Effect of emulsifiers on surface properties of sucrose by inverse gas chromatography

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Abstract

Inverse gas chromatography (IGC) was employed to characterize the changes in surface properties of sucrose particles coated with either lecithin or polyglycerol polyricinoleate. IGC was performed using polar and non-polar adsorbates at infinite dilution with the sucrose particles as the solid stationary phase. Coating the sugar surface with emulsifiers induced an increase in the lipophilicity of the sugar particles, i.e. a sharp decrease in the acidity of the surface. Yet the two emulsifiers induced a slightly different increase in the surface basicity. It was hypothesized that this observation was due to a difference in the molecular structure of the emulsifiers.
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1. Introduction

The surface properties of particles in a chocolate mass play a crucial role in the fluidity of the mixture, as they determine how the particles interact with each other and the fat phase. Thus, the surface properties have to be controlled in order to obtain the desired fluidity. This is done by the addition of emulsifiers that adsorb to the surface of the particles and thus reduce the interaction between them and, consequently, the viscosity of the mixture is decreased [1].

There are several existing methods for determining solid surface properties [2]. Among these, contact angle measurements are widely used. However, its applications are limited in the case of powders and fibers. For example, in order to measure the contact angle of a powder, a solution is to compress the particles to form a flat surface. This compression may cause changes in the surface properties and the rough microsurface produced would lead to a contact angle hysteresis reducing the accuracy of the results [3]. An alternative method that has been shown to be a valuable and sensitive tool in powder surface characterization is inverse gas chromatography (IGC). It has been employed extensively to characterize dispersive and non-dispersive interactions of fibers, mineral powders [4,5] and, more recently, organic powders in the pharmaceutical and food fields [6,7].

In this study, a range of polar and non-polar probes was employed to determine the influence of the two emulsifiers commonly used in chocolate, lecithin and polyglycerol polyricinoleate (PGPR), on

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the surface characteristics of sucrose. The surface properties calculated using IGC results, from the theory established in the literature, were the dispersive component of the surface free energy, γ_s^D [8], and the acid–base parameters K_a and K_b [9].

2. Experimental

2.1. Materials

Granulated sucrose (Sucreries Aarberg, Germany) was analyzed as received, having a median particle size of 228 μm and a specific surface area of 0.05 m²/g, or after milling with an air jet mill (Model 100AFG, Alpine, Augsburg, Germany) to a median particle size of 45 μm and a specific surface area of 0.34 m²/g. Both samples were 100% crystalline.

Standard soybean lecithin commonly used in chocolate manufacturing was provided by ADM (Germany). It is a complex mixture consisting of 40–45% (w/w) phospholipids, 10% (w/w) glycolipids, 40–45% (w/w) neutral lipids and 5% (w/w) free carbohydrates. The surface-active molecules are mainly the phospholipids. In lecithin, there are principally four phospholipid types present: phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol and phosphatidic acid.

Polyglycerol polyricinoleate (PGPR) is a polyglycerol ester of polycondensed ricinoleic acid of vegetable origin. It was type P4141 from Palsgaard (Denmark).

The probes employed for IGC were apolar probes, *n*-pentane (Merck, 99% purity), *n*-hexane (Merck, 98% purity), *n*-heptane (Merck, 99% purity), *n*-octane (Aldrich, 98% purity), and *n*-nonane (Aldrich, 99% purity), while the polar probes were chloroform (99% purity), tetrahydrofuran (THF) (99.5% purity), acetone (99.5% purity), diethyl ether (99.5% purity), ethyl acetate (99.5% purity) and toluene (99.5% purity). They were all obtained from Merck.

2.2. Sample preparation

Sucrose particles were modified by adsorption of emulsifiers onto their surfaces using the following procedure. Sucrose powder was dispersed in hexane containing the emulsifier in a proportion of 50% (w/w) sucrose powder, 50% (w/w) hexane and 2% (w/w) lecithin (or 1%, w/w, PGPR). Emulsifier was added in excess to ensure a full coverage of the sugar surfaces. In fact, around 0.3% (w/w) lecithin or PGPR is sufficient for full coverage. The excess emulsifier was removed by rinsing. The solution was mixed for 17 h and then filtered. Hexane (10 ml) was added to the filtered mass, the solution mixed again for 10 min and then filtered. This procedure was repeated twice. Excess hexane was evaporated using a rotavapour (Buchi, Switzerland). Finally, the remaining traces of solvent were removed from the powder by placing it in a vacuum oven for 12 h at 40 °C and 50 mbar.

