MICROENCAPSULATION OF ACID DYES IN LIPOSOMIC STRUCTURES OF LECITHIN AND SURFACTANTS

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ABSTRACT

The non-uniformity which occurs in the dyeing of polyamide, caused by the irregularities in the physico-chemical properties of the fibre, is reduced by the use of levelling agents. These agents block the accessible sites in the fibre, forcing a greater control in the rate of absortion of the dye on the fibre surface.

The objective of this work was the microencapsulation of the dye with lecithin from soy, with the formation of liposomes, as an alternative to levelling agents.

Since in the liposomes the concentration of lecithin is related to the dye concentration there is no risk of blockage of accessible sites.

Liposomes were prepared with soy lecithin at different concentrations, containing the commercial acid dye, CI Acid Blue 113. The levelling effect of the microencapsulated dyes was compared with the one obtained with levelling agents usually used in standard dyeing. The influence of surfactants in the stability of the liposomes and in the exhaution curves of the dyeing were also evaluated.

The dyeing of polyamide with microencapsulated acid dyes resulted in dyeings as uniformly dyed as with levelling agents, whether in laboratory or industrial conditions.

INTRODUCTION

In the dyeing of polyamide fibres with acid dyes, physical differences in polyamide fibres (continuous filaments) can cause unlevelness during dyeing, because the dye is rapidely absorved by the most accessible sites in the fibre. Phisical variations are of two types, namely *fine*, which are introduced during fibre processing (drawing, setting) and *gross,* which are due to variations affects in the count of the fibre or crimp whilst chemical variations in the fibre are introduced during polymer spinning .[8]

Although both pH and temperature control will promote level dyeing, these measures are not sufficiently effective in overcoming barré dyeing; consequently, dyeing auxiliaries are also used. Levelling agents can promote both levelness and coverage of fibre irregularities, blocking the accessible sites in the fibre and avoid the " strike" effect. These products reduce the initial rate of dye uptake and that the extent of this retardation in dyeing rate decreased with increasing duration of dyeing.

The present work is a study on the field of the microencapsulation technology in the dyeing process. Some work already been reported with encouraging results on the use of microencapsulation of disperse dyes with lecithin, with the formation of liposomes, as a way to control exhaustion and levelness in the dyeing with disperse dyes of polyester [4], wool with acid dyes [5] and wool with reactive dyes [1].

The ecological advantages of the liposomes has been discussed in earlier work, when applied to the dyeing of Polyamide fibres with acid dyes[9].

Liposomes are microscopic spherical vesicles that form when phospholipids are hydrated, the most common phospholips being phosphatidylcholine (PC), also know as lecithin: amphipathic molecules in which a glycerol bridge links a pair of hydrophobic acyl hydrocarbon chains, with a hydrofilic polar headgroup, phosphocholine. When mixed in water under low shear conditions, the phospholipids arrange themselves in sheets, the molecules aligning side by side in like orientation, “heads” up and “tails” down. These sheets then join tails-to-tails to form a bilayer membrane which encloses some of the water in a phospholip sphere.

Liposomes have come into wide use as models for biological membranes and as delivery sistems for hydrophylic and lipophilic substances.

Studies of the interactions between phospholipids and other amphiphiles, such as surfactants, may be beneficial in both developing techniques and furthering insight into phospholipid phase behaviour including the consequences of adding other non-phospholipid amphiphiles to lamellar phase lipids [6].

In phospholip-surfactants mixtures, the stage of aggregation, at equilibrium, of course depends on the components and composition of the mixture.

When the soluble amphiphile concentration is low, the surfactant is found associated with the phospholipid bilayers without much loss in the general structure [7].

The biotechnological applications of addition of surfactants to liposomes is directed towards increasing the entrapped volume for efficient loading of the drug and liposome fusion [2].

The first part of this work was the preparation of the liposomes with differents surfactants, in the second part we studied the effect of surfactants on the physical properties of lecithin liposomes and the exhaution curves of the dyeing.

The surfactants studied were:

- neutral surfactant : Triton X-100
- anionic surfactant : sodium dodecyl sulphate (SDS) and sodium laurate
- cationic surfactant: cetyl trimethyl ammonium bromide (CTAB)

All of them were used at a very low concentration (below the critical micelle concentration, cmc) when the vesicle is intact.

In the third part, after choosing the surfactant that best satisfies our demands, we studied its influence on the size of the liposome.

