Effective solubility parameters of sucrose monoester surfactants obtained by inverse gas chromatography

C.R. de Schaefer, M.E.F. de Ruiz Holgado, E.L. Arancibia *

Departamento de Química, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán, Avda. Independencia 1800, 4000-San Miguel de Tucumán, Tucumán, Argentina

ARTICLE INFO

ABSTRACT

Two products with a high content of sucrose monoesters were obtained from the commercial products P1670 and S1670, using liquid chromatography. The separation progress was monitored by thin layer chromatography (TLC). Differential scanning calorimetry (DSC) between 293.15 K and 473.15 K was used to define the transition phase temperature of the sucrose ester mixtures. Specific retention volumes of twelve probe solutes were measured at four different temperatures using sucrose monoester blends as stationary phases. These blends were characterized using DSC and inverse gas chromatography (IGC) techniques. The thermodynamic properties determined by IGC show an increase in the solubility in the surfactant mixture as the source fatty acid chain length increases, and a decrease in the solubility with an increase of the monoesters/diesters ratio. The values obtained from "effective solubility parameters" are explained by the presence of mesophases in the products analysed as stationary phases. The values of the effective solubility parameters are lower than those obtained for commercial surfactants.

Published by Elsevier B.V.

1. Introduction

Sucrose surfactants have a hydrophilic head, which is a disaccharide, and an hydrocarbon tail, usually derived from a fatty acid esterified on the carbohydrate [1,2]. By controlling the degree of esterification and the nature of the fatty acid, sucrose esters with a wide range of hydrophilic-lipophilic balance (HLB) can be prepared. Sucrose surfactants are chemically or enzimatically synthesized [3,4]. They have received an increasing attention due to the need to produce less toxic and highly biodegradable surfactants. Besides, they have shown excellent emulsifying, stabilizing and foaming abilities. All these properties make them an interesting alternative for the food industry [5,6].

With the aim of improving the solubility capacity of food systems, interesting studies of phase diagrams, solubilities and microstructures of sucrose monoesters have been made [7,8]. Surface properties of sucrose esters depend on the amount of substitution of the polar head by fatty acids. Commercial sucrose esters are mixtures of mono- and poly-substituted esters. The percentage of monoesters is commonly used to identify the sucrose esters mixtures and to give information about its hydrophilicity [9,10].

The values of the solubility parameters of two materials allow us to estimate their degree of miscibility. Thus, solubility parameters have been used in the selection of solvents for diverse applications [11–13]. The relation between solubility parameters and interfacial properties of sucrose monoesters for predicting solubility and hydrophobicity of the above mentioned esters has been reported [14]. The results obtained by Yanke et al. [14] presents the results of studies on interfacial tension of sucrose esters which show a decrease and a subsequent increase in the oil-water interfacial tension as the hydrocarbon chain length or the proportion of diesters and higher esters increase [15–17].

In previous studies, the physicochemical characterization of commercial sucrose monoesters was made by determining solubility and solubility parameters by inverse gas chromatography (IGC) [18,19].

In this paper, we have done the physicochemical characterization by using activity coefficients, solubility parameters and Flory–Huggins interaction parameters of two products of sucrose monoester blends with a high content of sucrose monoesters. The importance of this study is based on the comparisons that can be established between pure monoesters and commercial products (S1670 and P1670) as surfactants. This work is thus important for establishing correlations between HLB, monoesters content in sucrose derived surfactant and solubility parameters; this knowledge is necessary for the design of new emulsifiers

---

* Corresponding author.
E-mail address: earancibia@herrera.unt.edu.ar (E.L. Arancibia).

based on these surfactants. These studies, that can help in choosing the best systems for industrial purposes, have not been carried before.

IGC is a quick and efficient method to determine physico-chemical properties not only for solutions but for other systems (gas–liquid, gas–solid) as well [20–23].

2. Materials and methods

The studied surfactants are sucrose monoester blends with a small quantity of diesters. They were separated from Ryoto® sugar esters commercial surfactants P 1670 and S 1670 (donated by Mitsubishi–Kasei Food Corp. Japan) by liquid chromatography and used as stationary phases. These commercial surfactants are made of approximately 80% monoesters and 20% polyesters from the ester composition. Sucrose monoester blends will be identified as follows: MP (separated from P 1670 as powder), and MS (obtained from S 1670 as powder).

2.1. Liquid chromatography (LC) and thin layer chromatography (TLC)

Liquid chromatography (30×2 cm column, with 60 F254 silica gel, 70–230 mesh) was done by following the experimental procedures of Gupta et al. [24]. The column was loaded with up to 1 g of the commercial product. By collecting 10 mL fractions with an ethyl acetate–methanol gradient program (0–100% methanol), impurities were separated and the products MP and MS obtained.

The composition of collected fractions was studied by thin layer chromatography (TLC) using chloroform: methanol: water: acetic acid (70:28:2:2) to elute samples and 30% sulphuric acid aqueous solution as the developer [25]. The R_f value is a convenient way to express the position a substance on a developed chromatogram. The values of R_f obtained for monoesters (0.2), diesters (0.3) and polyesters (0.7) agreed with literature data [17]. The fractions of interest containing pure monoester isomers were evaporated using a vacuum evaporator.