2.3. Inverse gas chromatography

Inverse gas chromatography was carried out using a Carlo Erba/Fisons GC 8165 gas chromatograph. Nitrogen was used as the carrier gas. It was held at a constant pressure with the flow-rate measured using a soap bubble flow meter. The temperature of the oven housing the column was monitored and maintained isothermally throughout the experiment. The injection port temperature was held at 100 °C. The results presented in this paper were obtained at 30 °C. However, several analyses were performed between 20 and 50 °C. This was necessary to calculate the basic and acidic parameters of the surface powder (see the following section).

Each of the double-looped glass columns (Varian, USA), 1 m in length and 3 mm in internal diameter, was silanated in order that the glass surface would be hydrophobic and non-interactive with any gaseous probe [10].

The powder bed of sucrose particles (either coarse or fine) was packed homogeneously in the column with no air pockets. Silanated glass wool was plugged into each end of the column (around 3 cm). The powder bed was then allowed to settle for 16 h in the oven of the GC apparatus at a temperature of 40 °C with a nitrogen flow between 8 and 12 ml/min in order to condition the column.

The liquid probes were injected manually using a 10 μl syringe. The syringe was first rinsed with the liquid probe and then flushed out several times with

air to achieve infinite dilution conditions. A 1 μl volume of air containing the liquid vapor was injected. The eluted vapor was detected with a flame ionization detector. The retention times were taken from the time of injection to the maximum peak height. An average of five injections was recorded for each liquid probe, all of which were reproducible. Dead time was estimated by extrapolation according to Smith [11].

3. Results and discussion

The following classical relationship was used to calculate the dispersive component of the solid surface energy, γ_S^D [8]:

$$RT \ln V_N = 2N(\gamma_S^D)^{0.5} a(\gamma_L^D)^{0.5} + Cte \qquad (1)$$

where V_N is the net retention volume, N is Avogadro's number, a is the area of surface occupied by a molecule of vapor probe and γ_L^D the dispersive liquid surface energy. The plot of $RT \ln V_N$ as a function of $2Na(\gamma_L^D)^{0.5}$ for the alkanes is a straight line. The slope of the line is equal to the square root of the dispersive component of the solid surface energy. The values of a and γ_L^D of each probe are known and were taken from the literature [8,12].

When polar probes are used as adsorbates, both dispersive and specific interactions take place between the probe and the solid stationary phase. To a first approximation, the Gibbs free energy of adsorption, ΔG_{ads}^0, is decomposed into two components, dispersive, ΔG_{ads}^D, and specific, ΔG_{ads}^{spe}, which are considered independent as shown below:

$$\Delta G_{ads}^0 = \Delta G_{ads}^D + \Delta G_{ads}^{spe} \qquad (2)$$

The dispersive component corresponds to the value at the abscissa of the probe on the straight line of the alkanes. The specific component ΔG_{ads}^{spe} is represented graphically as the vertical distance between the alkanes' reference line and the polar probe. It is therefore easily calculated. The entropic part of this energy can be calculated by performing the experiment at different temperatures. This enables the enthalpy of adsorption to be deduced from ΔG_{ads}^{spe}. According to Riddle and Fowkes [13], this enthalpy

of adsorption can be used to calculate the polar character of the particle surface:

$$\Delta H_{ads}^{spe} = K_A \cdot DN + K_B \cdot AN^* \qquad (3)$$

where DN and AN^* are the donor and acceptor number characterizing the probe. Values of DN and AN^* can be found in the literature for different polar probes [8,9,13]. K_A and K_B are, respectively, the acidic and basic constants characterizing the surface of the powder.