EXPERIMENTAL

Liposomes preparation

The preparation of liposomes requires careful attention to ease of formulation, those we used were prepared in the following way: Commercial soya lecithin (Stern) containing 22% phosphatidylcholine, 20% phosphatidylethanolamine, 14% phosphatidylinositol, 10% phytoglycolipides, etc. was dissolved in diethyl ether. Commercial Acid Blue 113 came from Avocet, was purified in DMF (dimethylformamide).

An aqueous phase containing the dyebath components (dye 1% o.w.f., 2 g/l amonium sulfate, acetic acid to pH=5) was added to the lecithin solution. The resulting suspension was sonicated (Branson 5200, 50W) for 15 min at 20ºC , thereby obtaining an emulsion. The organic solvent was removed at 20ºC by rotary evaporation under vacuum.

Dyeing conditions

To the microencapsulated dye emulsion (1.0% o.w.f.), 2g/l of ammonium sulphate were added and the pH adjusted with acetic acid to

reach pH five and the dyebath ratio 50:1. The material to be dyed was polyamide 6.6 knitwear. Dyeing was started at 40ºC and the temperature raised to 98ºC at a gradient of 1º C/min, maintaining this temperature during 30 minutes to estabilish the equilibrium between the dye and the fibre. Using the same concentration (1.0% o.w.f.) polyamide 6.6 was dyed with 2% of Sandogene NH a cationic levelling agent together with Sandogene CN an anionic levelling agent (by Clariant). Both agents prevents the dyestuffs from being too rapidly absorved in a chemical way, the liposomes containing the dye, release it when the capsule collapsed with the raising of the temperature. At different temperatures, lecithin membranes can exist in different phases, and transitions from a tightly ordered phase (solid phase) to a liquid-crystal phase occurrs when the temperature is raised, and the freedom of movement of individual molecules is higher, thereby releasing the encapsulated dye.

Laboratory dyeing was done in a Ahiba Turbo Color dyeing machine. Dyebath exhaustion was determinated by spectrophotometry using a Unicam UV/VIS UV2 spectrophotometer. Liposomes aliquots (0.5ml) were periodically added to quartz cuvettes filled with 2 ml of aqueuos solution of 2% w/v Triton X-100 (Merck), supplemented with 5% sodium sulphate and acetic acid pH 5. Triton X-100 (non-ionic surfactant) solubilize the phospholipidic liposomes by means of mixed micelle formation [5], thus turning the liposome suspensions into a completely clear solution.

Influence of surfactants in the liposomes

In this work, we wanted to study the influence of surfactants in liposomes, in order to improve their resistence to temperature.

The surfactants were incorporated into liposomes by adding a definite volume from a stock surfactant solution in water to the emulsions before

sonication and the same method for the preparation of liposomes was followed.

By keeping the lipid concentration at 1g/L, the surfactant concentrations were varied, well below the cmc of all four surfactants [10]. It was also important to see which surfactant was the best, for the pretended effect (decrease dyeing rate without decrease final exhaustion).

The same procedure described above was followed, to study the effect of the surfactant in the exhaustion dye curves.

After, choosen the best surfactant we have studied its influence in the size of the liposomes.

Mean size of the liposomes preparations were determined with a Photon correlator spectrometer (Malvern Mastersizer S). Measurements were made at 25ºC with a detection angle of 90º.

Results and Discussion

So as to assess the effect of liposomes concentration on the exhaustion curves, dyeings were carried out using differents concentrations of soy lecithin.

The best concentration of lecithin to obtain a rate of dyeing approximate to that obtained with the levelling agents was found to be 1g/l (fig.2). With a higher concentration (1.5 g/l) differences in the exhaustion curves are not so significant but with (0.5 g/l) the retarding effect is not so good.

So as to choose the best surfactant to use in our work, we have tested four differents surfactants:

We have prepared microencapsulated dye with liposomes and CTAB. After dyeing, we observed that polyamide was completely unlevel. This fact is due to the complexation of the acid dye (anionic character) by CTAB, a cationic surfactant.

Microencapsulation with Triton X-100 was made with liposomes with differents concentrations well below cmc (0.24 mM/L), 0.02, 0.08, 0.16 mM. Comparing the exhaustion curves of these dyeings, we concluded that, there is no effect in the presence of this surfactant Fig.(3)

We have tested two different anionic surfactants, SDS and sodium laurate. After the preparation of the liposomes with SDS in differents concentrations below cmc (8.3 mM/L), 0.35, 1.70, 7.0 mM dyeings were carried out in the same way as above and we observed a great decreasing in the dyeing rate and in the final exhaustion of the bath. So that, we have made a dyeing with this surfactant and the dye without be microencapsulated, for as to see, if there is any effect of this surfactant in the general dyeing. The result was that, SDS with anionic character and a great ionic strengh, behave like a retarding agent competing with the dye in the bond with NH_3^+ groups of polyamide.