The results of the analysis of the fractions containing MP and MS blends using high performance liquid chromatography (HPLC) [25] showed chromatograms with two groups of peaks. In the chromatograms of the MP product, the first group of peaks accounted for 93% (by calculating the normalized areas under the peaks) while the second group is 7% of the total area. In the case of the MS product, the first group of peaks accounted for 33% and the second group for 67% of the total area. By comparing these to literature data on the composition of P1670 and S1670 [25], it can be inferred that the first group of peaks consist of sucrose monopalmitate isomers and the second group of peaks consist of sucrose monoesterate isomers.

The sucrose ester blends were analyzed by nuclear magnetic resonance (NMR) with a Bruker AC spectrometer at 200 MHz for ^{1}H NMR using CDCl$_3$ as solvent. Although those samples did not contain an important amount of diesters and polyesters, the NMR spectrum showed that they contained more than one isomer. This fact could be explained by considering the prevailing amount of esterificated monoesters in the positions 6 and 6′ of the sucrose molecule and also by the presence of a minor amount of diesters.

In the following scheme, the structure of sucrose monoesters is shown (Scheme 1):

The characteristics of the used sucrose monoester blends and those of the commercial surfactants from which the former were obtained have been included as a Supporting Material (S.M.) (Table I in Supplementary material).

Chemical Structure of Sucrose Monostearate
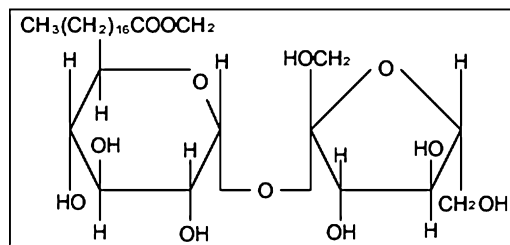
Scheme 1.

2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to define the transition phase temperature of the sucrose ester mixtures. DSC was performed using a Perkin Elmer DSC 6 calorimeter, between 293.15 K and 473.15 K, with a scanning rate of $10°$ min^{-1} and using of 5–10 mg for pure materials and 10–15 mg of other materials collecting over chromatography support.

The samples of MP and MS products analysed by DSC were deposited over Chromosorb W. The columns contained approximately 10% of MP or MS blends.

2.3. Inverse gas chromatography (IGC)

Measurements were performed using a Hewlett Packard, HP 6890 series, GC System, equipped with a flame ionization detector. Column temperatures were measured in a range between 338.1 K and 368.1 K with an iron–constantan thermocouple placed in the direct environment of the column. The temperature stability during experiments was of ±0.2 K.

Nitrogen was used as a carrier gas; flow rates were measured at the beginning of the experiments with an air-jacketed soap film flowmeter, placed at the outlet of the detector. Inlet pressures were measured with a micrometric syringe (through the injector septum) which was connected to an open branch mercury manometer.

The influence of the carrier gas on the retention of the probe solutes and the adsorption effect in the gas–liquid interface, which could be detected in a column with different percentages of stationary phase, were analyzed in the study of the commercial surfactant P1670 [18]. It was considered that the systems under study here (MP and MS products) show a similar behaviour, so the carrier gas flow was maintained between 20 and 60 ml/min, usually in the 40 ml/min zone.

Chromosorb W, AW, DMCS, 60/80, was used as a solid support and the sucrose monoester blends were dissolved in methanol. The packing was prepared in a rotary evaporator under a flow of dry nitrogen and was kept in a dry atmosphere, before filling the columns. The used columns were stainless steel tubes of 180 cm length and 0.23 cm id. Two columns were used to obtain the reported data: one for the MP product containing 2.2274 g of a 9.95% packing (w/w), and the other for the MS product containing 2.2204 g of a 11.41% packing (w/w).

The employed solutes were *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane, benzene, toluene, ethyl acetate, dichloromethane, trichlorometane and carbon tetrachloride. All solutes were of >99.0% purity (Merck) and used without further purification. Solutes were injected with 10 μL Hamilton syringes, as vapour in equilibrium with pure liquid. The peaks were symmetric for all the solutes and for the whole range of stationary phase concentrations. The injector was kept at 423. K and the detector at 453. K.
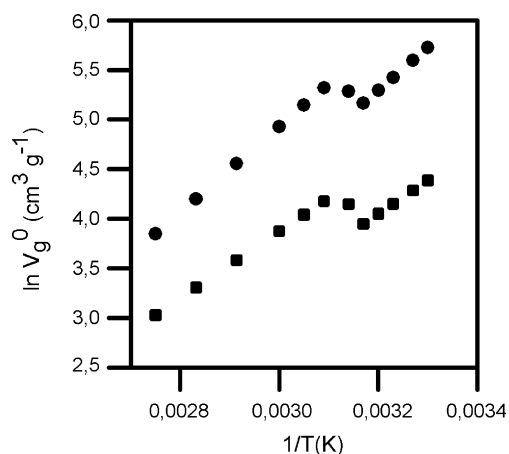
Fig. 1. Van't Hoff retention diagram for probe solutes in MP products: (●) *n*-octane; (■) carbon tetrachloride.

3. Results

Many studies on the thermodynamic behaviour of mixtures of sucrose esters with water have been made [9,26], in contrast to the few studies made on pure sucrose esters [27].

