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Hygrometric measurements for the evaluation of the stability of model food emulsions

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A non-destructive test is proposed, based on the measurement of the change in the relative humidity (%RH) needed to reach the equilibrium value (%ERH), which makes a comparative evaluation of the degree of dispersion between the aqueous and lipidic phase and the stability of emulsions. By measuring the rate to reach the %ERH, a kinetic index (k) has been introduced, describing the 'resistances' to the mass transport (water vapour) from the bulk emulsion to its surface and to the head space of the sample cell. To define this index a model of water adsorption to the gas–liquid interface of the bulk emulsion is described. The model is based on a formalism similar to that used to describe a Langmurian kinetic. In oil–in–water emulsions the destabilising processes (creaming, coalescence) during storage are implied in the formation of a 'barrier' which block the aqueous vapour or decrease the rate at which it comes to the surface. Thus, the corresponding k value of the model tends to decrease, and the decrease is higher for the more destabilised emulsified system. In the water–in–oil dispersed systems, the k index is able only to describe the degree of dispersion and partly loses the ability to indicate changes that take place in the bulk system with time. © 1997 Canadian Institute of Food Science and Technology. Published by Elsevier Science Ltd

Keywords: food emulsions, emulsion stability, hygrometric measurements.

INTRODUCTION

Many natural and processed foods, such as milk, cream, mayonnaise, butter and margarine, consist of an intimate mixture of at least two non-miscible phases in the form of finely or coarsely dispersed systems, defined as emulsions. Apart from water and oil (triglicerides), there may also be proteins, polar lipids, carbohydrates, dissolved salts, ethanol and preservatives in food emulsions (Dickinson, 1988; Robins and Wilson, 1994). In food processing the emulsification process permits incorporation in the same system of immiscible components (i.e. aroma compounds in soft drinks) as well as obtaining the essential properties of a chemical, physical, microbiological, nutritional, or organoleptic nature (Das and Kinsella, 1991).

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On the other hand, as is well known, emulsions are thermodynamically unstable systems due to an excess surface free energy where stability implies no tendency towards structural changes. In fact, after a time, the droplets of the inner phase tend to cluster together spontaneously, forming small or large flocs (flocculation), to coalesce giving larger spherical droplets and to cream (gravitational separation) leading to a layer of the lower density phase on the top of the emulsion (Kinsella, 1984; Leman and Kinsella, 1989). These different processes, which are responsible for the destabilisation and the ultimate oiling-off (breaking) of the emulsified system, are interrelated and can act simultaneously giving rise to numerous intermediate physical states, ranging from a perfectly uniform dispersion to completely separated phases. Meanwhile, the stability of an emulsion can be related to a kinetic concept (Dickinson and Stainsby, 1982) because the long-term stability of a dispersed system implies that the rate and extent of

change in its structure and properties is sufficiently low in real time (Tolstoguzov, 1992).

The rate at which the destabilisation occurs depends on different physical and chemical factors (droplet size and distribution, viscosity of the continuous phase, dispersed phase volume to total volume ratio, specific gravity of the phases, temperature, etc.) and on the presence of substances, generally recognised as emulsifiers, which form an interfacial film between the continuous and dispersed phase (Pearce and Kinsella, 1978; Leman and Kinsella, 1989). The key to stability lies in the properties of the surface-active components present in the system. Foods contain many surface active ingredients, the most important being proteins and low molecular weight emulsifiers. Proteins act as surfactants in many food emulsions due to their amphyphilic structure (Das and Kinsella, 1991; Damodaran, 1994).

Several methods have been proposed to estimate the emulsion stability; they have evaluated the chemical, physico-chemical and physical changes that in bulk emulsion occur either spontaneously, in the accelerated shelf-life tests or under thermal (high or low temperature) or mechanical stresses (Acton and Saffle, 1971; Pearce and Kinsella, 1978; Kato *et al.*, 1985; Leman and Kinsella, 1989). The phenomena causing the instability of the food emulsions occur during the different steps of the process and the storage and the resulting changes in general determine a decrease in the quality of the product. Thus, it is important to have rapid tests describing the state of the dispersion and the changes that could happen in the emulsions. They should able to be carried out in any step of the process and storage of food emulsion.

