THE USE OF POLYMERIZABLE SURFACTANTS IN EMULSION COPOLYMERIZATIONS FOR COATINGS APPLICATIONS

EL USO DE SURFACTANTES POLIMERIZABLES EN COPOLIMERIZACION EN EMULSION PARA APLICACIONES EN PINTURAS

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SUMMARY

In this paper results obtained in high solids content emulsion copolymerizations using polymerizable surfactants (surfmers) have been reviewed.

On the basis of the interpretation of the behavior of the surfmers (the conversion vs. time and their performance in stability tests and film properties), an optimal surfmer behavior has been defined, which means that all the added surfmer groups end up on the particle surface rather than being buried, which leads to inferior latex stability. One of the strategies that have been proposed to achieve this has been applied to prepare a well-defined styrene-butyl acrylate latex of which film can be easily be cast. Its properties in terms of mechanical stability, film water absorption, and film surfactant exhudation have been assessed and compared with these of a similar latex with sodium dodecyl sulfate. Other comonomer systems have been studied as well with the maleic surfmer. In these systems the surfmer behavior was less "optimum". For these latices both mechanical stability and water absorption was assessed.

Keywords: *polymerizable surfactants, surfmers, reactive surfactants, emulsion polymerization, latex, kinetics, film properties.*

INTRODUCTION

In the process of emulsion polymerization surfactants play a very significant role. They are very important for fast nucleation of latex particles, emulsification of monomer droplets and stabilization of the latex particles during the polymerization, and during the shelf life of the latex. When the latex is used in films and coatings however, the presence of surfactant can have negative effects. These effects are caused by the fact that the surfactant can desorb from the latex particle surface and can migrate through the product. For example they can desorb from the particle surface under high shear and cause mechanical instability or concentrate in aggregates **[1]**, increasing the water-sensitivity of the product Additionally in films exhudation of the surfactant **[2-4]** can take place towards the film-air (F-A) interface, or even towards the film-substrate (F-S) interface. This fact increases the water sensitivity of the film-air surface, and can have a negative effect on the adhesion properties of the film at the substrate interface.

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The use of reactive surfactants could be a solution to some of these problems, due to the fact that the surfactant moiety is bound covalently to the polymer material and the deabsorption from the latex particle surface is impeded. The migration in the polymer film is also impeded. These reactive surfactants can be the combination of a part with surfactant activity and a part with an initiating capacity called inisurf **[5-7]**. If the reactive group is a transfer agent it is called a transurf **[8]** and if the reactive group is polymerizable, it is a surfmer **[9,10]**. These have been described before as polymerizable surfactants and are the most promising possibility in emulsion polymerization. There are several examples which include anionic surfmers with sulfate or sulfonate head groups, **[11-17]** cationic surfmers **[18,19]** and non-ionic surfmers **[20,21]**. The reactive groups can be of different types, for example: allylics **[22,23]**, acrylamides **[16]**, (meth)acrylates **[21,24]**, styrenics **[14,25]**, or maleates.

Examples of emulsion polymerizations with surfmers can be found in refs. 13, 24-30 improvements in properties caused by the use of surfmers have been reported in several cases. For example in mechanical stability **[26]** and electrolyte stability of the latex **[24]**. Has been reported **[13]** that when a surfmer is used the surfactant migration is reduced and the water resistance **[12,14,20,31,32]** and adhesivity **[14,20,32]** are improved.

SCOPE OF THE PRESENT PAPER

This paper is part of a series **[10,33-35]** where several surfmers with very different reactivities in copolymerization have been investigated. We will firstly review results obtained in a styrene-acrylic monomer system with several surfmers with varying reactive groups: two maleic acid diesters, a methacrylic acid ester and a crotonic acid ester. The results include the analyses of conversion versus time of both surfmers and main monomers in high solids semicontinuous reactions, and the amount of coagulum formed and particle size.

This is followed by a review of results obtained **[35]** when using the maleic acid diesthers in other comonomer systems, to illustrate the fact of changing the reactivity of the main monomers. In the last part we will give the results of some tests that determine the performance of a few of these latices with respect to mechanical stability as well as the performance when applied as films (water sensitivity and surfactant exhudation). For this purpose two new styrene acrylic latices were prepared following a strategy as proposed in ref. 35 to obtain an ideal surfmer behavior, which means that all the surfmer is bound to the surface of the particles and that none is buried in the particles interior, where they can not contribute to the latex stability. These latices only differ in the nature of the surfactant: a bound maleic acid diester and the unbound sodium dodecyl sulfate.

EXPERIMENTAL

The experimental details of preparation of latices, surfactant and main monomer conversion, cleaning of latices and water ababsorption are given in ref. 10, 33 and 35.

For the mechanical stability test 25 g of latex was stirred at 12.000 rpm for 5 minutes and the coagulum formed was filtered through a # 63 mesh sieve. The residue was rinsed with water and dried. The weight of the residue was expressed in percentage based on the solid content of the emulsion.

Films from latices, for water ababsorption and spectral measurements, were cast on glass substrate and peeled off.