The MP product was analyzed by DSC from 293.15 K to 473.15 K. It showed a peak at 324.95 K, due to the transformation of an amorphous phase into a crystalline liquid phase, and two smaller peaks, one at 428.15 K and the other at 456.15 K. The MS product showed two peaks at 301.65 K and 308.25 K a small peak at 323.15 K and a bigger peak at 461.25 K.

In order to define the retention mechanism and the corresponding melting zones of the MP and MS products, an analysis of the retentive behaviour of two probe solutes, *n*-octane and carbon tetrachloride, was performed between 303.1 K and 373.1 K. The columns contained nearly 10% of stationary phases.

The retention diagram of ln V_g vs. $1/T$ for two probe solutes in MP and MS products coated on Chromosorb W, AW, DMCS, 60/80, are shown in Figs. 1 and 2. On heating the solid, the retention decreases until the solid-to-liquid crystal transition is reached. Then, there is an increase in retention which, decreases with an increase in temperature once the system phase change finished. The MP product shows a change in the chromatographic retention at the 318.1–323.1 K zone, which fits the DSC data, and the MS product exhibits a change in the retention close to 313.1 K. Both MP and MS show the classic retentive behaviour of phase transition in liquid crystals [28].
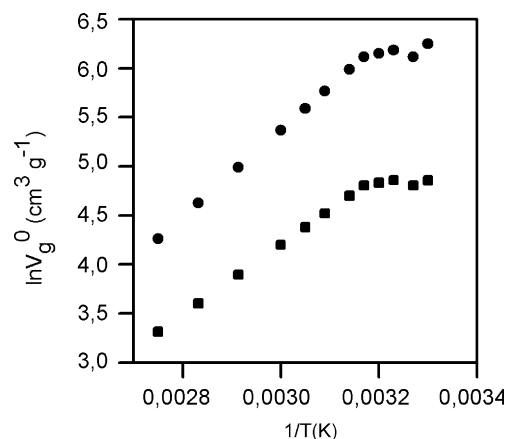

Fig. 2. Van't Hoff retention diagram for probe solutes in MS products: (●) *n*-octane; (■) carbon tetrachloride.

Retention times (t_R) were measured with a Chem Station system and the specific retention volumes (V_g^0) were calculated with the following expression [29]:

$$V_g^0 = \frac{j(F_f/w)(273.15/T_f)(t_R - t_0)(p_0 - p_w)}{p_0} \tag{1}$$

where j is James–Martin compressibility correction factor, p_0 represents the outlet column pressure, F_f is the flow rate measured at pressure p_0 and temperature T_f, w is the mass of stationary phase into the column, p_w is the water vapour pressure at T_f, and t_0 is the dead time (retention time of the methane peak).

Specific retention volumes were fitted to the following equation [29]:

$$\ln V_g^0 = \frac{\Delta H_s}{RT} + \text{constant} \tag{2}$$

where ΔH_s is the sorption heat. The values obtained for ΔH_s, as well as their respective standard deviations, were calculated using Marquardt-Levenberg's algorithm [30] and are shown in S.M. (Table II).

The weight fraction activity coefficient at infinite dilution of the solute Ω_1^∞ is related to V_g^0 according to the following equation [31]:

$$\ln \Omega_1^\infty = \ln \left(\frac{273.15R}{V_g^0 p_1 M_1} \right) - \frac{p_1(B_{11} - V_1)}{RT} \tag{3}$$

where V_1 and M_1 are the molar volume and the molar mass of the solute, respectively, p_1 is the saturated vapour pressure of the solute at temperature T, and B_{11} is the second virial coefficient of the solute in the vapour phase (calculated with Tsonopoulos correlation using critical constants tabulated in Reid et al.[32]). The vapour pressure was calculated using Antoine's equation and the coefficients were taken from Riddick et al. [33] and the solute densities at 323.15–373.15 K were estimated following Dreisbach's compilation [34].

In Table 1 we have included weight fraction based activity coefficient values at infinite dilution for each of the probe solutes at 338.1 K for the MS and MP products.

It has been suggested that $\Omega_1^\infty > 5$ are indicative of poor polymer-solvent systems [35], while lower values characterise good solubility. As shown in Table 1, Ω_1^∞ values for all systems are higher than these values except that of chloroform and one value of carbon tetrachloride in the MS product. Table 1 reveals that Ω_1^∞ values for all the solutes in the MP product are higher than those in the MS one, which are indicative of a lower solubility.

Table 1 also shows that hydrocarbons show higher values, indicating a weak interaction between the probe solute and the sucrose monoester blend. This fact shows that the ordering within the mesophase has an unfavourable effect on the mixing. The aromatic probes have lower values than the aliphatic ones, indicating that the former are more compatible. The chloride derivatives, on the contrary, show low values of Ω_1^∞, suggesting an interaction with the surfactants.

The methodology of IGC allows us to obtain Flory–Huggins interaction parameters [36], which reflect the interactions involved between a research material placed in the chromatographic column and the probe solutes injected in the column and transported by a carrier gas. The relation between the chromatographic retention data and the Flory–Huggins interaction parameter $\chi_{1,2}^\infty$ is given by [23,29,37]

$$\chi_{1,2}^\infty = \ln \Omega_1^\infty - \ln \frac{\upsilon_1}{\upsilon_2} - \left(1 - \frac{V_1}{V_2} \right) \tag{4}$$

where the molar volume relationship was neglected in relation to the unity and υ_1 and υ_2 are the specific volumes of the solute and the stationary phase, respectively.