In the present study, a non-destructive test is proposed based on the measurement of the change in the relative humidity (%RH) to reach the equilibrium value (%ERH) which makes a comparative evaluation of the degree of dispersion between aqueous and lipidic phase and the stability of the emulsion. By measuring the rate to reach the %ERH, a kinetic index (k) has been introduced which can describe the 'resistances' to the mass transport (water vapour), from the bulk emulsion to its surface and to the head space of the sample cell, that occur during the destabilisation of the emulsified system. To define this index, correlated to the 'state' of the water dispersion in the emulsion, the graph showing the increase of the relative humidity (%RH) in the head space as a function of the time has been related to an adsorption isotherm.

MATERIALS AND METHODS

Sample preparation

Oil–in–water emulsions were prepared at room temperature using two different emulsifiers, whey protein concentrate (WPC) and Tween 40 (Sigma Chemical Co., St. Louis, USA). Their concentration in the aqueous phase (distilled water) was 10 g litre^{-1} on a protein basis and 10 g litre^{-1}, respectively. Different amounts of commercial soy oil were added to the aqueous phases to obtain emulsions with two values of ϕ (where ϕ indicates the 'dispersed phase volume/total emulsion volume' ratio): 0.50 and 0.67. A commercial Whey Protein Concentrate (WPC) with a protein concentration of 825 g kg^{-1} was used for this purpose.

Two different water–in–oil emulsions were prepared: the first, using soy oil and whey protein dispersion (10 g litre^{-1} in protein); the second, using Span 80 (Sigma Chemical Co., St. Louis, USA) as emulsifier added to the oil phase before homogenisation, and distilled water as the aqueous phase. Emulsions with different values of ϕ, 0.10 and 0.20, were obtained.

To prepare the emulsions, the lipid and the aqueous phase were previously mixed in a blender and the resulting coarse emulsion (60 ml each time) was homogenised with a Polytron PT 20 (Kinematica, Luzern, Switzerland) at speed '5' for one minute.

In order to avoid microbial spoilage during storage, 4 g kg^{-1} of sodium benzoate was added to the aqueous phase before mixing.

Relative humidity (%RH) and equilibrium relative humidity (%ERH) measurements

A fixed volume (25 ml) of the emulsion sample was put into a hermetically sealed fitted plastic sample cell. A hygrometer (ROTRONIC HYGROSCOP DT, connected to a ROTRONIC DMS-100H probe, PBI, Milan, Italy) was used to measure the %RH during the period necessary to reach the %ERH. The measurement of the change in %RH over time was carried out following a well-established procedure, already described elsewhere (Lerici *et al.*, 1994). Briefly, the hygrometer and the sealed sample cell were put into a hermetic box in which the %RH of the air was kept at a very low value (about 10%) with dried silica gel. The cell containing the sample was opened immediately before the measurement of the %RH and then transferred into the hygrometer case which in turn, was closed with the head of the hygrometer lodging the water vapour probe. The measurements of the different model systems were carried out just after preparation and during storage (up to five days) at room temperature. The %RH values, recorded until the %ERH was reached, were represented both as a function of time, and as the rate of the %RH change, d(%RH)/dt, as a function of the corresponding %RH value. The rate at which the water vapour molecules leave the surface of a sample to pass into the surrounding atmosphere depends not only on the 'barriers' to the mass transfer present in the surface itself (i.e. lipid layers), but also on all the forces that act on the liquid water molecules (Hunter, 1993). The adsorption of pro-

teins at the gas–liquid interface has been studied by Guzman *et al.* (1986) and a kinetic model, based on a formalism similar to that used by Langmuir to describe adsorption at gas–solid interface, has been applied.

The Langmurian model was used to determine the excess surface concentration as well as the relative rates of adsorption and desorption of β-casein and lysozyme adsorption at the air–water interface (Hunter *et al.*, 1989, 1991). The behaviour of the release of water vapour from the bulk emulsion can be compared with this adsorption/desorption kinetic mechanism. Following the formalism used by Guzman *et al.* (1986), the number of sites covered by the water molecules is expressed as a function of the vapour pressure. Given the covering coefficient $\Gamma(0 < \Gamma < 1)$, the adsorption factor b,($b = K_a/K_d$, where K_a and K_d are the kinetic constants for adsorption and desorption, respectively), and the partial pressure of water vapour as P_a, the isotherm can be written:

$$\Gamma = b \cdot P_a/(1 + b \cdot P_a) \quad (1)$$

This is the Langmuir isotherm and it is the limit of our model for monolayer coverage by water vapour in which the energy of activation for adsorption and desorption can be considered constant. Adsorption and desorption calculations can be made from $d\Gamma dt$ leading to rather complicated equations. Instead of referring directly to the covering coefficient Γ, we can use the %RH in the headspace of the sample cell as a function of time. Indicating %RH with A, the desorption of water from an emulsion can be represented by the following empirical equation:

