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### Adhesion of food emulsions to packaging and equipment surfaces

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### Abstract

The adhesion of food emulsions to food contact surfaces is a problem of utmost importance in the recycling of packages and cleaning of industrial equipment. Bulk adhesion was measured experimentally by weighing the mass of food emulsion remaining on solid surfaces after contact (i.e., amount adhered or adhesion amount), a matter which is of industrial concern. Surfaces of different hydrophilicity have been tested: polytetrafluoroethylene (PTFE), low-density polyethylene (LDPE), poly(ethylene terephthalate) (PET), stainless steel and glass. Their polar free adhesion energy in contact with water ( $Wa_{water}^p$ ) varied in the range 0.8 to 7 mJ m<sup>-2</sup>.

The observed decrease in the bulk adhesion amount of oil-in-water (o/w) emulsions, when stabilized by whey protein isolates and soybean lecithin, with decreasing  $Wa_{water}^p$  may be explained by increasing hydrophilization of the outside of adsorbed protein layers formed on solid substrates. This phenomenon would be due to conformational rearrangements of the macromolecules by hiding their hydrophobic moieties in contact with hydrophobic substrates, leading to a consequent decrease in adhesion forces between emulsion droplets and the substrates.

A correlation was established between adhesion measurements and solid surface tension,  $\gamma_s$ , or its electron-donor component from the van Oss model,  $\gamma_s^-$ . Results could be interpreted on the basis of physicochemical mechanics which relates rheological and adhesive properties of emulsions to microscopic adhesion forces acting between liquid droplets and surfaces. The relative importance on adhesion amount of surface thermodynamical properties and emulsion rheology was demonstrated and several hypotheses for bulk adhesion mechanisms are forwarded. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Residues of food products adhering to surfaces are of high economic importance in the food industry. Indeed, food remaining in packages after consumption decreases product quality and makes consumers dissatisfied [1]. It also causes increased costs for recycling of packages, and the adhesion of products to equipment surfaces increases cleaning process costs. More specifically, widely used complex fluid foods — such as emulsions — cause these problems because they contain fat, as well as hydrocolloids as stabilizers, that are likely to adsorb on surfaces. Many sauces and dressings belong to this category.

Many theories address adhesion phenomena in general, such as mechanical interlocking, diffusion, electrostatics and thermodynamic adsorption [2], but only a few studies have attempted to apply

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such theories to predict the adhesion of food materials to solids. As reviewed earlier [3], studies on this subject often remain highly empirical, applied to specific food products [4,5] and only a few are concerned with fatty products or emulsions [6]. Thermodynamic adsorption theory has been used by McGuire and Kirtley [7] but applied to specific food components such as proteins, rather than to bulk products. This theory has mainly been applied to sanitary studies such as the adhesion of microorganisms [8,9], not food materials.

After having studied simple fatty food products such as edible oils [10], we chose in this work to study bulk adhesion of concentrated food emulsions with a mayonnaise-like composition, stabilized with lecithin and whey protein isolate. Our aim was to find surface and emulsion parameters responsible for bulk deposits adhered on surfaces after flow (called amount adhered or adhesion amount,  $M_{ad}$ ). If the link between the thermodynamic work of adhesion and true interfacial adhesion of the first molecular layers of an emulsion seems clear, we wanted to see if any relationship remained valid for bulk deposits, i.e., product remaining on the surface after mutual contact and flow when emptying a package or a bottle, for example. The effect of surface thermodynamics and physicochemical mechanics of emulsions on this global residue was investigated.

### 2. Experimental

#### 2.1. Materials

Solid surfaces were chosen for their use in food packaging and equipment and for their hydrophilic or hydrophobic properties. They were: Teflon (polytetrafluoroethylene, (PTFE)), low-density polyethylene (LDPE), poly(ethylene terephthalate) (PET), stainless steel (AISI 304) and glass.

Standard liquids used to calculate solid surface tension were: diiodomethane (Sigma, St Louis, MI, USA),  $\alpha$ -bromonaphthalene, cyclohexane (Prolabo, Paris, France), *n*-hexane, *n*-hexadecane, glycerol, formamide, ethylene glycol (OSI, Maurepas, France), and water (Chromanorm<sup>®</sup>, Prolabo, Paris, France) of the highest purity available.

Components of emulsions were virgin olive oil (Puget, Vitrolles, France), refined first-draft sunflower oil (Lesieur, Neuilly-sur-Seine, France) or soybean oil (Solior, Tourcoing, France), distilled water, soybean lecithin (OSI, Maurepas, France) and whey protein isolate (Armor Protéines, Saint-Brice-en-Cogles, France). Pure white vaseline oil OSI (Maurepas, France) was also used as a standard.

### 2.2. Emulsions

Oil-in-water (o/w) emulsions were prepared for each oil comprising 70% oil, 1% lecithin and 1.5% proteins, which are industrial proportions [11]. Lecithin and proteins were dissolved in water under gentle stirring. Preparation of emulsions was carried out under 0.9 bar vacuum in an industrial research food mixer (UMC 5 Electronic, Stephan, Troyes, France), thermostated at  $20\pm1^{\circ}$ C. Agitation speed was varied in the range 800-3000 rev min<sup>-1</sup>. The aqueous phase was first mixed with half of the oil for an initial time between 30 and 90 s, then the rest of the oil was added by vacuum at 1.71 min<sup>-1</sup> and mixed further for a final time of 4 or 6 min. Conductimetric measurements confirmed the emulsions as o/w.

