SOLUBILITY PARAMETERS, HYDROPHILE-LIPOPHILE BALANCE, AND SOLUBILITY IN SUCROSE DERIVATIVE SURFACTANTS OBTAINED BY GLC.

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Abstract

Specific retention volumes of different solvents were measured on columns containing two sucrose derivative esters as stationary phase. Henry's constants were calculated and the solubility in the surfactants was obtained. The solubility parameters of the surfactants were obtained at different temperatures. The relation between solubility parameter and hydrophilic - lipophilic balance was discussed and the results obtained in both surfactants are presented.

Resumen

Se midieron los volúmenes de retención específicos de distintos solventes en columnas que contenían derivados de esteres de sacarosa como fases estacionarias. Se calcularon las constantes de Henry y se ha obtenido la solubilidad de los solventes en dos esteres de sacarosa. Se calcularon los parámetros de solubilidad de los surfactantes a diferentes temperaturas. Finalmente, se ha discutido la relación entre parámetro de solubilidad con el balance hidrofílico - lipofílico y se analizaron los resultados obtenidos en ambos surfactantes.

Introduction

The emulsification efficiency has been empirically determined by Griffin [1] through the hydrophilic – lipophilic balance system (HLB), based on a series of emulsion tests in which the efficiency of different surfactants was numerically evaluated on an arbitrary empirical scale. It has been found that there is an optimum value of HLB for the emulsification process when using a series of surfactants in a particular system. However, it is necessary to establish the maximum stability capacity of an emulsion, according to the chemical interactions involved.

It has been shown that the solubility and aggregation characteristics of surfactants are related to their solubility parameters [2] and to those of the solvents in which they were dispersed [3].

Solubility parameters have not been exhaustively used in the characterization of the surfactants, despite the theories that discuss the behavior of the emulsifier in water/oil systems in terms of the cohesive energy density of the components of the system [3].

Inverse gas chromatography has been used in the characterization of physicochemical properties of a number of liquid and solid materials [4-9]. The term "inverse" means that the substance under study is placed in a chromatographic column as stationary phase and the retention data of a series of test solutes are measured. The physicochemical parameters calculated from retention data describe the molecular interaction between the studied material and the solute.

Fatty acid esters of sucrose are non-ionic surfactants, which have a hydrophilic group, the sucrose, and a lipophilic group, the hydrocarbon chain of a fatty acid. Those surfactants are widely used as additives in food industry because of their special properties as emulsifier agents: tasteless, odorless and non-toxic. They are also adequate for cosmetic and medical applications because of their excellent biodegradability and a wide range of HLB obtained by changing the characteristics of the fatty acid used in their preparation.

In this paper, two sucrose derivative surfactants were used as stationary phase and the emulsification efficiency has been determined through the solubility parameters.

Theoretical relationships

The solubility parameters of a volatile substance can be calculated from the basic equation:

$$\delta = \left(\frac{\Delta H_v - RT}{v_1^0} \right)^{1/2} \tag{1}$$

where ΔH_v is the vaporization enthalpy, R the gas constant, T the absolute temperature and v_1^0, the molar volume.

The equation (1) cannot be applied to low volatility or non-volatile species, and alternative methods should be used. One of them is that presented by Di Paola- Baranyi [10,11] to evaluate the solubility parameters of polymeric substances, by using the interaction solute-solvent parameter $\chi_{1,2}^\infty$ of the Scatchard-Hildebrand theory.

In that procedure, the expression $\chi_{1,2}^\infty$ is used in the following way.

$$\chi_{1,2}^\infty = \frac{v_1^0 (\delta_1 - \delta_2)^2}{RT} + \chi_S^\infty \tag{2}$$

where δ_1 and δ_2 are the solute and the solvent solubility parameters, respectively, and χ_S^∞ is the entropic factor of the interaction parameter. Dividing equation (2) by v_1^0, it is possible to obtain the following relation:

$$\frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{v_1^\circ} = \left(\frac{2\delta_2}{RT} \right) \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^\infty}{v_1^\circ} \right) \tag{3}$$

By plotting the left-hand side of the above equation *vs.* δ_1, it is possible to obtain δ_2 for the non-volatile substance from the slope of the resulting straight line. The infinite dilution activity coefficients for concentrations expressed as weight fractions (Ω_1^∞) were calculated according to Patterson [12]:

$$ln\,\Omega_1^\infty = ln\left(\frac{273.15R}{p_1^0 V_g^0 M_1}\right) - \frac{p_1^0\left(B_{11} - v_1^0\right)}{RT} \tag{4}$$

where p_1^0, M_1, V_g° and v_1^0 represent vapor pressure, molar mass, specific retention volumes and the molar volume of the solute, respectively. B_{11} is the second virial coefficient for solute-solute interactions in the vapor phase. The vapor pressures were calculated by Antoine equation and the coefficients were taken from Riddick et al [13]. The solute densities at 50-95ºC were estimated from Dreisbach compilation [14]. The second virial coefficients of the solutes used were calculated with Tsonopoulos correlation using critical constants tabulated in Reid et al [15].