$$A = k \cdot t/(1 + k \cdot t) \quad (2)$$

which can be rearranged as:

$$A/(1 - A) = k \cdot t \quad (3)$$

This function holds validity in a limited range of time, over which it loses its linearity. For the range of time here considered, the k constant is the slope of the curve obtained representing the term $A/(1–A)$ as a function of the recording time. In such a context, the k factor assumes the value of an index able to point the 'degree of freedom' of the water vapour molecules (corresponding to the highest branch of the adsorption isotherm) (Hunter, 1993). The factor k, having the dimensions of the inverse of time, may also be related to the 'frequency' with which the water molecules leave the bulk emulsion. The k data referred to in this paper are the average of at least five measurements.

Emulsion stability evaluation

The stability of the oil–in–water emulsions was evaluated by turbidimetry, according to Pearce and Kinsella (1978). The mean data reported are the average of at least five replicates. Creaming behaviour in quiescent emulsion samples of 100 mm height was monitored visually for time-dependent changes in the thickness of cream and serum layers.

Statistical analysis

The data were submitted to one-way analysis of variance (CoStat, Cohort Software, Berkeley, USA). When significant effects were determined by the ANOVA procedure, the Student-Newman-Keuls procedure was used in order to perform multiple comparisons of the detected means.

RESULTS AND DISCUSSION

The measurements of the equilibrium relative humidity (%ERH) using a hygrometric probe assume that the water vapour pressure of the sample in the headspace of the cell reaches a steady state. As is well known, in a hygrometric cell the rate at which the %ERH is reached depends on various factors; at constant values of headspace volume of the sample in the cell, temperature, total pressure and initial composition of the air, it can be summarised as:

1. the difference of the water vapour pressure between the sample and the atmosphere in the head space.
2. the transfer rate of the water vapour from the surface of the sample to the atmosphere in the headspace

If we consider the general characteristics of an emulsified system, it could be considered that, in a system with fixed composition of the aqueous and lipidic phase, at constant temperature, pressure and headspace volume, differences in the rate to reach the %ERH are only due to a difference in the state of dispersion of the lipidic and aqueous phase in the higher layers of the sample or to any change that takes place there with time. In fact, in the extreme states of dispersion of a specific oil–in–water (o/w) emulsion, i.e. perfect uniformity and completely destabilised with phase separation and free oil on the top, the rates to reach the %ERH will be the maximum and the minimum, respectively. On the other hand, in the case of the water–in–oil (w/o) emulsions, the %RH change towards the equilibrium value depends on the degree of dispersion because in a perfect emulsified system the water is completely 'entrapped' as small droplets in a waterproof continuous phase. In such a case, the increase of the %RH in the headspace will be very slow, whereas the presence of the water not completely emulsified and 'free' on the surface could determine a behaviour similar to that of a freshly made oil-in-water emulsion.

In Fig. 1 the extreme of states of dispersion in the oil-in water (Fig. 1a) and water-in-oil (Fig. 1b) and the corresponding hypothetical trend of the %RH towards the equilibrium value (%ERH) are drawn. Figure 2 reports the recorded trends of the %RH towards the equilibrium versus time of the WPC dispersion (10 g kg^{-1} on protein basis, no lipid), the WPC and Tween 40 oil–in–water emulsions ($\phi = 0.67$) and a model imitating a completely destabilised oil-in-water emulsion ($\phi = 0.67$) with the two phases separated (oiling-off), just after their preparation. The model of the oiling-off was prepared with the protein aqueous dispersion covered with an appropriate volume of oil. The values of ERH% of the whey protein aqueous dispersion, of the corresponding $\phi = 0.67$ emulsion and of the Tween 40 $\phi = 0.67$ emulsion were 99.6, 98.5 and 98.7, respectively.