3.1. Effect of lecithin

Table 1 shows the effect of lecithin coating on the surface properties of standard and milled sucrose. As expected, milling significantly increased the dispersive component of sucrose due to the creation of more, new energetic surfaces [7]. Interestingly, when jet milled sucrose was coated with a layer of phospholipids, the dispersive component of the surface energy was significantly reduced to the value of granulated sucrose. The dispersive component was not altered when granulated sucrose was coated with lecithin.

Lecithin greatly decreased the acidic (acceptor) character of sucrose originating from the hydroxyl groups of the molecule. It also slightly changed its basic characteristics (Fig. 1). The decrease in the acidic character may be explained by the apolar chain of the phospholipids in lecithin. The increase in the basic character may be due to phospholipids such as phosphatidylethanolamine. In general, adsorbed lecithin increases the lipophilicity of sugar particles, thus inducing an increase in the fluidity of fat-based suspensions like chocolate.

Another observation that can be made from Table 1 is that particle size does not influence the polar

Table 1
Effect of adsorbed lecithin at the sucrose surface

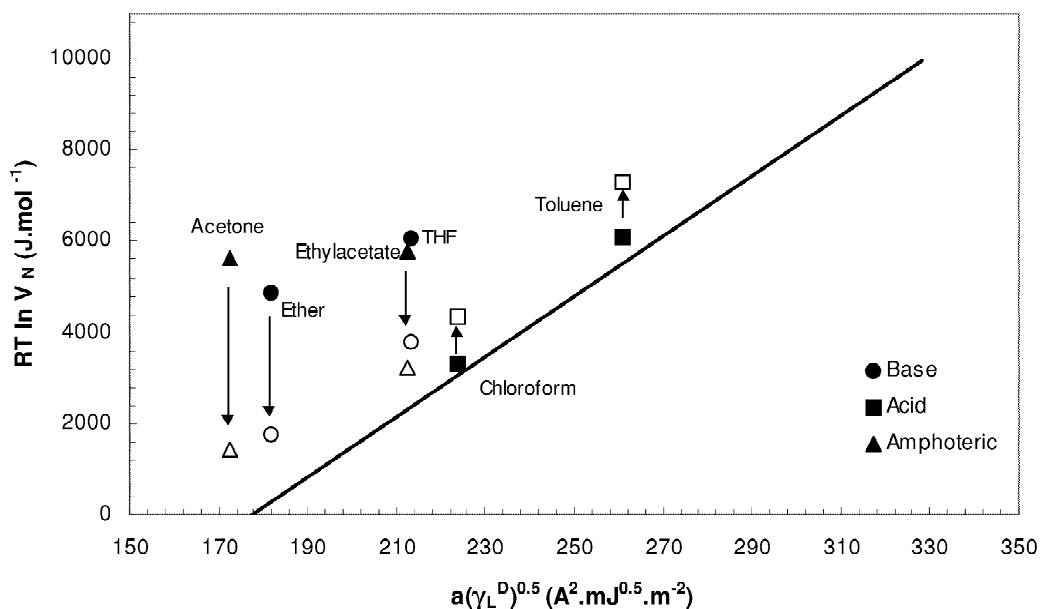|	Granulated sucrose		Jet milled sucrose	
	Without lecithin	With lecithin	Without lecithin	With lecithin
γ_S^D (mJ/m^2)	30.3	30.6	36.5	30.9
$K_A \cdot 10^{-2}$	18	15	19	16
$K_B \cdot 10^{-2}$	23	28	22	26

Fig. 1. Free energy of adsorption ($RT \ln V_n$) as a function of the dispersive surface energy of the vapor probe: effect of adsorbed lecithin at the granulated sucrose surface. (●) Without lecithin, (○) with lecithin.

properties of the material. This is demonstrated by the similar K_A and K_B values of granulated and jet milled sucrose with and without lecithin.

3.2. Effect of PGPR

PGPR and lecithin are two emulsifiers that have different fluidization effects in chocolate-like suspensions. PGPR mainly reduces the yield value of chocolate, while lecithin alters the plastic viscosity. Thus it was interesting to compare the surface energetics of PGPR-covered sucrose to that of lecithin.