#### 2.3. Amount of emulsion adhered

Experimental amount of emulsion adhered to surfaces  $(M_{ad})$  was measured with the device described by Ould Eleya and Hardy [12] and improved by Michalski et al. [9] (Fig. 1). Emulsion was held back at the top of a tilted solid surface, then was allowed to flow down and the weight remaining on the solid surface after flow had stopped was measured, so that:

 $M_{\rm ad} = {\rm deposit \ weight/surface} \ ({\rm g \ m^{-2}})$  (1)

The end of flow time was determined by weighing product dropping down with a precision balance (Precisa 400M, PAG, Zürich, Switzerland). Usually flow time was 15 min for glass, stainless steel and PET, and 5 min for LDPE and PTFE.

This method is not aimed to measure the force



Fig. 1. Device for measuring amount of emulsion adhered ( $M_{ad}$ ) at 20±1°C: (a) product release, (b) product flow and determination of the end of flow time and (c) weighing of the remaining residues.

acting between the first molecular layers of the liquid or droplets and the solid surface, but to measure the global adhesion amount resulting from adhesion and cohesion strengths. This global adhesion after drainage corresponds to food remaining on packaging when consumers attempt to empty it.

### 2.4. Surface and interfacial tension

Surface tension of pure standard liquids was measured with a Krüss K10ST tensiometer (Krüss, Hamburg, Germany) equipped with a platinum plate, according to the Wilhelmy method. To calculate the surface tension components for pure standard liquids, interfacial tension measurements were performed with a platinum ring according to the Du Nouy method described by Harkins and Jordan [13]. Between each measurement, the plate and ring were rinsed with ethanol and distilled water before being red-hot burned. Glass cups containing samples were cleaned by rinsing and soaking for 10 min in acetone (OSI, France), then rinsing with ethanol and distilled water and drying for 10 min in an oven (110°C). Surface tension components of pure standard liquids used to characterize solid surfaces, listed in Table 1, were consistent with the literature [14–16].

#### 2.5. Contact angles

The contact angle of pure liquids on solids was measured with an assembly including a precision video camera coupled to image analysis, as described by Michalski et al. [9]. Measurements,

Table 1

Surface tension of pure standard liquids at  $20 \pm 1^{\circ}$ C (mN m<sup>-1</sup>)

	$\gamma_{\mathbf{L}}$	$\gamma_{\rm L}^{\rm LW}$
Diiodomethane	50.8	50.8
α-Bromonaphthalene	44	44
<i>n</i> -Hexane	18.7	18.7
Cyclohexane	25.1	25.1
<i>n</i> -Hexadecane	27.3	27.3
Water	72.4	21.5
Glycerol	64.7	38.7
Formamide	58.3	32.5
Ethylene glycol	48	32.5

Average of 10 measurements. Device maximum error:  $0.1 \text{ mN m}^{-1}$ .

performed at  $20 \pm 1^{\circ}$ C, were repeated 10 times. A Fortran program was written to calculate contact angles. The program determined the top and triple points of the drop and then calculated three angles: the theoretical contact angle and the two actual contact angles on the right and left sides of the drop.

For a proper measurement of  $\theta$ , solid and liquid must be in equilibrium and the surface should be clean and homogeneous. Our cleaning procedure, using ethanol and a 4% RBS detergent bath (Société Traitements Chimiques des Surfaces, Lille, France) was described in detail in [9].

It should be stressed that there are difficulties in applying contact angle measurements for the determination of real solid surface properties. Indeed, in real systems, an adsorption layer of the liquid used can be formed on the solid, around the liquid drop, and the contact angle would be different whether it is advancing or receding. However, as a first indication, rapid measurement of the contact angle of a pure liquid on a solid when the drop is advancing gives a good estimate of the differences between the surface properties of different solids, especially their hydrophilicity using water contact angle.

### 2.6. Rheology

Rheological characterization of the emulsions was performed by using a controlled-stress rheometer (CarriMed, Rheo, Palaiseau, France). The device was equipped with a 6 cm diameter cone at a  $2^{\circ}$  angle. Measurements, at  $20\pm1^{\circ}$ C, were performed at a stress increase speed of  $20 \text{ Nm}^{-2} \text{min}^{-1}$ , until a shear rate of  $1000 \text{ s}^{-1}$ was reached. Flow curves analysis was performed by the software furnished with the rheometer.

### 2.7. Fat droplet size

The size of emulsion fat droplets was measured by a light diffraction granulometer (MasterSizer, Malvern, Worcestershire, UK). Emulsions were diluted to 1/1000 but no dilution or agitation speed effects were found on the measurements in this range.