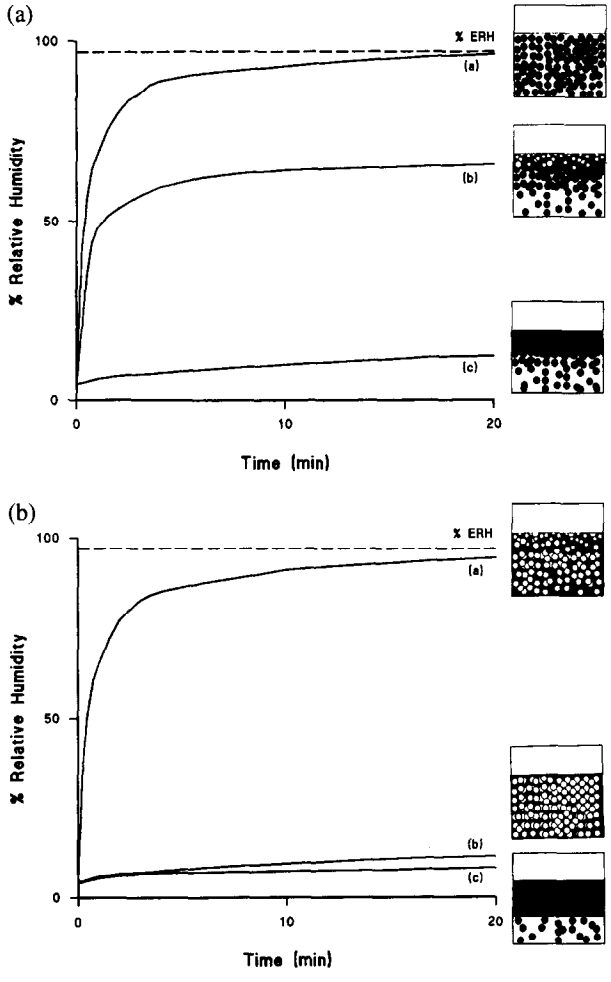

Fig. 1. (a) Hypothetical trends of the %RH in the head-space of a hygrometer during the time needed to reach the %ERH of oil-in-water model emulsions at different levels of dispersion and stability. (i) perfectly dispersed; (ii) not perfectly dispersed or partially destabilised; (iii) destabilised; □: aqueous phase; ■: oil phase.
(b) Hypothetical trends of the %RH in the head-space of a hygrometer during the time needed to reach the %ERH of oil-in-water model emulsions at different levels of dispersion and stability. (i) not perfectly dispersed; (ii) perfectly dispersed; (iii) destabilised; □: aqueous phase; ■: oil phase.

The protein dispersion and the emulsions showed a similar behaviour, indicating that partial vapour pressure in the surface of the emulsions is comparable to that of the protein dispersion. Although the emulsified systems of the Fig. 2a contain the same amount of oil, the change of the RH% towards the ERH % value as a function of the recording time of Tween 40 emulsion was slower than the WPC emulsion. This result could be related to a different state of dispersion of the emulsified systems considered. The effects of the emulsifier and of the oil ratio on the absorbance of the freshly made emulsions are reported in Table 1. At the same value of ϕ, the type of emulsifier used significantly affected the values of absorbance and, thus, the degree of dispersion of the lipidic phase of the freshly prepared emulsions. Tween 40 produced o/w emulsions with higher values of absorbance than WPC, whilst no difference was found between the $\phi = 0.50$ and $\phi = 0.67$ WPC emulsions. The higher interfacial area of the dispersed oil droplets in the case of the Tween 40 emulsions, which slowed the mass transfer of the aqueous vapour from the surface of the sample to the head space of the hygrometric cell, could be implied in the lower RH% change towards the %ERH. On the other hand, the increase of the vapour pressure in the headspace of the model of the completely destabilised emulsion is significantly less, especially for values of %RH above 20. The different behaviour of this sample is explained as being due to the presence of a continuous lipid layer on the top of the model sample acting as a 'barrier' against the reaching of the water vapour equilibrium.

The trends of the %RH in the head-space of water-in-oil emulsions, at different composition and volume ratios as a function of the time, are shown in Fig. 2b. Although some differences among the %RH curves of the water-in-oil emulsions under study were shown, the trend in all cases is more similar to that of an aqueous dispersion than that of a well-dispersed water-in-oil emulsion. The presence of water not perfectly homogenised in the bulk dispersed system, could account for this behaviour and the effect is more evident in the w/o emulsions prepared with whey proteins than in those containing Span 80. On the basis of these results, it could be reasonably supposed that, for a given oil-in-water emulsion, a lower degree of emulsification or of processes causing destabilisation, regarding especially the higher part of the bulk emulsion and its superficial layer, determines the curves of the %RH change ranging between those of the two groups of samples considered.

