight-chained hydrocarbons from pentane to dodecane as an oil phase. *Journal of Colloid and Interface Science 240*, 272-276.

Prokop, R.M.; Jyoti, A., Eslamian, M., Garg, A., Mihaila, M., del Río, O.I., Susnar, S.S.; Policova, Z.; Neumann, A.W. (1998). A study of captive bubbles with axisymmetric drop shape analysis. *Colloid Surface A*, 131, 231-247.

Ross, S., Morrison, I.D. (1983). On the alleged ideality of Szyszkowski-Langmuir adsorption. *Journal of Colloid and Interface Science 91*, 244-247.

Serrano-Saldaña, E., Domínguez-Ortiz, A., Pérez-Aguilar, H., Kornhauser-Strauss, I., Rojas-González, F. (2004). Wettability of solid/brine/n-dodecane systems: experimental study of the effects of ionic strength and surfactant concentration. *Colloid Surface A 214*, 343-349

Stalder, A.F., Melchior, T., Müller, M., Sage, D., Blu, T., Unser, M. (2010) Low-bond axisimmetric drop shape analysis for surface tension and contact angle measurement of sessile drops. *Colloid Surface A 364*, 72-81.

Uskoković, V. (2008). Surface charge effect involved in the control of stability of sols comprising uniform cholesterol particles. *Materials and Manufacturing Processes 23*, 620-623.

Wang, H.H. (2001). Analytical model of atherosclerosis. *Atherosclerosis 159*, 1-7.

Weinberg, R.B., Cook, V.R., DeLozier, J.A., Shelness, G.S. (2000). Dynamic interfacial properties of human apolipoproteins A-IV and B-17 at the air/water and oil/water interface. *Journal of Lipid Research 41*, 1419-1427.

Xie, A.J., Shen, Y.H., Xia, B., Chen, H.B., Ouyang, J.M. (2005). Thermodynamic study of bilirubin/cholesterol mixtures at the air/water interface. *Thin Solid Films 472*, 227-231.

Zdziennicka, A., Janczuk, B. (2010). Wettability of quartz in presence of nonionic surfactants and short chain alcohol mixtures *Journal of Colloid and Interface Science 343*, 594-601.

Zdziennicka, A., Szymczyk, K., Janczuk, B. (2009). Correlation between surface free energy of quartz and its wettability by aqueous solutions of nonionic, anionic and cationic surfactants. *Journal of Colloid and Interface Science 340*, 243-248.

Zisman, W.A. (1964) Relation of the equilibrium contact angle to liquid and solid constitution. In: *Contact Angle, Wettability, and Adhesion*, (F. Fowkes ed., Advances in Chemistry), Pp. 1-51. American Chemical Society: Washington, DC.