#### 3. Results

#### 3.1. Surface tension of solid surfaces

Solid surface energetical properties can be estimated on the basis of the work of adhesion. The thermodynamic work of adhesion, *Wa*, may be defined as the reversible work, per unit surface, to separate two phases that initially have a common interface. In the absence of an adsorption layer on the solid surface after separation of the liquid from the solid, *Wa* is given by the Dupré energy equation [17]:

$$Wa = \gamma_{\rm L} + \gamma_{\rm S} - \gamma_{\rm SL} \tag{2}$$

where  $\gamma_L$  is liquid product surface tension,  $\gamma_S$  solid surface tension and  $\gamma_{SL}$  solid–liquid interfacial tension. *Wa* is positive in the case of adhesion and may be expressed by a combination of Young's force equation [18] and the Dupré equation (Eq. (2):

$$Wa = \gamma_{\rm L}(\cos\theta + 1) \tag{3}$$

where  $\theta$  is the contact angle at the solid/liquid interface. Eq. (3) allows us to calculate *Wa* by measuring  $\gamma_{\rm L}$  and  $\theta$  as described in the Experimental section. By using this equation with a range of standard liquids, it is then possible to calculate the solid surface tension ( $\gamma_{\rm S}$ ) and the Lifshitz–van der Waals ( $\gamma_{\rm S}^{\rm LW}$ ) and acid–base ( $\gamma_{\rm s}^+$ ,  $\gamma_{\rm s}^-$ ) components from the van Oss model (Table 2). Moreover, an index of solid hydrophilicty is also given by  $Wa_{\rm water}^p$  (polar part of the work of adhesion for water), according to Krisdhasima et al. [20], based on the contact angle of water on the solids:

$$Wa_{\text{water}}^{\text{p}} = \gamma_{\text{water}}(\cos\theta + 1) - 2(\gamma_{\text{water}}^{\text{LW}}\gamma_{\text{S}}^{\text{LW}})^{1/2}$$
(4)

From Tables 1 and 2 and contact angles of the pure liquids, solid surface tension was calculated (Table 3), as well as the surface tension parameters,  $\gamma_{\rm S}^{\rm LW}$ ,  $\gamma_{\rm S}^+$  and  $\gamma_{\rm S}^-$ , and the hydrophilicity index,  $Wa_{\rm water}^p$  (Table 4). The solids chosen lie in a wide range of hydrophilicity and acid–base interaction ability. Their polarity increases in the order PTFE < LDPE < PET < stainless steel < glass. The solids were found to have mostly an electron-donating ability, which is in agreement with van

Table 2			
Van Oss model [19]	expressing the work	of adhesion and	solid surface tension

Wa expression	Components	$\gamma_{\rm S}$ expression
$\overline{2(\gamma_{\rm L}^{\rm LW}\gamma_{\rm S}^{\rm LW})^{1/2} + 2(\gamma_{\rm L}^{+}\gamma_{\rm S}^{-})^{1/2} + 2(\gamma_{\rm L}^{-}\gamma_{\rm S}^{+})^{1/2}}$	LW: Lifshitz-van der Waals (London, Debye, Keesom) +: electron acceptor -: electron donor	$\gamma_{\rm S}^{\rm LW} + \gamma_{\rm S}^{\rm acid-base} = \gamma_{\rm S}^{\rm LW} + 2(\gamma_{\rm S}^-\gamma_{\rm S}^+)^{1/2}$

Table 3

Solid surface tension at  $20 \pm 1^{\circ}$ C using the van Oss model [19]

	$\gamma_{\rm S} \ ({\rm mN} \ {\rm m}^{-1})$
PTFE	24.1
LDPE	37.9
PET	46.3
Stainless steel	44.0
Glass	49.5

Table 4

Solid surface parameters at  $20 \pm 1^{\circ}$ C using van Oss model [19] and Krisdhasima et al.'s hydrophilicity index [20] (mN m<sup>-1</sup>)

	$\gamma_{\mathbf{S}}^{\mathbf{L}\mathbf{W}}$	$\gamma_{s}^{+}$	$\gamma_{s}^{-}$	$Wa_{water}^{p}$
PTFE	23.6	3	0	0.8
LDPE	36.9	1.1	0.25	6.2
PET	44.7	0.05	14.3	36.4
Stainless steel	40.1	0.2	19.3	41.3
Glass	36.8	0.85	47.5	78

Oss [21] for polymers. Moreover, differences between solids were more likely to be due to the  $\gamma_s^-$  surface parameter, which almost vanished for LDPE or PTFE but reached 47.5 mN m<sup>-1</sup> for glass. It should be noted that the van Oss model, known as the acid–base approach, is supposed to be the one fitting best with reality as it splits the proton donor and acceptor terms, allowing us to describe asymmetrical interactions. Indeed, it may be used for non-polar, monopolar as well as bipolar surfaces. It describes interactions with more precision than simple global polar terms and has proved to be the most reliable in predicting the solubility of polymers, compared with previous models [7,22–24].

Additionally, it was observed that adsorption on glass of lecithin and proteins, contained within the concentrated stabilized emulsions, caused the surface to be less hydrophilic. Indeed, the contact angle of a sunflower oil drop on clean glass in water was  $134.8^{\circ}$  compared with  $54^{\circ}$  for glass that had been exposed to a lecithin+protein solution. Also, lecithin and proteins hydrophilized LDPE, as the contact angle was  $50.5^{\circ}$  against  $28^{\circ}$  on a clean surface.