The surface properties of sucrose with PGPR are presented in Table 2. Again, the emulsifier reduced

the dispersive component of the milled sucrose, making the particles less energetic. This value is similar to that of lecithin. Emulsifiers probably minimize the dispersive surface energy of the milled sucrose back to the original non-altered dispersive surface energy.

PGPR also increases the lipophilicity of the sucrose, as shown in Fig. 2. The significant drop in acidic character of the particles with PGPR is similar to that of lecithin, even if the PGPR molecule differs from the phospholipid molecule in the length of its apolar chain, which is around three times longer.

On the other hand, the basic character of sucrose is greater with PGPR than with lecithin. This might be linked to the presence of oxygen atoms in poly-condensed ricinoleic acid.

4. Conclusions

The results indicate that the adsorption of emulsifiers (either lecithin or PGPR) increases the lipophilicity of the sucrose particles via a strong decrease in the acidic character of the surface. This induces a decrease in the sucrose–sucrose interactions and thus

Table 2
Effect of adsorbed PGPR at the sucrose surface

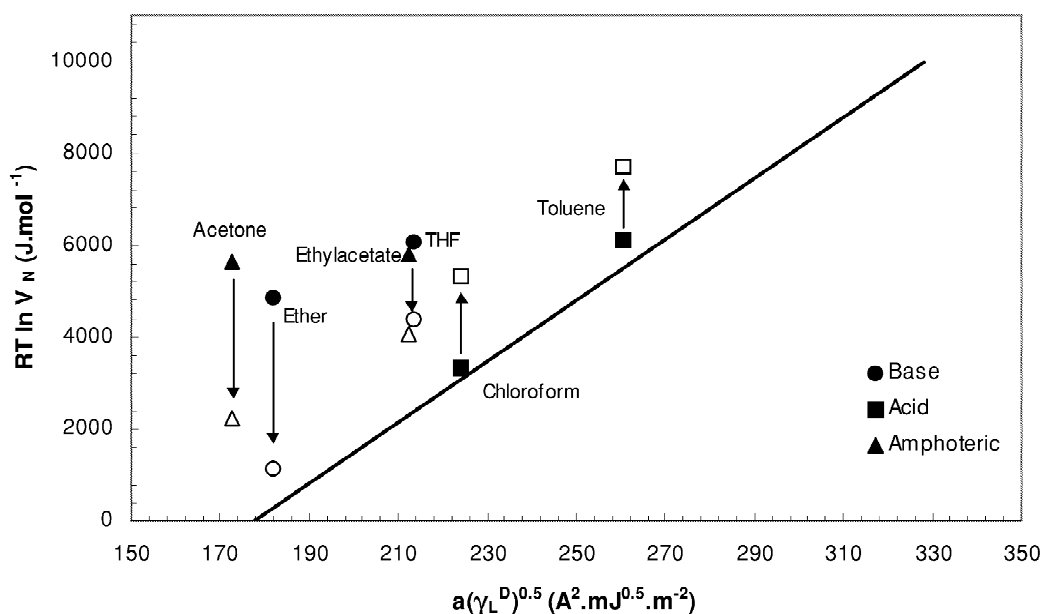|	Granulated sucrose		Jet milled sucrose	
	Without PGPR	With PGPR	Without PGPR	With PGPR
γ_S^D (mJ/m^2)	30.35	31.05	36.46	29.98
$K_A \cdot 10^{-2}$	18	15	19	16
$K_B \cdot 10^{-2}$	23	33	22	29

Fig. 2. Free energy of adsorption ($RT \ln V_n$) as a function of the dispersive surface energy of the vapor probe: effect of adsorbed PGPR at the granulated sucrose surface. (●) Without PGPR, (○) with PGPR.

explains the increased fluidity of the fat-based suspension.

Whilst the dispersive component and acidic character for both emulsifiers were comparable, the basic character exhibited a slight difference. It is hypothesized that this is linked to the presence of oxygen atoms in poly-condensed ricinoleic acid.

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