The different stabilities of the emulsions could be evaluated testing the effect of the storage time on the %RH change in the head space of these dispersed systems. Indeed, the repetition of the measurements on the same emulsions during the period of storage at room temperature showed a more or less pronounced decrease in the %RH values reached at the same recording time

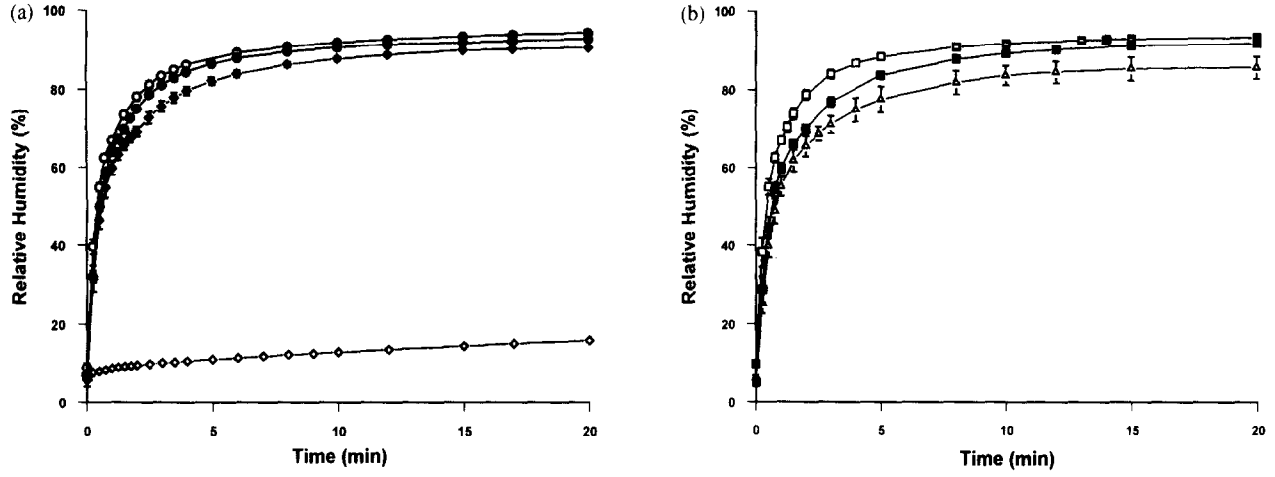

Fig. 2. (a) %RH trend of WPC aqueous dispersion, $\phi = 0.67$ oil–in–water emulsions and oiling off model as a function of recroding time (mean data of at least five measurements). (○) WPC aqueous dispersion; (●) $\phi = 0.67$ WPC emulsion; (◆) Tween 40 emulsion; (◇) $\phi = 0.67$ oiling-off model. (b) %RH trend of water-in-oil emulsions as a function of the recording time (mean data of at least five measurements). (□) $\phi = 0.2$ WPC; (■) $\phi = 0.1$ WPC; (△) $\phi = 0.2$ Span 80.

in comparison with those of the samples freshly prepared. As an example, Fig. 3 reports the change of trends of the %RH in the head space of the water-in-oil, $\phi = 0.2$ WPC during storage (up to 96 h) as a function of the recording time. The %RH changes in the headspace of the hermetically sealed sample in the hygroscopic cell could be also studied in terms of rate, d(%RH)/dt as a function of the corresponding %RH.

Figure 4, records d(%RH)/dt of w/o and o/w emulsions freshly prepared and after 48 h of storage as a function of the corresponding value of %RH. Figures 4(a) and (b) are representative of two different behaviours: one for the protein dispersion and the freshly made emulsions, and the other for the completely destabilised sample. The %RH change at the corresponding %RH value of the former showed a marked decrease with the increase of the %RH reached in the headspace of the hygrometric cell, less pronounced at the values near to the %ERH. In contrast, the model sample of the emulsion with oiling-off and completely separated phases presented very low rate values, even in the %RH range between 10 and 20, as expected. The change of the %RH trend observed in the emulsions during storage also affected the corresponding rate values and, as a consequence, the stored samples presented d(%RH)/dt values lower than the fresh ones, especially in the range 20–80%RH, as shown in Figs 4(c) and (d) for the samples stored for 48 h. In particular, it was noted that the w/o emulsion prepared with Span 80 after this storage time presented a trend comparable to that of the model of the oiling-off while the w/o WPC showed only a decrease in the rate of the %RH change.