Table 1
Values of activity coefficients at infinite dilution in terms of weight fraction (Ω_1^∞) in MP and MS products at 338.1 K

Solutes	Ω_{MP}^∞	Ω_{P1670}^∞ [a]	$\Omega_{MP}^\infty/\Omega_{P1670}^\infty$	Ω_{MS}^∞	Ω_{S1670}^∞ [b]	$\Omega_{MS}^\infty/\Omega_{S1670}^\infty$
Hexane	16.6	7.82	2.13	10.9	6.31	1.73
Heptane	14.9	7.24	2.06	9.80	5.66	1.73
Octane	13.7	6.37	2.15	8.84	5.40	1.64
Benzene	9.64	5.32	1.81	7.46	4.37	1.71
Toluene	8.94	4.75	1.88	6.72	4.40	1.53
Cyclohexane	12.8	6.64	1.93	9.00	5.29	1.70
Methylcyclohexane	11.6	5.70	2.04	8.02	4.70	1.71
Dichloromethane	7.28	3.88	1.87	5.87	3.25	1.81
Trichloromethane	4.05	2.15	1.89	3.06	1.82	1.68
Carbon tetrachloride	5.29	2.34	2.26	3.84	2.27	1.69
Ethyl acetate	12.9	8.27	1.56	11.2	8.93	1.26

[a] Calculated values from reference [18].
[b] Calculated values from reference [19].

The $\chi_{1,2}^\infty$ parameter can be considered as an indicator of the behaviour of the solute, which acts as a solvent in the stationary phase. High values of this parameter correspond to substances that behave as poor solvents. The values of $\chi_{1,2}^\infty$ in Table III in Supplementary material for all the probe solutes in the different products are higher than 0.3 and lower than 2.0. The latter is critical for the miscibility of small molecules [38]. The values of the interaction parameters are lower in the MS product than in the MP product. This fact shows that the solubility in these systems increases with the hydrocarbon chain length, i.e., when the hydrophobicity of the surfactant increases.

The solubility parameter model has been successful in describing the thermodynamic properties of solutions, especially when the materials in the column and the volatile solutes are non-polar.

The relationship between the solubility parameter of two components and the interaction parameter $\chi_{1,2}^\infty$ is given by [39,40]:

$$\chi_{1,2}^\infty = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{5}$$

where $\chi_{1,2}^\infty$ has free energy characteristics; that is,

$$\chi_{1,2}^\infty = \chi_H^\infty + \chi_S^\infty \tag{6}$$

The estimated solubility parameters of the surfactants are obtained using a combination of the lattice model of solutions and the solubility parameter theory [39,40]:

$$\chi_{1,2}^\infty = \frac{V_1(\delta_1 - \delta_2)^2}{RT} + \chi_S^\infty \tag{7}$$

where χ_S^∞ is the entropic factor of the interaction parameter, and δ_1 is the solubility parameter of the solute. The solubility parameter of the surfactant, δ_2, can be calculated by fitting $\chi_{1,2}^\infty$ and δ_1 to the following equation:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{1,2}^\infty}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^\infty}{V_1}\right) \tag{8}$$

The plot of the first term of the above equation versus δ_1 allows us to get the solubility parameters for each one of the sucrose surfactants at different temperatures. The values of δ_1 were calculated at each temperature by a derivative expression of the Haggenmacher equation [41].

The solubility parameters of the two sucrose monoester blends used in this experiment, at 338.1 K, together with the slope, the ordinate values of the linear equation ($\delta_2 = a - bt$) (where t is the temperature in °C) and their standard deviations were all included in Table IV in Supplementary material.

The solubility parameter values for both products in (MPa)$^{0.5}$ at 298.15 K, MP(16.23) and MS(16.21), calculated by using Eq. (8),

are lower than the corresponding parameters obtained for surfactants P1670(16.8) and S1670(16.8) taken from the literature [18,19], which have been recalculated from the interaction parameters $\chi_{1,2}^\infty$ using relation (4).

4. Discussion

In Table 1, we have presented weight fraction based activity coefficient values at 338.1 K obtained for commercial surfactants [18,19] together with the activity coefficient values of the MP and MS products. The activity coefficient values at infinite dilution for each of the probe solutes for the MS and MP blends are higher than the corresponding values obtained for the source commercial surfactants, reveling a lower solubility of these solutes in the MS and MP products.

The relationship between both activity coefficients for hydrocarbons is constant, with values close to 1.7 in the case of the relation $\Omega_{MS}^\infty/\Omega_{S1670}^\infty$ and close to 2.0 for the relation $\Omega_{MP}^\infty/\Omega_{P1670}^\infty$. The polar probe solutes have values quite similar to those mentioned above, except in the case of ethyl acetate in both relations. Even though these values are far from 1.14 found by Kelker [42] (for the relation between activity coefficients for hydrocarbons in 4,4′-azoxyanisole between the mesophase and an isotropic liquid), the constancy of the indicated values shows similar kind of interactions between the probe solutes and both phases.