# 3.2. Rheological and interfacial parameters of emulsions

According to rheological measurements, the emulsions were found to follow an Herschel–Bulkley flow model, like numerous food sauces and dressings [25]:

$$\tau = \tau_0 + K\sigma^n \tag{5}$$

where  $\tau$  is the shear stress,  $\tau_0$  the yield value of the shear stress from which flow begins, *K* the plastic viscosity or consistency index,  $\sigma$  the shear rate and *n* the flow index. These parameters are listed in Table 5 in order of increasing apparent viscosity:

 $\eta_{app} = \tau / \sigma$  at a particular shear stress (6)

We have chosen oils with different Newtonian viscosities as components, in order to produce emulsions with different sizes of fat droplet ( $d_{50}$ , Table 5) and apparent viscosities. The higher viscosity of olive oil compared with the other oils resulted in larger fat droplets, as during the mixing process the agitation speed was not as efficient as with others oils in dispersing the fatty phase. Moreover, for sunflower oil emulsions, we controlled mixing parameters in order to make the properties of the emulsions vary at constant emulsion composition. The lower agitation speed of emulsions sunflower 4 and 5 resulted in a lower apparent viscosity because dispersion of the oil

Table 5

( $\tau_0$ ), plastic viscosity (K), flow index (n), average diameter of fat globules ( $d_{50}$ ) and continuous phase surface tension ( $\gamma_L$ )						
Emulsion	$\eta_{app}$ at 15 Pa (mPa s)	$\tau_0 (N m^{-2})$	K (Pa s")	п	d <sub>50</sub> (μm)	$\gamma_L \ (mN \ m^{-1})$
Sunflower 5	40.0	0.370	0.253	0.700	_	31.7
Olive 1	48.3	0.278	0.216	0.735	33.7	30.8
Vaseline 1	48.5	0.265	0.147	0.801	42.0	40.5
Sunflower 4	50.9	0.333	0.244	0.716	_	36.2
Vaseline 2	51.0	0.262	0.128	0.831	_	43.4
Olive 2	54.5	0.251	0.177	0.776	_	32.7
Soybean 2	73.7	0.230	0.223	0.780	_	42.5
Soybean 1	75.1	0.189	0.228	0.779	11.1	42.8
Sunflower 2	76.6	0.195	0.224	0.779	_	41.2
Sunflower 1	80.9	0.182	0.335	0.732	11.4	37.4
Sunflower 3	81.6	0.210	0 247	0.776		39.5

Physicochemical parameters of emulsions at  $20+1^{\circ}$ C: apparent viscosity at a shear stress of 15 Pa  $(n_{res})$  shear stress yield value

phase was then less efficient. As for vaseline oil emulsions, this low dispersion of the oil phase resulted in a higher yield stress  $\tau_0$ , certainly because the oil droplets' specific surface was smaller. This resulted in a higher concentration of lecithin and proteins in the continuous phase, which can result in the presence of a yield stress. These various oils and mixing parameters were chosen to prepare emulsions of controlled rheological parameters, in order to study their effect on final deposits. The surface tension of the continuous phase was also measured (Table 5).

### 3.3. Effect of solid surface parameters on the amount of emulsions adhered

The amount of emulsion adhered  $M_{ad}$  was found to increase with solid surface tension as shown in Fig. 2. In addition, Fig. 2 shows the existence of a minimal, critical solid surface tension for each emulsion at which deposits begin to be formed. There is a sharp increase in the adhesion ability of a given emulsion beginning with some minimum value of  $\gamma_{s}$ . Moreover, for vaseline 1 and sunflower 4 emulsions, the adhesion amount reached a plateau value, suggesting the role of an emulsion parameter in limiting final residues. Solid surface tension seems to play a key role in amount of emulsion adhered, which is in agreement with Eq. (2). However, as the correlation is not very clear, it may not be the most important surface parameter.



Fig. 2. Effect of solid surface tension  $\gamma_s$  on amount of emulsion adhered  $M_{ad}$ :  $\bullet$ , olive 1;  $\blacksquare$ , sunflower 4;  $\times$ , soybean 2;  $\triangle$ , vaseline 1.

Experimental adhesion was also found to increase with surface hydrophilicity, as calculated by  $Wa_{water}^{p}$  (Fig. 3,  $R^{2}$  coefficients are given in Table 6). However, for some emulsions, the increase of  $M_{\rm ad}$  did not follow a linear trend but reached a plateau value. This indicates that for these emulsions, as also observed in Fig. 2, there must be other important parameters overwhelming the effect of surface properties; these may be rheological such as apparent viscosity or yield stress.



Fig. 3. Effect of  $Wa_{water}^p$ , an index of surface hydrophilicity, on amount of emulsion adhered  $M_{ad}$ : black circles: olive 1, white circles: olive 2, small black squares: sunflower 1, small white squares: sunflower 2, medium white squares: sunflower 3, medium black squares: sunflower 4, large white squares: sunflower 5, +: soybean 1,  $\times$ : soybean 2, white triangle: vaseline 1, black triangles: vaseline 2.