A first series of tests on the influence of sodium laurate on the exhaustion curves indicated an increasing of the resistence of the liposome to the colapse. Comparing the exhaustion curves of these three dyeings we can see that the sodium laurate by itself has pratically no retarding effect but the dyeing using microencapsulated dye with lecithin and sodium laurate has a much better retarding behavior than when only using microencapsulted dye with lecithin.

When a low concentration of surfactant is added to phospholipid bilayers in an aqueous medium, the surfactant distributes between the bilayers and the solution, and their general structure remains nearly the

same. The liposomes can accommodate some surfactant without being disrupted, although there may be other changes, namelly in its size. Measuring the mean vesicle size distribution of the liposome suspensions after preparation with and without surfactant, we found:

Sodium laurate concentration	Mean size of liposomes
without	0.95 μm
0.4 g/l	71.39 μm

Table I. Mean size of liposomes

Conclusions

The dye exhaustion was directly dependent on the lecithin concentration, where an optimum concentration of lecithin was used to substitute two commercial levelling agents in the control of the rate of dye uptake.

Sodium laurate influence the behavior of the liposome, increasing its retarding effect in the polyamide dyeing.

With liposomes prepared with lecithin and sodium laurate, the uniformity of colour obtained was comparable to that obtained with levelling agents. The colour difference between the material dyed with differents procedures, was measured in a ACS Spectro Sensor II reflectance spectrophotometer applying the CIElab colour difference formula, and the results were not significative.

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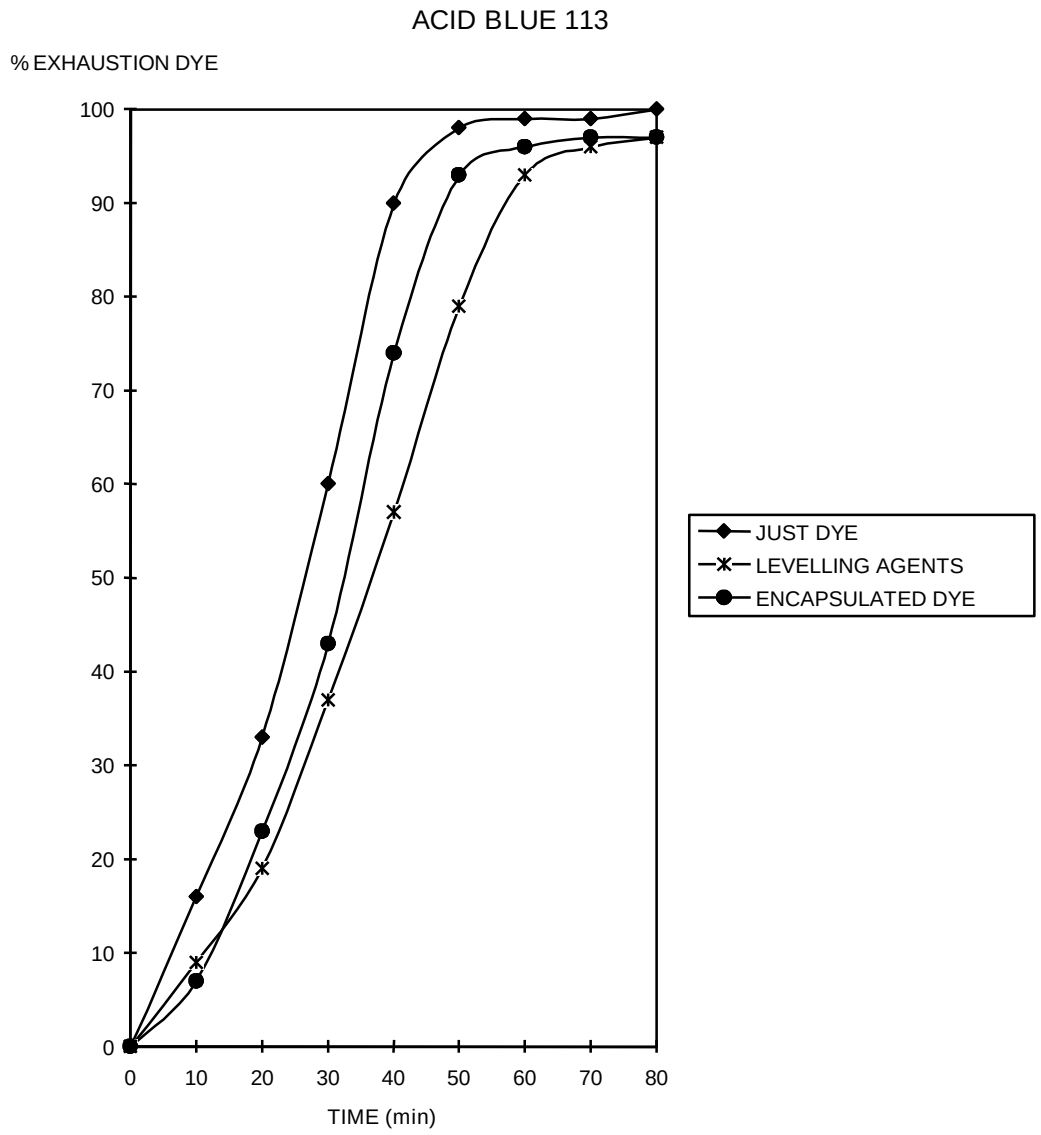