Huang et al. [43] have pointed out that the use of transference properties between two solvents could screen the influence of the interaction of the pure liquid solute when comparing thermodynamic properties. Fig. 3 shows a graph of the activity coefficient logarithm at infinite dilution obtained in the S1670 product vs. those obtained in the MS product. Fig. 3 also contains the values obtained in the MP product vs. those obtained in P1670. A linear relationship in the logarithmic graph provides a simple way of comparing the kind of interactions between the two surfactants and the probe solutes. A high correlation coefficient has been found in both graphs, with a noticeable separation of the ethyl acetate in the two cases. (An explanation of the behaviour of this probe solute is included in a related paper to be submitted). A constant value of transference Gibbs energy can be predicted from Flory's theoretical treatment in liquid crystals [44–46].

Due to the organized structure of the molecules of sucrose monoester blends in a mesophase, we can assume that the molecules of the probe solutes have different accessibility to the surface of the anisotropic solvent. This does not occur in the case of commercial products P1670 and S1670 (which show the behaviour of an isotropic liquid above the fusion zone), where the test molecules have free access to the whole surfactant molecules. Huang et al. [46] pointed out that in these cases the measured
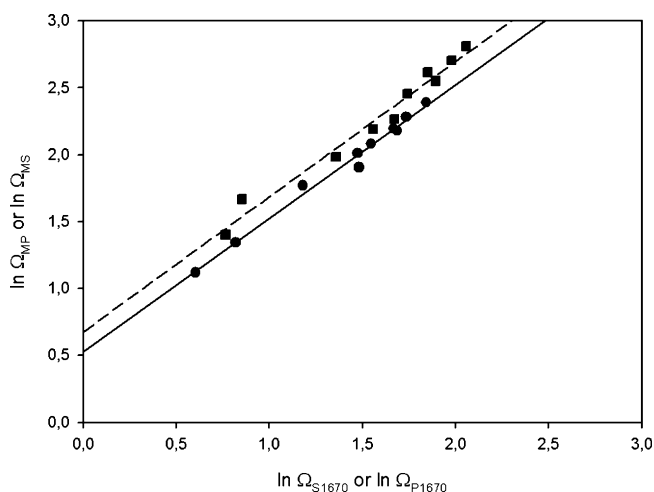
Fig. 3. Logarithm of weight fraction activity coefficient at infinite dilution of the probe solutes in MP or MS products as a function of logarithm of the weight fraction activity coefficient at infinite dilution of the solutes in P1670 or S1670 surfactants at 338.1 K: (●) solutes in MS/S1670; (■) solutes in PM/P1670.

Fig. 4. Logarithm of activity coefficient ratios of probe solutes as a function of molar volume of solutes at 338.1 K: (▼) solutes in SM/S1670 system; (△) solutes in PM/P1670 system.

solubility parameter could be the result of the interaction with functional groups. This solubility parameter is called the "effective solubility parameter" of the liquid crystal phase and can be estimated from the IGC measurements.

When the content of sucrose diesters and polyesters decreases in the MS and MP products, the hydrophilic nature of these mixtures should be greater than that of commercial surfactants S1670 and P1670 and thus, their solubility parameters should be higher as well. We do consider that this difference is a result of the presence of a mesophase and we could conclude that the solubility parameters obtained are similar to the so-called effective solubility parameters of Huang et al. [46].

Two explanations have been mentioned for the deviations of the solubility parameter model in the treatment of the data obtained for liquid crystals [47]: one is related to the effect of free volume and the other is the effect of the orientation of probe solutes in the stationary phase.

To study the possible reasons of the deviation of the solubility parameter model found in our results, we have plotted the activity coefficients relation logarithm of the MP/P1670 and MS/S1670 systems as a function of the molar volume and the solubility parameter of the probe solutes. In both cases, as it is seen in Figs. 4 and 5, the values are grouped around a constant value close to 1.4, with only the deviations of the polar solutes. From this point of view, it appears to be no tendency that could be related to the molecular size or an effect of interaction energy with the solutes.

Following Huang [47], we have compared the experimental values of the free energy of solution fitted by effect of size to their predicted values based on the solubility parameters. In Eq. (7) χ_{12}^{∞} represents the size-corrected free energy of solution and it is estimated as $RT\chi_{12}^{\infty}$, being the enthalpy of solution estimated on the basis of Eq. (7) as $RT\chi_H = (\delta_1 - \delta_2)^2 V_1$. The entropic term, estimated from the difference of these two terms, can be a negative or positive value and it represents the deviation from the solubility parameter model. Huang [47] found more appropriate to call this new entropic term "residual free energy of solution" because it includes interactions with enthalpic and entropic characteristics.