Table 6  $R^2$  coefficients of  $M_{ad}$  versus  $Wa_{water}^p$  and  $\gamma_s^-$  curves

Emulsion	Wa <sup>p</sup> <sub>water</sub> curves	$\gamma_{\rm S}^-$ curves
Sunflower 1	0.812	0.675
Sunflower 2	0.976	0.905
Sunflower 3	0.926	0.750
Sunflower 4	0.952	0.739
Sunflower 5	0.909	0.893
Soybean 1	0.939	0.831
Soybean 2	0.894	0.881
Olive 1	0.768	0.878
Olive 2	0.818	0.921
Vaseline 1	0.813	0.711
Vaseline 2	0.890	0.606

# 3.4. Effect of emulsion rheological parameters on adhesion amount on solids

The adhesion amount was found to correlate with the apparent viscosity at a 15 Pa shear stress, which is the approximate stress undergone by the emulsions during the first moments of flow, but only below a certain yield value  $\tau_0^*$ . Below  $\tau_0^*$ , for

emulsions olive, soybean and sunflower 1, 2 and 3,  $M_{ad}$  increased with increasing apparent viscosity (Fig. 4) because the yield stress was apparently too small to have a significant effect. This low yield stress may even be an artefact resulting from rheometer precision below a certain shear rate. Above  $\tau_0^*$  (of the order of  $\tau_0$  for the vaseline emulsions), for sunflower 4 and 5 and vaseline oil emulsions (Table 5), the amount adhered increased with yield value rather than with viscosity, because flow was harder to continue when stress was decreasing at the end of flow (Fig. 5). Moreover, the adhesion amount of emulsions also decreased with increasing fat droplet size, as depicted in Fig. 6.

### 4. Discussion

### 4.1. Physicochemical mechanics approach to the adhesive properties of dispersed systems

According to the thermodynamics of microscopic liquid films, the specific adhesion free



Apparent viscosity at 15 Pa, η<sub>app</sub> (mPa.s)

Fig. 4. Effect of apparent viscosity of emulsion at a shear stress of 15 Pa on amount of emulsion  $M_{ad}$  adhered on glass ( $\Box$ ), stainless steel ( $\blacksquare$ ), PET ( $\bigcirc$ ), LDPE ( $\bullet$ ) and PTFE ( $\triangle$ ) for olive, soybean and sunflower 1–3 emulsions.



Fig. 5. Effect of yield stress of emulsion  $\tau_0$  on amount of emulsion  $M_{ad}$  adhered on glass ( $\Box$ ), stainless steel ( $\blacksquare$ ), PET ( $\bigcirc$ ), LDPE ( $\bigcirc$ ) and PTFE ( $\triangle$ ) for vaseline and sunflower 4 and 5 emulsions.

energy  $\Delta_{ad}F(H)$  between condensed media separated by a thin liquid film (e.g., an emulsion droplet and a solid) of thickness *H* is defined from the isotherm of the disjoining pressure  $\Pi(h)$  operating between the condensed phases in the liquid



Fig. 6. Effect of average diameter  $d_{50}$  of emulsion fat globules on amount of emulsion  $M_{ad}$  adhered on glass ( $\Box$ ), stainless steel ( $\blacksquare$ ) and PTFE ( $\triangle$ ) for emulsions 1.

film of thickness *h* [26]:

$$\Delta_{ad}F(H) = \int_{H}^{\infty} \Pi(h) \,\mathrm{d}h \tag{7}$$

A negative value of  $\Delta_{ad}F(H)$  signifies attraction between the media. For emulsion droplets, the absolute value of  $\Delta_{ad}F(H)$  increases when they have a higher affinity for the solid, in the continuous phase (i.e., their contact angle on the surface is decreasing).

 $\Delta_{ad}F(H)$  results from molecular attraction, due to van der Waals' forces, and electrostatic repulsion between charged surfaces ( $\Delta_{ad}F = \Delta_{ad}F^{LW} + \Delta_{ad}F^{EL}$ ; DLVO theory). It is also due to steric interaction between adsorption layers of surfactants and polymers. For low-molecular-weight surfactants, the DLVO  $\Delta_{ad}F(H)$  isotherm (Fig. 7) is usually characterized by two adhesion minima and a coagulation barrier for electrically charged surfaces, resisting to the adhesion of droplets to solids.

It should be noted that, in aqueous media, van Oss takes the acid-base interaction energies into account  $(\Delta_{ad}F = \Delta_{ad}F^{LW} + \Delta_{ad}F^{EL} + \Delta_{ad}F^{AB})$ . Indeed, electrostatic repulsion is then almost always accompanied by acid-base repulsion and a reduction in  $\zeta$ -potential, especially for amphoteric polymers such as proteins and phospholipids present in our emulsions [21]. This leads to an extended DLVO theory with different  $\Delta_{ad}F$  energy isotherms, the profile of which depends on the



Fig. 7. Free adhesion energy  $\Delta F_{ad}$  isotherm according to the DLVO theory (\_\_\_\_\_), with repulsive electrostatic (- - -) and attractive van der Waals' (\_\_\_\_\_) interactions.

properties of the continuous phase (hydrophilic character, ionic strength, etc.) and no longer has both primary and secondary minima of attraction. At this point, we cannot suggest a hypothesis for the adhesion profile of our emulsions as we have not yet measured the specific interaction forces.

The adhesion force  $f_a^*$  between an emulsion droplet of radius *R* and a plane surface through a microscopic emulsion film of thickness *H* is then related to the specific adhesion free energy by the following equation:

$$f_{a}^{*} = 2\pi v_{a} R \varDelta_{ad} F(H) \tag{8}$$

where  $v_a$  is a parameter which is a function of the deformability of emulsion droplets [26]. Thus, the specific adhesion free energy between an emulsion droplet and a surface governs the adhesion force at a larger scale.