From expression (2), $\chi_{1,2}^\infty$ has Gibbs' energy characteristics and it expresses the sum of energetic and entropic contributions. Starting from the athermal mixing model of Flory-Huggins and from equation (4) it is possible to calculate $\chi_{1,2}^\infty$ from chromatographic data.

$$\chi_{1,2}^\infty = ln\left(273.15R\Big/p_1^0 V_g^0 M_1\right) - \frac{p_1^0\left(B_{11} - v_1^0\right)}{RT} - \left(1 - \frac{v_1^0}{v_2^0}\right) - ln\left(\frac{v_1^0}{v_2^0}\right) \tag{5}$$

The specific volume of the surfactant was used instead of the molar volume and the density of the solid was determined by the picnometric technique at different temperatures.

Materials and methods

The product identified by S1670 for Ryoto (Mitsubishi-Kagaku Foods Corp.), correspond to sucrose stearate with 25 % of di and tri-esters. The M1695 (also provided by Mitsubishi-Kagaku Foods Corp.) corresponds to sucrose miristate with 20 % of di and tri-esters. Both of them were used as stationary phase. Chromosorb W, AW, DMCS, 60/80 was used as a solid support and the surfactants 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 columns used were stainless steel tubes of 0.53 cm (internal diameter) and 100 cm length, containing packing with 10.22% (w/w) of S1670 and with 10.13% (w/w) of M1695.

Chromatographic measurement was performed in a Perkin-Elmer Sigma 300 gas chromatograph, equipped with a thermal conductivity detector. Hydrogen was used as carrier gas and flow rates were measured at the beginning or at any moment of the experiment with an air-jacketed soap film flowmeter placed at the outlet of the detector.

Inlet pressures were measured with a micrometry syringe (through the injector septum), which was connected to a mercury manometer of open branch. Solutes were injected with Hamilton syringes, as vapor in equilibrium with pure liquid. The injector was kept at 150 ºC and the detector at 180 ºC.

Retention times (t_R) were measured with an electronic integrator Perkin-Elmer LCI100 and the specific retention volumes (V_g°) were calculated with the following expression [16]:

$$V_g^o = j(F_f / w)(273{,}15 / T_f)(t_R - t_0)(p_0 - p_w) / p_0 \qquad (6)$$

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 vapor pressure at T_f and t_0 is the dead time which was measured by using the air peak obtained with the thermal conductivity detector.

Results and discussion

Various experiments were carried out to analyze the effect of the carrier gas flow and the temperature on the chromatographic retention. Adsorption effects over the gas-liquid interface were considered irrelevant in a similar sucrose derivative as stationary phase study [17]. The retention measurements of different solvents were made at four different temperatures: 50, 65, 80 and 95ºC. The heats of solution (ΔH_k°) were calculated using the following expression:

$$ln V_g^\circ = \frac{\Delta H_k^\circ}{RT} + cte \qquad (7)$$

They correspond to the process of transference of one solute mole from an ideal gaseous phase at a pressure of 1 atm. to a hypothetical solution of unit molar fraction with a typical interaction of an infinitely diluted solution [18]. The ΔH_k° obtained, as well as their respective standard deviations, were calculated using Marquartd-Levenberg's algorithm [19] and are quoted in Tables 1 and 2. The heats of solution were obtained with an average deviation of 2%. Similar values for the rest of the hydrocarbons were found in both stationary phases. For chloride derivatives of methane and ethyl acetate, heats of solution values obtained in M1695 are slightly larger than those obtained in S1670.