The second cause of the deviation of the model is the so-called orientation entropy [48] that includes the effect of the specific interaction between the probe solute and the stationary phase, and an effect of geometry of the probe solutes when passing from pure liquid solutes to the stationary phase.
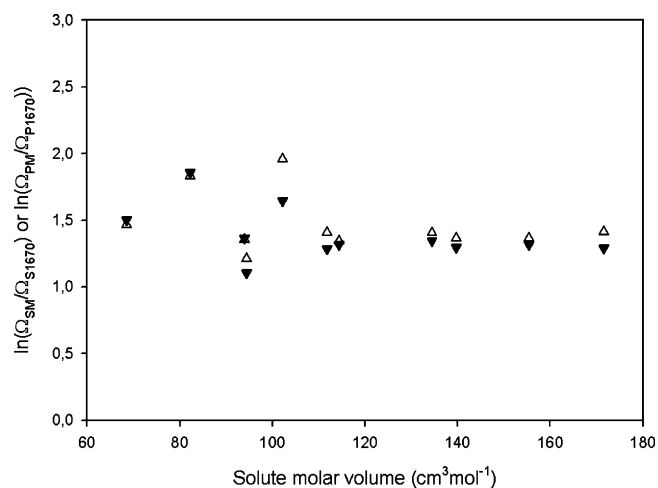
In Table 2 we have included the terms for $RT\chi_H$ and for the residual free energy (RFE) for the MP and MS products and we have also added those calculated for P1670 and S1670 with data from the literature [18,19].

The values of residual free energy of the probe solutes in the MS and MP products observed in Table 2 are positive and higher if compared to the values obtained in commercial surfactants S1670 and P1670.

Residual free energy terms for aliphatic hydrocarbons in the MP and MS products and in surfactants P1670 and S1670 at 338.1 K are shown in Fig. 6. The average percentage of increase in the value of the RFE for hydrocarbons (aliphatic, aromatic and cycloalkanes) in MS relative to S1670 is 70% and 62% in the case of MP and P1670 products. This would reveal the presence of a higher ordering in the MS and MP products than in the commercial products S1670 and P1670 when used as stationary phase in IGC.

In the polar probe solutes, the dispersion of values is large, ranging from small percentages for ethyl acetate to greater than 100% for chloroform. This is an evidence of the presence of specific interaction effects for this chlorinated derivative of methane with the mesophase in the case of the MS and MP products.
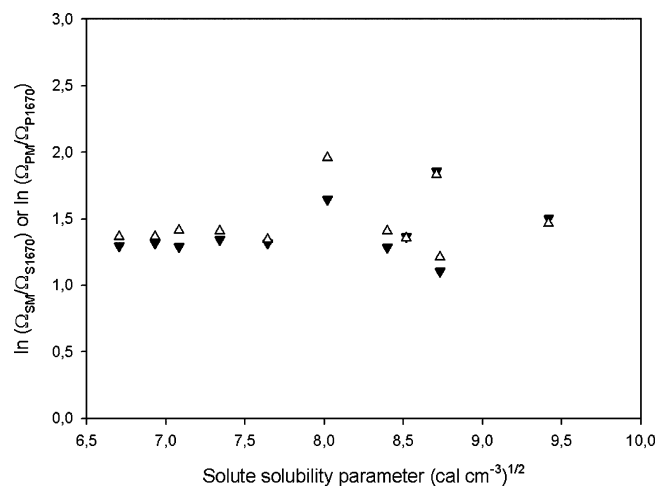
Fig. 5. Logarithm of activity coefficient ratios of probe solutes as a function of solubility parameters of solutes at 338.1 K: (▼) solutes in SM/S1670 system; (△) solutes in PM/P1670 system.

Table 2
$RT\chi_H$ and the residual free energy (RFE) of solution (cal mol^{-1}) of the probe solutes in MP and MS products and P1670 and S1670 surfactants at 338.1 K

Solutes	MP		P1670[a]		MS		S1670[b]	
	$RT\chi_H$	RFE	$RT\chi_H$	RFE	$RT\chi_H$	RFE	$RT\chi_H$	RFE
n-Hexane	17.	895.	65.	340.	17.	587.	77.	156.
n-Heptane	2.	867.	33.	325.	2.	556.	42.	148.
n-Octane	0.	832.	16.	301.	0.	511.	23.	157.
Benzene	201.	543.	121.	221.	202.	344.	107.	80.
Toluene	201.	487.	114.	150.	202.	269.	100.	19.
Cyclohexane	39.	840.	7.	362.	40.	551.	4.	230.
Methylcyclohexane	11.	774.	0.	305.	11.	496.	2.	147.
Dichloromethane	383.	443.	282.	174.	383.	271.	265.	45.
Trichloromethane	225.	313.	143.	−33.	225.	97.	130.	−155.
Carbon tetrachloride	95.	646.	41.	153.	96.	405.	33.	112.
Ethyl acetate	266.	752.	171.	549.	266.	632.	155.	590.

[a] Calculated values from reference [18].
[b] Calculated values from reference [19].

The analysis of the values obtained in the enthalpic term ($RT\chi_H$) in Table 2 shows a notorious decrease when passing from the values obtained in P1670 to MP and from S1670 to MS in aliphatic hydrocarbons. If only dispersive interactions are taken into account, it must be assumed that the greater hydrophilic character of the monoesters is present here.

The same reasoning applied to the behaviour of aliphatic hydrocarbons would explain the values found in the polar solutes for the enthalpic term in MS and MP with relation to the commercial products. There is an increase in the values of the enthalpic term in all the probe solutes with the notorious case of the high increase for cyclohexane and methylcyclohexane in both cases. We could point out that the rotational effects [49] could be mainly responsible for these values as they facilitate the arrangement of these molecules in the mesophase in relation to what occurs in the isotropic phase.