According to the concept of physicochemical mechanics, the adhesional strength  $P_{ad}$  of a concentrated emulsion formed by droplets of mean radius *R* may be expressed to a first approximation as the product of the mean adhesion force  $f_a^*$  and the density of number of contacts *n* between emul-

sion droplets and the solid (Fig. 8). For a narrow droplet size distribution, n may be estimated as  $1/R^2$ , yielding [26]:

$$P_{\rm ad} \approx |f_{\rm a}^*|n \approx |\mathcal{A}_{\rm ad}F(H)|/R \tag{9}$$

Thus, all of the physicochemical factors affecting the specific adhesion free energy in the emulsion film also affect the global adhesion strength of such emulsions. The adhesion amount of emulsions after flow,  $M_{\rm ad}$ , increases then with increasing  $P_{\rm ad}$ .

The effect of R on  $P_{ad}$  (Eq. (9) explains our findings that  $M_{ad}$  increased with decreasing average droplet size,  $d_{50}$  (Fig. 6). It also explains the effect of related rheological parameters such as viscosity (Fig. 4) which induces heavier residues, as it increased with decreasing  $d_{50}$  at low yield stress.

# 4.2. Specific surface phenomena acting on $M_{ad}$ involved in real systems

In real conditions of emulsions stabilized by lecithin and proteins, the specific modification of surfaces by adsorption layers of these species must be taken into account, as it affects the behavior of thin liquid films. Particularly, proteins tend to adsorb on hydrophobic, low-energy surfaces such as polymers, inducing conformation changes. Their hydrophobic moieties tend to adsorb irreversibly on these surfaces, together with the adsorption of lecithin, leaving hydrophilic sites in contact with the aqueous phase. Thus, the hydrophobic surface is hydrophilized (see Results section) and droplets interact with the surface precoated with proteins and lecithin. Moreover, there is a competition between protein and lecithin. As the protein has more hydrophobic sites, its desorption energy is expected to be greater, which means that the surface will be covered more by proteins than by lecithin. On the contrary, adsorption of proteins on hydrophilic, high-energy surfaces is lower and leads to no major conformation change [20,27]. In this case, hydrophilic sites interact with the surface and hydrophobic moieties are left at the interface with water, but this adsorption layer is not as tight and as continuous as on hydrophobic solids. Thus it leaves open sites for both the



Fig. 8. Effect of adhesion force  $f_a^*$  on adhesion pressure  $P_{ad}$  of the emulsions.

adsorption of lecithin on its hydrophilic head and direct interactions between hydrophilized oil droplets and the solid.

This could explain the observed effect of surface hydrophilicity (Fig. 3), as interactions between solid and hydrophilized droplets are thermodynamically favored on hydrophilic surfaces such as glass. Morover, as the adsorption layer is more loose than on low-energy solids, these direct interactions with droplets are more likely to occur (Fig. 9). Oil droplets may also interact directly with hydrophobic protein moieties, leading to an enhanced spreading. There is thus an increase of  $|\Delta_{ad}F(H)|$ , and consequently of  $P_{ad}$  (Eq. (9), explaining high  $M_{ad}$  (Figs. 2–4). Conversely, on hydrophobic surfaces, the adsorption of native proteins and phospholipids on their hydrophobic moieties is favored and droplets interact with the adsorption layer rather than with the solid directly (Fig. 9). Because of steric repulsion between the adsorption layer on the solid and that on the droplets, interactions between these layers can induce a lower free energy of adhesion  $|\Delta_{ad}F(H)|$ . This results in a lower adhesion force on these hydrophobic solids, as observed on LDPE or PTFE for which  $M_{ad}$  is low (Figs. 2–4). The same phenomenon was also observed on living cells [21].

Moreover, in the case of blends of proteins and phospholipids, additionally to the competition for adsorption of low- and high-molecular-weight species, surfactant-polymer complexes are formed [28]. Their adsorption at solid surfaces competes with that of simple species and droplets. Finally, phospholipids such as lecithin are likely to form



Decreasing contact angle of oil droplets

Fig. 9. Effect of surface hydrophilicity, increasing from PTFE to glass, on the adhesion of emulsion droplets.



Fig. 10. Formation of symmetric (A) and non-symmetric (B) liquid films during emulsion flow on hydrophobic and hydrophilic surfaces.

micelles, vesicles and lamellar structures in the aqueous phase and on the surface [29], which certainly play a role in adhesion of the emulsions.

# 4.3. Suggestions explaining the effect of surface hydrophilicity on $M_{ad}$

The effect of surface hydrophilicity on  $M_{ad}$  can also be explained on the basis of symmetry of the emulsion films on different solids. In the case of hydrophobic surfaces, a "symmetric" aqueous film is formed during flow (Fig. 10) as the hydrophobic fragments of the proteins and lecithin tend to leave water for hydrophobic media (air or solid). The velocity profile is thus likely not to vanish on the surface (slip effect). An easy glide of this aqueous layer on the solid and low amount adhered are thus expected. In the case of hydrophilic surfaces, a "non-symmetric" aqueous film is formed, in which emulsion droplets are "anchored" to the surface. This may be due to two effects: the attractive forces between hydrophilic sites covering emulsion droplets and the hydrophilic solid, and the

lower tendency of native proteins to adhere on high-energy solids [27], which makes the anchoring of emulsion droplets easier. This makes flow more difficult as the speed distribution is no longer homogeneous. Moreover, this effect was certainly increased by the anchoring of liposomes on the surface, because for example phosphatidylcholine is likely to form vesicles in the aqueous phase [29].