Transmission spectra of films and surfactants were performed in the common way. The attenuated total reflectance (ATR) spectra of film-air and film-substrate interfaces were performed using a KRS-5 crystal. The spectrum were normalized with respect to the 852 cm^{-1} band due to the C-C skeletal mode of the C-C main chain.

RESULTS AND DISCUSSIONS

The surfmers used in the work are summarized in Table 1. Sodium dodecyl sulfate (SDS) was used as a non-polymerizable reference surfactant.

The systems investigated include the following:

I) Styrene (S)/butyl acrylate (BA)/acrylic acid(AA) (49.5/49.5/1 (w%)).
II) Vinyl acetate (VAc)/VEOVA10/AA (69/30/1 (w%))
III) VAc/BA/AA (79/20/1 (w%))
IV) Methyl methacrylate (MMA)/BA/VAc (50/35/15 (w%))

Table 1

Name, code, chemical structure and cmc value of surfactants used

surfactant	code	chemical structure	cmc (g/L)
Sodium 3-sulfopropyl dodecyl maleate	M12	$C_{12}H_{25}OOC-CH=CH-COOC_3H_6SO_3Na$	0.693
Sodium 3-sulfopropyl tetradecyl maleate	M14	$C_{14}H_{29}OOC-CH=CH-COOC_3H_6SO_3Na$	0.12/0.085
Sodium 11-crotonoyl undecan-1-yl sulfate	CRO	$NaSO_4C_{11}H_{22}OOC-CH=CH(CH_3)$	4.9
sodium 11-methacryloyl undecan-1-sulfate	MET	$NaSO_4C_{11}H_{22}OOC-C(CH_3)=CH_2$	2.5
sodium dodecyl sulfate	SDS	$C_{12}H_{25}\ SO_4Na$	1.15

These systems are of practical interest and at the same time the monomers present widely different reactivities in copolymerization (Table 2).

Table 2

Reactivity ratios of surfmers (or corresponding monomers) with main monomers

Surfmer or equivalent monomer	styrene	butyl acrylate	vinyl acetate	methyl methacrylate
	r_S , $r_{surfmer}$	r_{BA} , $r_{surfmer}$	r_{VAc} , $r_{surfmer}$	r_{MMA} , $r_{surfmer}$
Diethyl maleate (M14 or M12)	8-10 , 0[36]	>>10 , 0*	0.04 , 0.17[36]	354 , 0[37]
Methyl crotonate (CRO)	26 , 0.01[38]	-	-	-
Dodecyl/methyl methacrylate (MET)	0.53 , 0.30[36]	0.32 , 2.6[39]	-	-

* estimated on the basis of results of a reaction between BA and M14 (33), where M14 did not polymerize at all in the presence of BA.

I) The styrene/butyl acrylate/acrylic acid system.

Three surfmers differing in the nature of the polymerizable group were used. One of the surfmers is an ester of methacrylic acid (MET), one is an ester of crotonic acid (CRO), and the third is a diester of maleic acid (M14). The methacrylic derivative is an example of a very reactive surfmer, the crotonic derivative an example of a generally non-reactive surfmer. The maleic derivative was chosen for its intermediate reactivity and for the fact that it cannot homopolymerize (in the aqueous phase). This feature is common to all maleic diesters [40,41]. The intrinsic reactivity of the polymerizable groups in the surfmers can provide a basic idea about the suitability of the surfmer. One can see in Table 2, that on the basis of the reactivity with S, the MET surfmer can be expected to be the most reactive, and the CRO surfmer the least reactive. In order to maximize the differences between the performance in the emulsion polymerizations, the concentrations of the surfmers were chosen in such way that the system were close to the stability limit.

In Table 3 the amount of coagulum obtained in some reactions are given together with the particle diameter.

When MET is used as the surfmer, the amount of coagulum increases and reaches 24 %, an unacceptable level. This could be due to the fact that the MET can homopolymerize and is quite reactive with the main monomers (see Table 2) in contrast to M14. This fact could lead to polyelectrolyte formation in the aqueous phase, which in turn could destabilize existing particles by bridging flocculation or, if the amount of polyelectrolyte is significant with respect to the amount available for adabsorption on the latex particle surface, the minimum coverage for stabilization is not attained.

If we compare the reactions M14B1 and CRO, in which the initiator was charged completely at the beginning, it can be seen that the surface tension is lower in the case of CRO, which also has less coagulum. This may be caused by the fact that CRO is less reactive than M14, so that when all M14 is charged in the beginning, more of this surfmer may become buried in the particle, whereas the less reactive CRO remains at the particle surface.