Fig. 2 - Exhaustion curves of C.I. Acid Blue 113 (1.0% o.w.f.) of three differents dyeings

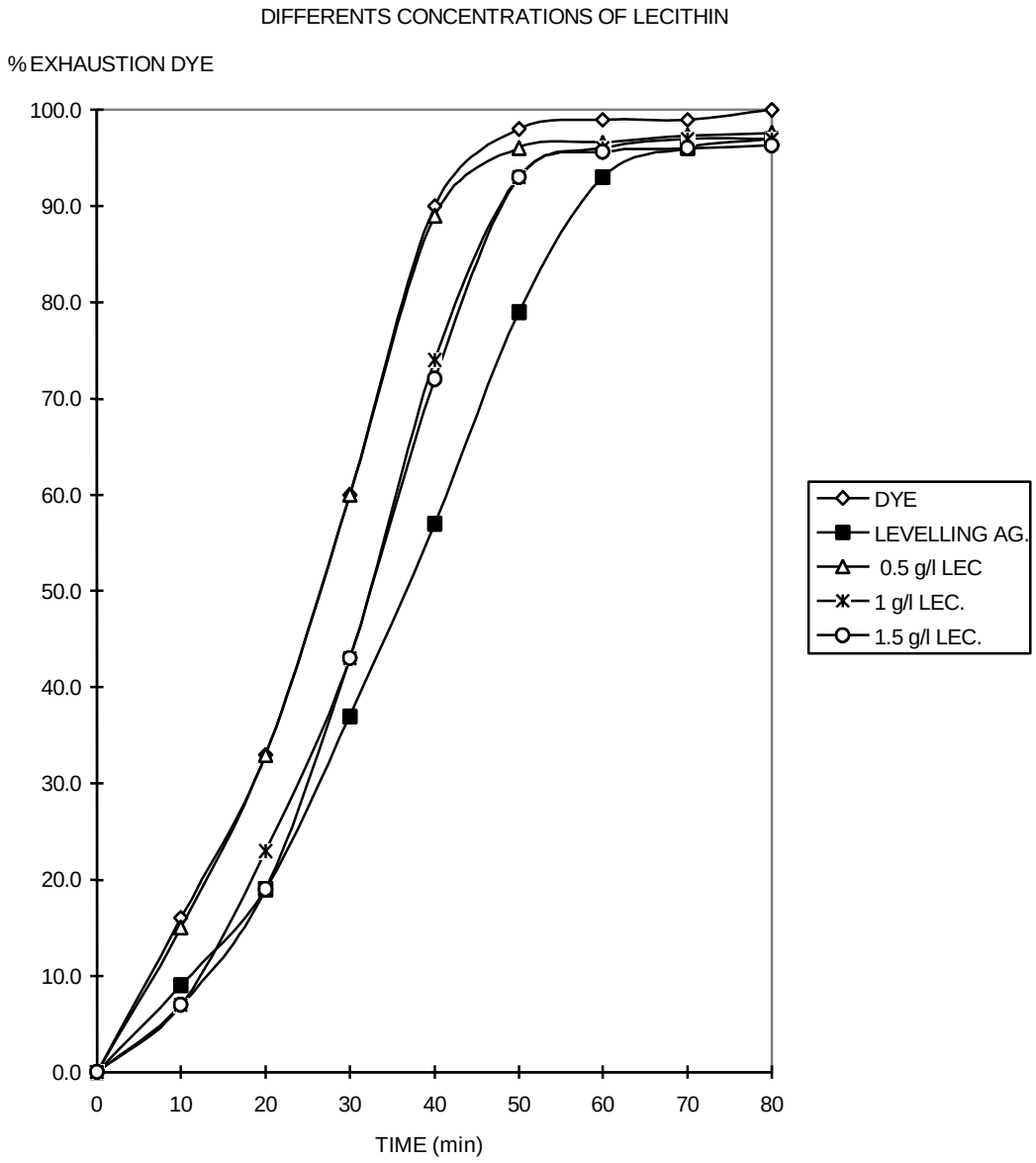

Fig. 3 - Exhaustion curves of C.I. Acid Blue 113 using differents concentrations of lecithin