The sudden increase of  $M_{ad}$  with increasing solid surface tension (Fig. 2) may also be explained by a sharp transfer from symmetric to non-symmetric liquid films, due to a brutal inversion of the thermodynamically favorable adsorption state of proteins and lecithin on solids. This transition may not be explained clearly by solid total surface tension, but rather by the presence of acid–base surface tension components. Indeed, we have shown that surface tension differences between solids were mostly given by their acid–base components, which almost vanish for LDPE and PTFE. It is precisely on these surfaces that the adhesion amount is very low. Then, on more hydrophilic surfaces, adhesion amount increased with increas-



Fig. 11. Effect of  $\gamma_s^-$ , the electron-donor component of solid surface tension, on the amount of emulsion adhered  $M_{ad}$ : black circles: olive 1, white circles: olive 2, small black squares: sunflower 1, small white squares: sunflower 2, medium white squares: sunflower 3, medium black squares: sunflower 4, large white squares: sunflower 5, +: soybean 1, ×: soybean 2, white triangles: vaseline 1, black triangles: vaseline 2.



Fig. 12. Effect of emulsion yield stress  $\tau_0$  on final liquid film thickness (*h*).

ing electron-donor component  $(\gamma_s^-)$  as shown in Fig. 11 ( $R^2$  coefficients are given in Table 6). Thus it seems that, from a certain value of acid-base surface free energy components, proteins adsorb

on their hydrophilic rather than hydrophobic moieties, explaining the greater adhesion on higher energy solids.

These results confirm the importance of acid– base interactions in the adhesive process, even for polymer surfaces as developed in many recent theoretical studies [30], and the usefulness of splitting solid surface tension into different parameters to better understand interfacial interactions.

# 4.4. Suggestions explaining the effect of rheology on $M_{ad}$

As seen in the Results section, to explain the residual adhesion amount one must also account for rheological parameters. According to Figs. 4 and 5, there seems to be a combined effect of an emulsion's apparent viscosity  $\eta_{app}$  and yield stress  $\tau_0$ . For products having equivalent yield values, below 0.25 Pa, adhesion amount increased with increasing viscosity. However, from a certain threshold yield stress (which seems to be of the

order 0.26 Pa), the difficulty of starting flow at low shear stress has the most important effect on the final weight, for a given solid. The range of residual amount may then be estimated by the mechanical equilibrium condition (Fig. 12):

$$\rho g \sin \alpha h = \tau_0 \tag{10}$$

where h is residue thickness per unit surface,  $\rho$  is emulsion density and  $\alpha$  tilting angle. As we found that  $\tau_0$  varied in the range 0.26–0.37, we can approximate h between 20 and 35 µm, i.e.,  $M_{\rm ad}$ between 20 and 35 g m<sup>-2</sup> which is the range that was found for emulsions having  $\tau_0$  above the critical value (Fig. 5) on wetted solids. Finally, it seems that  $M_{\rm ad}$  is increasing with apparent viscosity if other parameters are kept constant and, as well,  $M_{\rm ad}$  is increasing with shear stress yield value, with other parameters kept constant. One may though notice that for low-energy solids such as PTFE and LDPE, there is no effect of rheological parameters on  $M_{\rm ad}$ . Thus surface thermodynamics seems to be more important than rheological properties on these low-energy solids, as it prevents wetting in the first moments of contact. As well, the amount adhered on glass is only weakly dependent on rheology, as the thickness of deposits may not increase indefinitely. There is thus a balance between a solid surface tension parameter and both apparent viscosity and shear stress yield value.

### 4.5. Tentative mechanism of $M_{ad}$ formation

We can suggest that for hydrophobic, lowenergy solids, for which there is a low wetting, surface thermodynamical parameters are the driv-



Fig. 13. Hypothesis concerning of the combined effect of solid surface tension and emulsion rheological properties on adhesion of emulsion films to hydrophobic (a) and hydrophilic (b, c) surfaces.

ing force for residual adhesion, as they prevent the presence of a continuous liquid film (Fig. 13(a)). Therefore, whatever the rheological parameters of the emulsions, the amount adhered is expected to be very low. This interpretation is illustrated by the existence of the critical solid surface tension after which deposits begin to be formed (Fig. 2).

For medium hydrophilicity and surface energy solids, such as stainless steel and PET, both rheological parameters and surface tension factors determine final  $M_{ad}$  (Fig. 13(b)). Indeed, in the gravity field, the rate of thinning of the relatively thick emulsion layers is determined by the apparent viscosity of the emulsion (Fig. 4). If the thickness of the emulsion layer diminishes and becomes of the order or less than the capillary length,  $l_{\rm c} = (\gamma_{\rm L}/\rho_g)^{1/2} \approx 1 \text{ mm} (\rho \text{ is the density of the emul-}$ sion), then the rate of thinning is expected to be influenced also by the surface tension forces (the well-known Marangoni effect). For emulsions being characterized by yield stress  $\tau_0$ , the rate of thinning will tend to zero for a layer thickness of  $h \approx \tau_0 / \rho g$  (final residual weight of  $\tau_0 / g$ , Figs. 5 and 12). For negligible  $\tau_0$ , film thinning may lead to its desaggrgation in multiple droplets [31], as observed on PET and stainless steel. This instability takes part in the limitation of  $M_{ad}$  on mediumenergy, partially wetted surfaces (Fig. 5).