The %RH data of the model systems under study were elaborated according to eqn 3 reported in the 'Material and Methods' section and Fig. 5 shows some examples of the slopes (k) of the curves obtained representing $A/(1-A)$ as a function of the recording time, t. The values of the k and the results of the analysis of the variance of the samples under study, just after their preparation and during storage at room temperature, are reported in Table 2. The state of dispersion, the composition of the freshly made model systems having the same f and the storage time affected ($P \leqslant 0.01$) the k values. At time zero (freshly made models) the mean k values ranged between a minimum of 0.017, corresponding to the oiling-off model, to a maximum of 1.532 of the w/o $\phi = 0.20$ WPC emulsion. This value is close, even though significantly different, to that of the whey protein concentrate dispersion. Indeed, these two extreme k values could be related to a different degree of

Table 1. Absorbance mean values of oil-in-water emulsions just after preparation and after 96 h of storage at room temperature (mean data of at least 5 determinations)

		Time (h)			
		0		96	
o/w emulsion	ϕ	$\bar{x}$	s_x	$\bar{x}$	s_x
WPC	0.50	0.235a	0.009	0.207a	0.032
Tweeen 40	0.50	0.476b	0.007	0.441b	0.007
WPC	0.67	0.229a	0.003	0.236a	0.009
Tween 40	0.67	0.541c	0.006	0.539c	0.007

Means followed by different letters in the same column and within the same sample are signficantly different at $P \leq 0.01$.

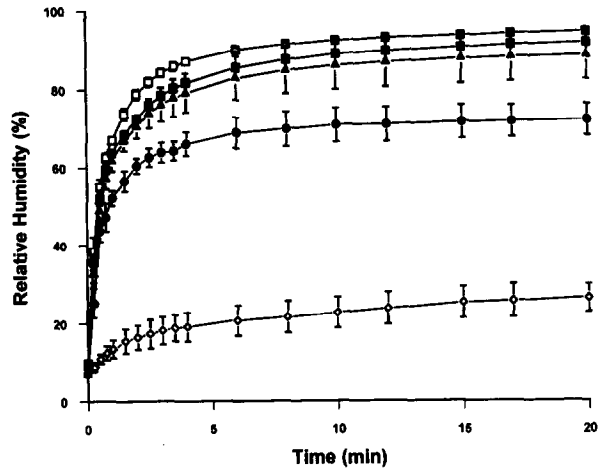

Fig. 3. Change of %RH trend of $\phi = 0.2$ w/o WPC emulsions during storage at room temperature (□) freshly made; (■) 24 h; (▲) 48 h; (●) 72 h and (◇) 96 h.

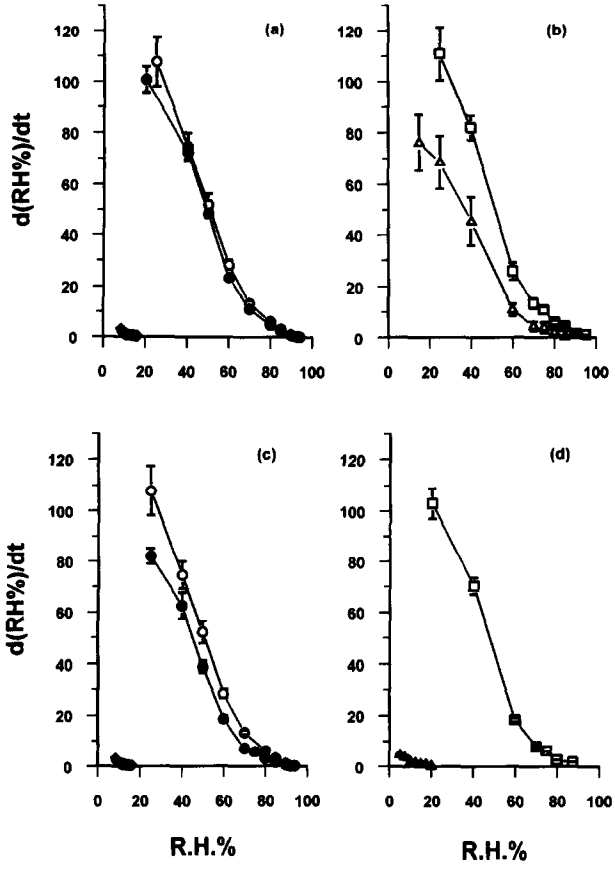

Fig. 4. d(%RH)/dt versus the corresponding %RH of the WPC dispersion, o/w and w/o emulsions just after preparation and after 48 h of storage. (a) and (c): WPC dispersion and o/w model emulsions. (b) and (d) w/o model emulsions. (a) and (b) freshly made. (c) and (d) after 48 hours of storage (○) WPC aqueous dispersion; (●) $\phi = 0.67$ WPC emulsion; (◇) oiling-off model; (□) $\phi = 0.2$ WPC; (△) $\phi = 0.2$ Span 80.

freedom of the water vapour molecules to the mass transfer into the headspace of the hygrometric cell. The lowest k value of oiling-off model, of an emulsified totally destabilised system, indicates the presence of a