The solubility parameters estimated by Yanke et al. model [14] differ from those experimentally obtained by IGC in this laboratory (considering that MP and MS products are equivalent to sucrose monoesters), in about 50% (MP 58%, MS 55%).

Although the solubility parameters obtained by Yanke's model do not agree very well to the systems studied here our results are qualitatively consistent with their model. The hydrophobic character decreases and the solubility of the probe solutes decreases in the products with a high content of sucrose monoesters, unlike the behaviour of commercial products P1670 and S1670 which show a greater hydrophobic character and a higher solubility of the non-polar probe solutes.
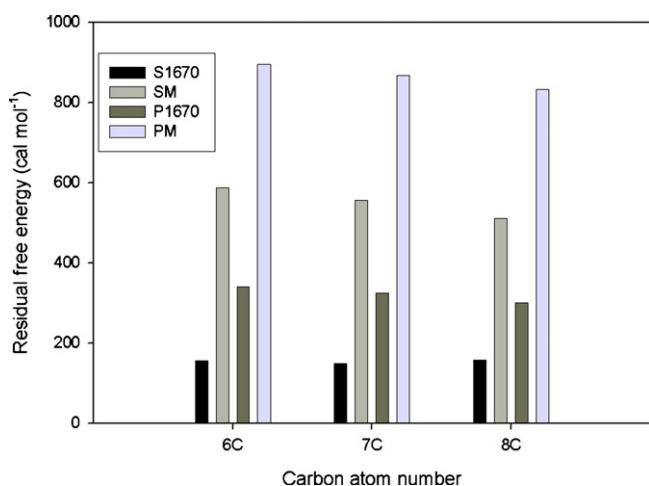
5. Conclusions

The thermodynamic characterization of two products obtained from commercial sucrose ester surfactants was performed by the first time using IGC. The interaction parameters allowed the calculation of the solubility parameter values. The values obtained from "effective solubility parameters" can be explained by the presence of mesophases in the products analysed as stationary phases. The values of effective solubility parameters are lower than the solubility parameter values obtained in commercial surfactants and than those obtained by an incremental method.

The high residual free energy values obtained in products with a high content of sucrose monoesters indicate a higher ordering when compared to commercial surfactants P1670 and S1670.

The presence of a mesophase could account for the absence of correlation (usually found for non-ionic surfactants) between the HLB number (hydrophilic-lipophilic balance) and the solubility parameter values of blends with high sucrose monoester content. These comparisons can help in choosing the best systems for industrial purposes.

Fig. 6. Comparison of residual free energy of solution values of aliphatic hydrocarbons in MP and MS products and P1670 and S1670 surfactants as a function of the number of carbon atoms of solutes at 338.1 K.

List of symbols

a	intercept of linear equation
b	slope of the linear equation
B_{11}	second virial coefficient
F_f	flow rate measured by flowmeter
ΔG^e	partial molar excess Gibbs energy of solution
ΔH_s	sorption heat
j	james-Martin compressibility correction factor
M_1	molar mass of the solute
p_0	outlet column pressure
p_w	water vapour pressure at T_f
p_1	saturated vapour pressure of the solute
R	universal gas constant
R_f	retention relation in TLC.
t	temperature($^\circ$C)
t_0	dead time of the column
t_R	retention time
T	absolute temperature (K)
T_f	flowmeter temperature
V_g^0	specific retention volume
υ_1	specific volume of the solute
υ_2	specific volume of the stationary phase

V_1	molar volume of the solute
V_2	molar volume of the stationary phase
w	mass of the stationary phase

Greek symbols

δ_1	solubility parameter of the solute
δ_2	solubility parameter of the stationary phase
$\chi_{1,2}$	flory-Huggins interaction parameter
χ_H	enthalpic contribution of the interaction parameter
χ_S	entropic contribution of the interaction parameter
Ω_1	weight fraction activity coefficient
∞	infinite dilution state

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2008.08.002.