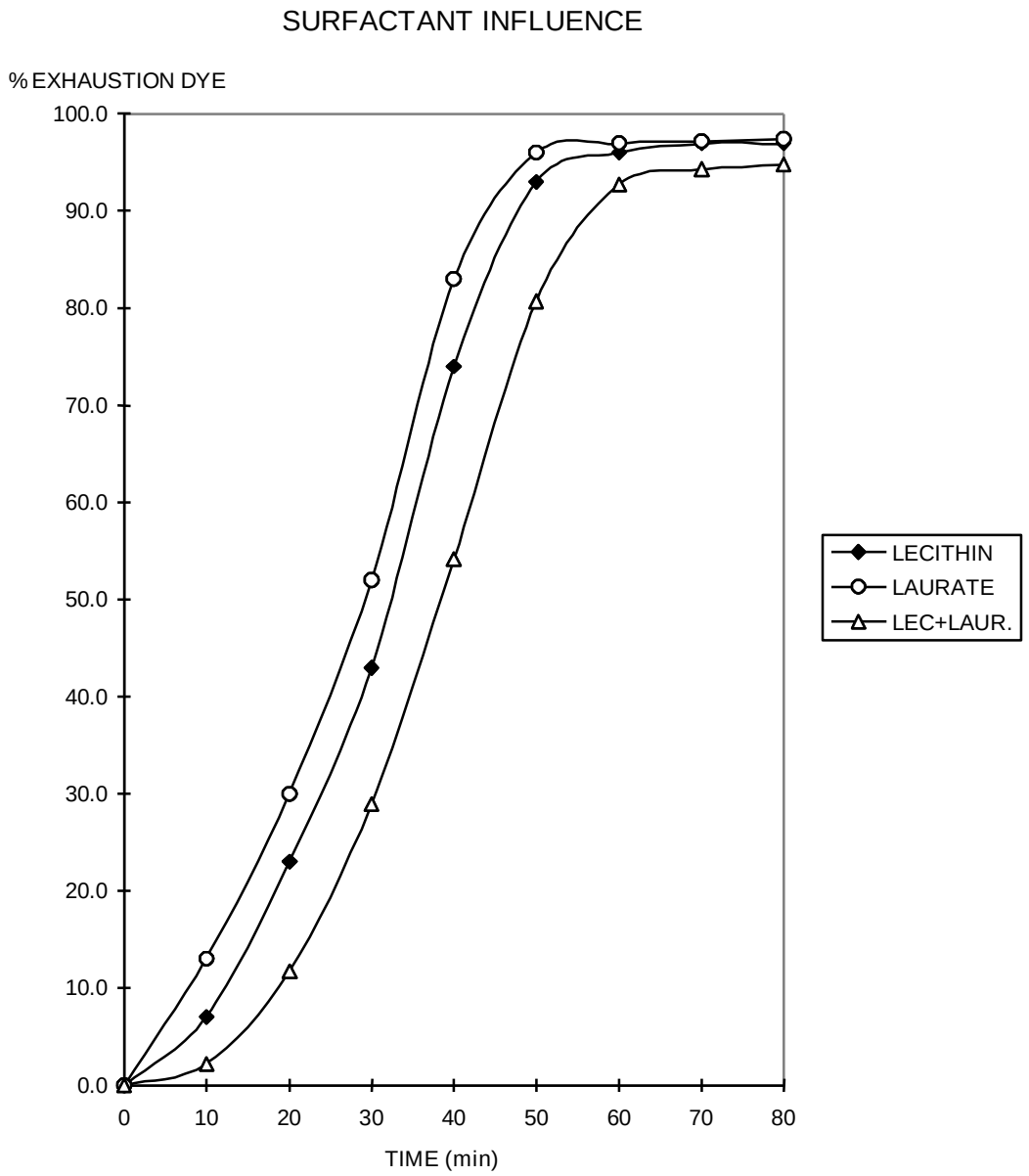

Fig. 4 - Exhaustion curves of C.I. Acid Blue 113 using microencapsulated dye with lecithin, microencapsulated dye with lecithin and sodium laurate and only with sodium laurate.