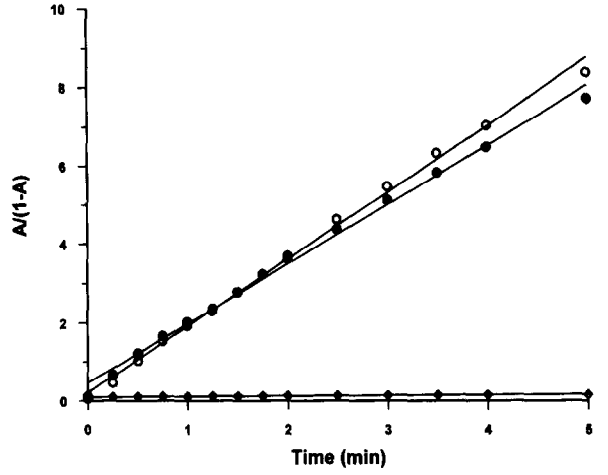

Fig. 5. Examples of slopes of the curves obtained representing $A/(1-A)$ as a function of the recording time. (○) WPC aqueous dispersion; (●) $\phi = 0.67$ WPC emulsion; (◇) oiling-off model.

'waterproof barrier' to the aqueous vapour transfer, whilst the higher k values are representative of a state where no hurdles to the mass transfer of the vapour molecules into the atmosphere of the hygrometric cell are present, except those present in the dispersion due to the dissolved solutes. In the case of the o/w emulsions, WPC and Tween 40 produced emulsified systems with significantly different k values, and this result could be related to the different degree of dispersion of the oil phase (see Table 1). However, immediately after their preparation, k was not affected by the lipidic fraction present in the emulsions having different emulsifying agents ($P > 0.05$). No meaningful differences were noted between the o/w WPC emulsions (both $\phi = 0.50$ and $\phi = 0.67$) and the WPC dispersion. At time zero the mean k values of the differently prepared w/o emulsions were significantly different and also different from those of the o/w emulsions. In general, storage caused a decrease of the k values of the emulsions whose intensity reflected the characteristics and the relative stability of the emulsified system.

After 24 h the k values of the o/w WPC emulsions (both $\phi = 0.50$ and $\phi = 0.67$) were lower and significantly different from those of the freshly prepared samples; longer storage time did not have a further effect. A more limited decrease of the k value was observed in the case of both of the o/w Tween 40 emulsions, indicating that only minor changes occurred in the higher layers of the emulsion which, thus, had a higher stability. The decrease in the k value is particularly remarkable for the w/o emulsion made with Span 80 and no differences ($P > 0.05$) were found between the k value of this sample after 24 h of storage and the model of the completely destabilised emulsion.

No differences ($P > 0.05$) occurred in the k value of the protein dispersion and the model mimicking the oiling-off of an emulsion during storage time. The vari-

Table 2. k Values of oil-in-water and water-in-oil emulsions of different composition just after preparation and during storage (mean data of at least 5 replications)

		Storage times (h)									
		0		24		48		7296			
Sample	ϕ	$\bar{x}$	s_x	$\bar{x}$	s_x	$\bar{x}$	s_x	$\bar{x}$	s_x	$\bar{x}$	s_x
WPC dispersion (1% protein)		1.398ij	0.035	1.407j	0.011	1.396j	0.052	1.419j	0.010	1.420j	0.019
Oiling-off model		0.018a	0.003	0.017a	0.001	0.018a	0.002	0.018a	0.002	0.017a	0.003
Oil-in-water emulsions											
WPC	0.50	1.317ij	0.195	0.858efg	0.034	0.985h	0.112	0.819efg	0.039	0.795efg	0.018
WPC	0.67	1.251i	0.050	0.859efg	0.008	0.856efg	0.024	0.846efg	0.029	0.828efg	0.019
Tween 40	0.50	0.816efg	0.004	0.815efg	0.029	0.813efg	0.019	0.801efg	0.021	0.764def	0.013
Tween 40	0.67	0.852efg	0.024	0.836efg	0.014	0.771def	0.019	0.736de	0.009	0.715de	0.002
Water-in-oil emulsions											
WPC	0.10	0.991h	0.042	0.846efg	0.056	0.474c	0.099	0.346b	0.050	0.119a	0.129
WPC	0.20	1.532k	0.128	0.924gh	0.011	0.907fgh	0.038	0.346b	0.071	0.030a	0.005
Span 80	0.20	0.648d	0.059	0.033a	0.009	0.021a	0.002	0.018a	0.002	0.018a	0.003