References

[1] I.R. Vlahov, I. Vlahova, R.J. Linhart, J. Carbohydr. Chem. 16 (1997) 1–10.
[2] P. Gouéth, P. Gogalis, R. Bikanga, P. Godé, D. Postel, G. Ronco, P. Villa, J. Carbohydr. Chem. 13 (1994) 249–272.
[3] A. Ducret, A. Giroux, M. Trani, R. Lortie, J. Am. Oil Chem. Soc. 73 (1996) 109–113.
[4] D.B. Sarney, E.N. Vulfson, Trends Biotechnol. 13 (1995) 164–172.
[5] J.M. Franco, M. Borjano, A. Guerrero, J. Muñoz, Food Hydrocolloids 9 (1995) 111–121.
[6] C.C. Akoh, J. Am. Oil Chem. Soc. 69 (1992) 9–13.
[7] O. Glatter, D. Orthaber, A. Stradner, G. Scherf, M. Fanun, N. Garti, V. Clement, M.E. Láser, J. Colloid Interface Sci. 241 (2001) 215–225.
[8] M. Fanun, E. Wachtel, B. Antalek, A. Aserín, N. Garti, Colloids Surf. A: Physicochem. Eng. Asp. 180 (2001) 173–186.
[9] A.-S. Muller, J. Gagnaire, Y. Queneau, M. Karaoglanian, J.-P. Maitre, A. Bouchu, Colloids Surf. A: Physicochem. Eng. Asp. 203 (2002) 55–66.
[10] Ryoto Sugar Ester Technical Information, Mitsubishi-Kasei Food Corporation, 1998.
[11] A. Abbasian, S.R. Ghaffarian, N. Mohammadi, M.R. Khosroshahi, M. Fathollahi, Progr. Org. Coat. 49 (2004) 229–235.
[12] C.M. Hansen, Progr. Org. Coat. 51 (2004) 109–112.
[13] Y.H. Lang, Z.M. Cao, X. Jiang, Talanta 66 (2005) 249–252.
[14] L. Yanke, Z. Shufen, Y. Jinzong, W. Qinghui, Colloids Surf. A: Physicochem. Eng. Asp. 248 (2004) 127–133.
[15] M. Ferrer, F. Comelles, F.J. Plou, M.A. Cruces, G. Fuentes, J.L. Parra, A. Ballesteros, Langmuir 18 (2002) 667–673.
[16] S. Soultani, S. Ognier, J.M. Engasser, M. Ghoul, Colloids Surf. A: Physicochem. Eng. Asp. 227 (2003) 35–44.
[17] M.J. Donnelly, J.D. Bu'Lock, J. Am. Oil Chem. Soc. 65 (1988) 284–287.
[18] C.R. de Schaefer, M.E.F. de Ruiz Holgado, E.L. Arancibia, J. Colloid Interface Sci. 239 (2001) 222–225.
[19] C.R. de Schaefer, M.E. Ferreyra de Ruiz Holgado, E.L. Arancibia, J. Argentine Chem. Soc. 90 (2002) 55–63.
[20] A. Voelkel, J. Janas, J.A. Garcia Domínguez, J. Chromatogr. A 654 (1993) 135–141.
[21] P. Choi, T. Kavassalis, A. Rudin, J. Colloid Interface Sci. 180 (1996) 1–8.
[22] M.K. Kozłowska, U. Domańska, M. Lempert, M. Rogalski, J. Chromatogr. A 1068 (2005) 297–305.
[23] K. Adamska, A. Voelkel, J. Chromatog. A 1132 (2006) 260–267.
[24] R.K. Gupta, K. James, F.J. Smith, J. Am. Oil Chem. Soc. 60 (1983) 1908–1913.
[25] M.H. Moh, T.S. Tang, G.H. Tan, Food Chem. 69 (2000) 105–110.
[26] H. Kunieda, N. Kanei, A. Remoto, I. Tobita, Langmuir 10 (1994) 4006–4011.
[27] V.M. Sadtler, M. Guely, P. Marchal, L. Choplin, J. Colloid Interface Sci. 270 (2004) 270–275.
[28] G.J. Price, S.J. Hickling, I.M. Shillcock, J. Chromatog. A 969 (2002) 193–205.
[29] J.R. Conder, C.L. Young, Physicochemical Measurement by Gas Chromatography, John Wiley & Sons, N.Y, 1979.
[30] D.W. Marquardt, J. Soc. Ind. Appl. Math. 11 (1963) 431–441.
[31] D. Patterson, Y.B. Tewari, H.P. Schreiber, I.E. Guillet, Macromolecules 4 (1971) 356–359.
[32] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases & Liquids, 4th ed., Mc Graw Hill, Boston, Massachusetts, 1987.
[33] A.R. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents Techniques of Chemistry, 4th ed., Wiley-Interscience, New York, 1986.
[34] R.R. Dreisbach, Advances in Chemistry Series, vol. 15, Am. Chem. Soc., Washington, DC, 1955.
[35] J. Klein, H.-E. Jeberien, Macromol. Chem. 181 (1980) 1237–1249.
[36] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y., 1953.
[37] D.D. Deshpande, D. Patterson, H.P. Schreiber, C.S. Su, Macromolecules 7 (1974) 530–535.
[38] T.L. Hill, Statistical Mechanics, McGraw-Hill, New York, 1956.
[39] G. DiPaola-Baranyi, J.E. Guillet, Macromolecules 11 (1978) 228–235.
[40] K. Ito, J.E. Guillet, Macromolecules 12 (1979) 1163–1167.
[41] K.L. Hoy, The Hoy, Tables of Solubility Parameters, Solvents & Coatings Materials, S. Charleston, W. Virginia, 1985.
[42] H. Kelker, Ver. Bunsengen Physik. Chem. 67 (1963) 698–703.
[43] J.-C. Huang, R.J. Sheehan, S.H. Langer, J. Phys. Chem. B 109 (2005) 1736–1743.
[44] P.J. Flory, Proc. Roy. Soc., London A 234 (1956) 73–89.
[45] P.J. Flory, Adv. Polym. Sci. 59 (1984) 1–36.
[46] J.-C. Huang, J. Coca, S.H. Langer, Fluid Phase Equilib. 253 (2007) 42–47.
[47] J.-C. Huang, J. Applied Polymer Sci. 89 (2003) 1242–1249.
[48] S.H. Langer, R.J. Sheehan, J.-C. Huang, J. Phys. Chem. 86 (1982) 4605–4618.
[49] L.C. Chow, D.E. Martire, J. Phys. Chem. 75 (1971) 2005–2015.