A frequent way to express the solubility of a vapor in a liquid is by following Henry's law. It is assumed that the vapor phase is ideal on the column and that the fugacity of the solvent f_1 in the liquid phase is proportional to its concentration in fraction weight. Newman and Prausnitz showed that Henry's constant is given by [20]:

$$H_1 = \lim_{w_1 \to 0}\left(f_1 \middle/ w_1 \right) = \frac{273.15R}{M_1 V_g^\circ} \qquad (8)$$

Solute	V^o_g (cm^3 g^{-1})	ΔH_k (kJ mol^{-1})	Ω^∞_1	$\chi^\infty_{1,2}$
n-Hexane	77.56	28.2 ± 0.7	6.50	2.03
n-Heptane	206.1	32.1 ± 0.4	5.92	1.91
n-Octane	522.6	36.1 ± 0.2	5.72	1.86
Benzene	177.5	30.2 ± 0.9	4.50	1.53
Toluene	569.1	38.9 ±0.2	3.55	1.30
Cyclohexane	137.9	29.1 ±0.9	5.51	1.77
Methylcyclohexane	265.5	32.6 ± 1.1	4.79	1.64
Dichloromethane	58.92	27.5 ± 1.3	3.27	1.20
Trichloromethane	157.6	31.0 ± 1.4	1.79	0.63
Carbon tetrachloride	155.6	29.4 ± 0.4	2.33	0.91
Ethyl acetate	73.71	30.5 ± 0.3	9.42	2.25

Table 1. *Specific retention volume, solution heat, infinite dilution activity coefficients, and* $\chi^\infty_{1,2}$ *solvent parameter in S1670 at 50ºC.*

Solute	V^o_g (cm^3 g^{-1})	ΔH_k (kJ mol^{-1})	Ω^∞_1	$\chi^\infty_{1,2}$
n-Hexane	56.37	27.5 ± 0.2	9.266	2.438
n-Heptane	158.2	34.5 ± 0.3	6.731	2.088
n-Octane	428.5	39.1 ± 0.4	5.808	1.920
Benzene	135.0	31.2 ± 0.7	6.158	1.865
Toluene	403.4	36.5 ± 0.2	5.238	1.697
Cyclohexane	100.7	28.9 ± 0.7	7.802	2.154
Methylcyclohexane	220.9	32.6 ± 1.1	5.992	1.861
Dichloromethane	54.64	31.4 ± 0.7	3.983	1.388
Trichloromethane	181.8	43.6 ± 0.3	1.952	0.698
Carbon tetrachloride	210.9	32.9 ± 0.5	3.044	1.154
Ethyl acetate	133.6	41.6 ± 1.5	5.407	1.699

Table 2. *Specific retention volume, solution heat, infinite dilution activity coefficients,* $\chi^\infty_{1,2}$ *solvent parameter in M1695 at 50ºC.*

If a value of 1 atm. is assumed for the partial pressure of the solvent in Henry's law, it is possible to write [21]:

$$\frac{1}{H_1(atm)} = c_1 \equiv S_1 \tag{9}$$

where S_1 is the solubility of the solvent in the surfactants. The solubility of the hydrogen used as a carrier gas is negligible here. On the other hand, fractions in weight have been used but they could be transformed into the most common molar fraction in a direct way if the molecular mass of the surfactants was known. The results for Henry's constants and

the solubilities expressed as weight of the solvent times weight of the solution are included in Table 3.

Table 3 shows how hydrocarbons solubility, in both stationary phases, increases as their molar mass increases. Comparing both sucrose derivatives, the solubility of these solutes is higher in S1670. The opposite is found with chloride derivatives of methane and ethyl acetate, in which the solubility is higher in M1695.

Values of $\chi_{1,2}^{\infty}$ obtained in chromatographic experiences at 50ºC, are included in Tables 1 and 2. Those values allowed the calculation of the surfactant solubility parameter δ_2 by means of equation (3). The representation of the left hand side of that expression *vs.* the solvent solubility parameter (δ_1) is shown in Figure 1, and it corresponds to M1695 when it is used as stationary phase. Solvent solubility parameter (δ_1) values were calculated at different temperatures using the expression from Haggenmacher. The equation is given by [22]:

$$\delta_T = \left[\frac{RT}{v_1} \left(1 - \frac{p_r}{T_r^3} \right) \left(\frac{2.303BT}{(t+C)^2} - 1 \right) \right]^{1/2} \tag{10}$$