Means followed by different letters in the same column and within the same sample are signficantly different at $P \leq 0.01$.
ϕ: dispersed phase volume/total emulsion volume rate; $\bar{x}$: mean; s_x: standard deviation.

ety of k values obtained from the %RH trends of the samples under study, and the different changes with storage time, could essentially be related to the degree of the dispersion and to the stability of the aqueous phase in the bulk system. Because in the range of time considered in the aqueous protein dispersion, no change in the composition occurred and the model of the completely destabilized emulsion was already at the lowest energy level, the state of the aqueous phase does not show changes and neither does the respective k value. The excess of interfacial energy between the aqueous and lipid phases is implied with the thermodynamic instability of the freshly prepared emulsions. As a consequence, these systems tend towards a reduction of this energy, decreasing the total surface area to a minimum value by creaming, flocculation, droplet coalescence and, finally, oiling-off. In the present study, during the storage time at room temperature, the oil-in-water emulsion showed a progressive formation of a layer of aqueous phase on the bottom and creaming of the oil droplets, more pronounced in the case of WPC emulsions. The turbidimetric measurements of the same samples after 96 h did not indicate significant differences ($P > 0.05$) in the absorbance (i.e. in the interfacial area of the oil droplets) compared to that of the emulsions just after their preparation, as reported in Table 1. The visual observation of the water-in-oil emulsions prepared with the WPC dispersion showed coalescence of the aqueous droplets and phase separation with a progressive appearance of free oil on the top of the aqueous phase within a few hours, as a spot at the beginning and then as a continuous layer. This fact was indeed expected because of the use of proteins as emulsifying agents which were not effectively able to stabilise these kinds of emulsions. Nevertheless, both these emulsions reached a k value which can be compared to that of the model of the completely destabilised emulsion after only 96 h, probably due to the presence of very small water droplets kept on the top of the emulsion by the proteins.

On the other hand the w/o emulsion made with Span 80 showed good stability in the same period of storage with no phase separation. The relatively high value of k of the freshly made emulsion could be due to the presence of free water, but the evaluation of the k value after 24 h demonstrated the true degree of dispersion of this w/o emulsion. Thus, in the evaluation of a dispersed system having a specific chemical composition and structure during the storage time, a decrease of the k value may be related to the presence of 'barriers' to the transport of water vapour molecules from the surface to the atmosphere. In general, in oil-in-water dispersed systems the destabilising processes are implied in the formation of a 'barrier' (creamed oil droplets or free oil in the higher layer of the emulsion) which block the aqueous vapour or decrease its rate of coming to the surface and, as consequence, reaching the head space. This means that, as time goes by, the corresponding k value of the model samples calculated from the %RH curves towards the ERH% tend to decrease, and the decrease is higher for the more destabilised emulsified systems. The meaning of the k value in the water-in-oil dispersed systems is different. Here it becomes an index describing the degree of dispersion and loses, in part, the ability to indicate changes that take place in the bulk system.

CONCLUSIONS

In the head space of a sample, the rate of the %RH change from a very low value towards its equilibrium (%ERH) depends on the presence or the formation of 'barriers' to the water mass transfer. In the case of oil–in–water emulsified systems, these 'barriers' can arise from destabilising processes. On the other hand, the degree of dispersion of the oil phase, as a consequence

of the different emulsifying capacity of the emulsifying agent, can also affect the %RH trend, as shown for the WPC and Tween 40 o/w emulsion. Instead, the characteristic dispersion of the water in the water–in–oil emulsions creates constraints to the diffusion of the water towards the headspace itself. The analysis of the curves of the %RH change in the sample head space in terms of the rate to reach the %ERH, d(%RH)/dt, as a function of the corresponding %RH value, can describe the degree of dispersion of an emulsion, as demonstrated by the different behaviours of the model samples considered. Using the Langmuir adsorption isotherm, an index (k) was determined giving an indication of the forces acting between the water molecules in an aqueous system and of the barriers to the water mass transfer from a sample to its head space. Thus, in the case of emulsions, model or real emulsified foods, the changes in the aqueous phase in the dispersed system (and of the lipid phase) due to the destabilising processes can be evaluated by the change of the k value during their shelf-life. Finally, on the basis of our results, it is possible to conclude that the method described could be useful to distinguish the emulsions on the basis of the different mechanism of destabilisation. In fact, a creamed emulsion and an emulsion with true instability (coalescence and oiling-off) will show a different trend of the k value both during storage of the freshly prepared emulsion and after shaking of the destabilised emulsified system.

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