For soilds with high hydrophilicity and high surface energy such as glass, wetting is complete and stable. There can be a continuous and tight first adsorption layer due to the primary adhesion minimum (Fig. 10). Thus, once spreading is performed,  $M_{ad}$  is governed by rheological effects (Fig. 13(c)). However, this dependence is not as important as for medium-energy solids because the maximum residual mass for the mechanical equilibrium to be maintained is reached more easily, as there are no more surface instability effects.  $M_{ad}$  increases then only in the limits of physical equilibrium conditions.

### 5. Conclusion

These first results of our study show the importance of both surface energetics and physicochemical mechanics on the bulk amount of food emulsions adhered to surfaces. They suggest the relative importance of the emulsion's rheological behavior compared with surface energetical properties on the adhesion amount, depending on the nature of the solid: hydrophobic or hydrophilic, low-energy or high-energy. The importance of acid-base interactions in the adhesive process was also highlighted. The formation of residues of concentrated emulsions on solid substrates is thus a complex colloid-chemical process.

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### References

- C.C. Lai, in: J.I. Gray, B.R. Harte, J. Miltz (Eds.), Food Product–Package Compatibility, 1986, p. 258.
- [2] K.W. Allen, J. Phys. C 7 (1993) 1511.
- [3] M.C. Michalski, S. Desobry, J. Hardy, Crit. Rev. Food Sci. Nutr. 37 (1997) 591.
- [4] S.R. Saunders, D.D. Hamann, D.R. Lineback, Lebensm. Wiss. Technol. 25 (1992) 309.
- [5] H. Nishino, M. Tanaka, M. Yokoyama, Nipp. Suis. Gakk. 56 (1990) 1239.
- [6] I.B. Checkmareva, V.G. Babak, R.I. Dzhafarova, Izv. Vyss. Ucebn. Zaved. Pis. Technol. 2 (1985) 3.
- [7] J. McGuire, S.A. Kirtley, J. Food Eng. 8 (1988) 273.
- [8] L. Boulange-Peterman, B. Baroux, M.N. Bellon-Fontaine, J. Adhesion Sci. Technol. 7 (1993) 3.
- [9] H. Busscher, Surface free energies and the adhesion of oral bacteria, Thesis, University of Gröningen, 1985.
- [10] M.C. Michalski, S. Desobry, M.N. Pons, J. Hardy, J. Am. Oil Chem. Soc. (1998) 75, in press.
- [11] G. Hoffman, The Chemistry and Technology of Edible Oils and Fats and their High Fat Products, Academic Press, London, 1989.
- [12] M. Ould Eleya, J. Hardy, in Proc. Food Preservation 2000 (US Army Natick Research, MA, 19–21 October 1993), Science and Technology Corporation, Hampton, VA, 1993, p. 877.
- [13] W.D. Harkins, H.F. Jordan, J. Am. Chem. Soc. 52 (1930) 1751.
- [14] D.W. van Krevelen, Properties of Polymers, 3rd edn, Elsevier, Amsterdam, 1990.
- [15] J.R. Dann, J. Colloid Interface Sci. 32 (1970) 302.

- [16] C.J. van Oss, R.J. Good, H.J. Busscher, J. Dispers. Sci. Technol. 11 (1990) 75.
- [17] A. Dupré, Théorie Mécanique de la Chaleur, Gauthiers-Villars, Paris, 1867.
- [18] T. Young, Philos. Trans. R. Soc. London 95 (1805) 65.
- [19] C.J. van Oss, M.K. Chaudhury, R.J. Good, Chem. Rev. 88 (1988) 927.
- [20] V. Krisdhasima, J. McGuire, R. Sproull, J. Colloid Interface Sci. 154 (1992) 337.
- [21] C.J. van Oss, Interfacial Forces in Aqueous Media, Marcel Dekker, New York, 1994.
- [22] D.K. Owens, R.C. Wendt, J. Appl. Polym. Sci. 13 (1969) 1741.
- [23] S. Wu, J. Adhesion 5 (1973) 39.
- [24] C. Germain, Thèse de doctorat, Université Lyon I Claude Bernard, 1994.

- [25] R. Byron-Bird, G.C. Dai, B.J. Yarusso, Rev. Chem. Eng. 1 (1982) 1.
- [26] V.G. Babak, Colloids Surfaces A: Physicochem. Eng. Aspects 85 (1994) 279.
- [27] F. MacRitchie, J. Colloid Interface Sci. 38 (1972) 484.
- [28] E. Dickinson, in: E.D. Goddard, K.P. Ananthapadmanabhan (Eds.), Interactions of Surfactants with Polymers and Proteins, CRC Press, Boca Raton, FL, 1993, p. 295.
- [29] O.R. Fennema, Food Biochemistry, 2nd edn, Marcel Dekker, New York, 1985.
- [30] K.L. Mittal, H.R. Anderson, Jr. (Eds.), Acid-Base Interactions: Relevance to Adhesion Science and Technology, VSP, Utrecht, 1991.
- [31] A. Sharma, ReiterG., .Co, J. Colloid Interface Sci. 178 (1996) 383.