where p_r and T_r are the reduced pressure and reduced temperature, respectively. Critical constants and Antoine equation constants were obtained from the literature [13, 14].
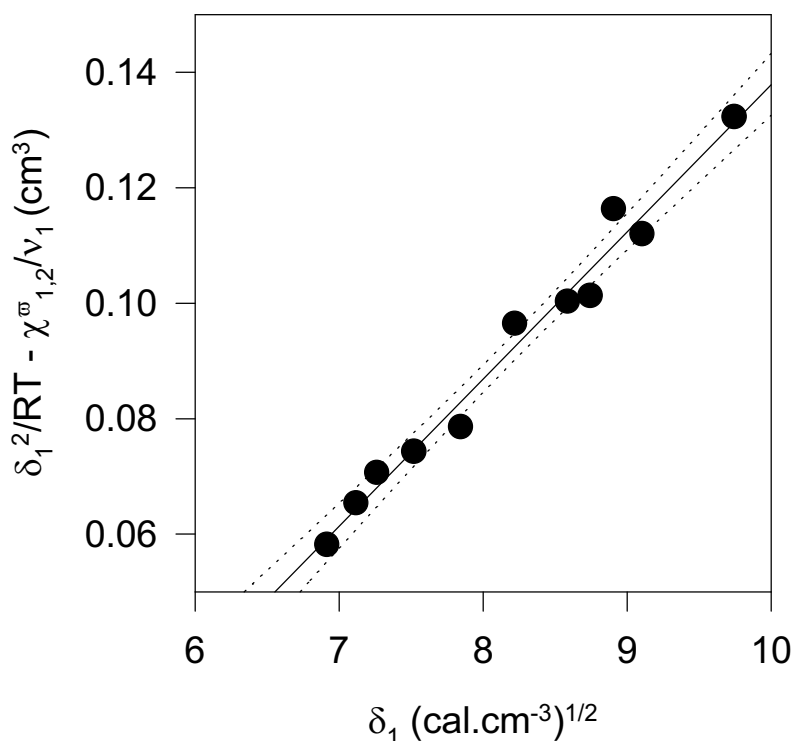
Figure 1. *Determination of the M1695 solubility parameter at 50ºC from $\chi_{1,2}^{\infty}$ calculated from chromatographic data.*

Figure 1 shows that at 50ºC for all the studied solutes the straight lines have a correlation coefficient higher than 0.97 and from the slope at 50ºC, the values of the solubility parameters for each one of the surfactants were obtained.

$$M1695: \delta_2 = 8.60 \pm 0.03 \ (cal \ mol^{-1})^{1/2}$$
$$S1670: \delta_2 = 7.94 \pm 0.02 \ (cal \ mol^{-1})^{1/2}$$

Solute	M1695		S1670	
	H(atm)	S	H(atm)	S
n-Hexane	4.614	0.217	4.000	0.250
n-Heptane	1.414	0.707	1.274	0.785
n-Octane	0.458	2.184	0.436	2.295
Benzene	2.126	0.470	1.598	0.626
Toluene	0.603	1.658	0.498	2.009
Cyclohexane	2.644	0.378	2.306	0.434
Methylcylohexane	1.033	0.968	1.033	0.968
Dichloromethane	4.837	0.207	5.114	0.195
Trichloromethane	1.033	0.968	1.370	0.730
Carbon tetrachloride	0.691	1.448	1.109	0.902
Ethyl acetate	1.905	0.525	3.352	0.298

Table 3. *Henry's constants and solubility in different surfactants*

From the values at the other experimental temperatures, it is possible to express the dependence of δ_2 on *t* (ºC), for each one of the surfactants, by the equations:

$$\delta_2^M = 10.506 - 0.0382 \ t$$
$$\delta_2^S = 9.113 - 0.0237 \ t$$

From the extrapolation at 25ºC the value of δ_2 is 9.55 (cal mol^{-1})$^{1/2}$ for M1695 and the value of δ_2 is 8.52 (cal mol^{-1})$^{1/2}$ for S1670. The obtained values have not been checked with literature values, because they were not found in bibliography. There is a correlation between surfactant solubility parameters and HLB due to Little [23] that leads to the calculation of the HLB coefficient, if the surfactant solubility parameter (δ_2) is already known.

$$HLB = 54 \left(\frac{\delta_2 - 8.2}{\delta_2 - 6.0} \right) \tag{10}$$

HLB values obtained in the present work for surfactants at 25ºC were 18.5 for M1695 and 8.1 for S1670. The literature value [24] for both surfactants is 16. The different composition in esters of these surfactants, 25% of di and poli-esters in S1670 and 20% in

M1695, could explain the differences in HLB values when this coefficient is obtained through solubility parameters determined by gas-liquid chromatography.

Conclusions

Chromatographic values of V_g^0 allowed the calculation of solubility and solubility parameters of sucrose derivative surfactants. The correlation between those parameters and the HLB coefficient [23], led to the analysis of the behavior of non-ionic surfactants. The obtained values agree with the literature values for one of the sucrose derivatives within the experimental error estimation. The difference in ester composition of S1670 could explain the disagreement found. Additional search is carried out in this direction.

Acknowledgements

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