Table 3

Amount of coagulum^{a} and diameter^{b,c} of latex in non-seeded reactions in the S/BA/AA system (50% solid content), with SDS and various anionic surfmers, using KPS as initiator and at 80 °C.

reaction code	initiator charge/feed	surfactant	coagulum (%)	diameter (nm)
SDS	50/50	SDS (1 w%)^{d}	1.1	99
M141	50/50	M14 (1 w%)	2.5	152^{c}
M142	50/50	M14 (2 w%)	0.5	130^{c}
M145	50/50	M14 (5 w%)	0.6	102^{c}
MET	50/50	MET (1 w%)	24	-
M14B1	100/0	M14 (1 w%)	5.6	129
CRO	100/0	CRO(1 w%)	1.5	186

^{a} % on total monomer; ^{b} from light scattering; ^{c} from transmission electron microscopy
^{d} based on monomers.

In case of the maleates (M14 and M12) the results indicate that the level of conversion is between that of the crotonate and methacrylate surfmers. This is in line with its general copolymerization reactivity. In Table 4 the properties of some latices of system I with maleate surfmers are presented.

Table 4

Properties of latices of system I

Code	Monomers (w%)	solids content (%)	surfmer, w%	final particle size (nm)	coagulum (w%)*
30IM141	S/BA/AA (49.5/49.5/1)	30	M14, 1	98	1.3
50M142	S/BA/AA (49.5/49.5/1) seed S/BA (50/50)	50	M14, 2	114	1.4
50M122	S/BA/AA (49.5/49.5/1) seed S/BA (50/50)	50	M12, 2	109	1.2

* w% based on monomers.

Figure 1 shows an example of a seeded semi-continuous reaction with M14 (50M142S) and the equivalent reaction with M12 (50M122S).

The evolution of the total conversion of the main monomers with time is virtually the same for both reactions, due to the fact that these are seeded reactions. An equivalent reaction with SDS gave conversion results identical to 50M142. The use of the maleate surfmers in these reactions does not seem to affect the kinetics.

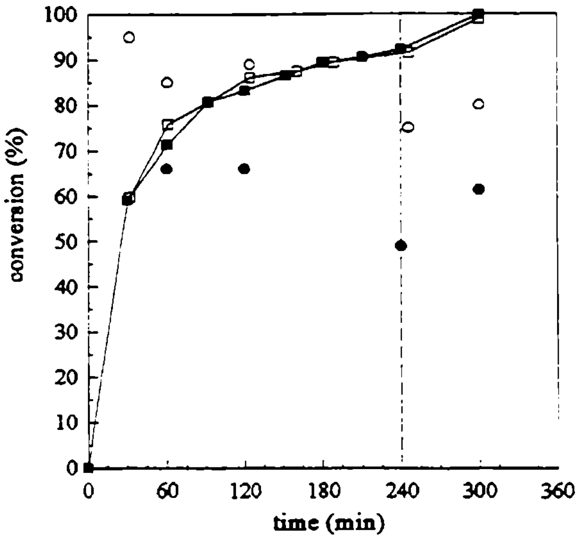

Fig.1. System I. Main monomer conversion (squares) and surfmer conversion (circles) versus time in reactions 50M142 (with M14 as surfmer, open symbols) and 50M122 (with M12 as surfmer, closed symbols).

It can be seen that M14 had a relatively high conversion throughout the reaction and a final conversion of 80 %. The conversion of M12 is somewhat lower and its final conversion is 62 %, which is perhaps due to the higher water solubility of M12. Anyway, the pattern of the conversion versus time shows the same characteristics for both maleates.

It was observed in a non-seeded reaction with a final particle size of 98 nm (30IM141 in Table 5), that the conversion of M14 during the reaction reached levels higher than 95 %. The surface-charge density analysis showed that only 40 % of the original M14 surfactant groups were present at the particle surface, indicating that a large proportion remains buried in the particle interior due to the high conversion of M14 from the beginning of the reaction. This is corroborated by the results of other reactions with styrene and M12 or M4 **[34]**, where the surfmers reached very high levels of conversion at low overall conversion.

II) The VAc/VEOVA10/AA system

We applied M12 as a surfmer in the monomer system VAc/VEOVA10/AA (Table 5).

In Figure 2 are shown the conversion results of the reaction 30IIM12. It can be seen that in reaction 30IIM12 the conversion of M12 is very high from the beginning.

The amount of coagulum is not very high, however, and no signs of instability were observed. This can be a result of the fact that the solids content was low. A reaction at 50 % of solids (50IIM12 in Table 5) was carried out, using a seed of latex to ensure a similar particle size to that of 30IIM12. The conversion of the main monomers (not shown here) follows the same pattern as in 30IIM12, but as indicated in Table 5, the amount of coagulum is quite high and at the same time, the particle size is much higher than expected on the basis of the number of seed particles.

Table 5

Properties of latices of system II

Code	monomers (w%)	Solids content (%)	surfmer, w%	final particle size (nm)	coagulum (w%)*
30IIM12	VAc/VEOVA10/AA (69/30/1)	30	M12, 1	128	0.6
50IIM12	VAc/VEOVA10/AA (69/30/1) seed VAc/VEOVA10 (75/25)	50	M12,2	>170	15

* w% based on monomers.

This indicates that the reaction 50IIM12 is unstable, probably because of the high conversion of the surfmer. This high conversion is somehow expected if we look the reactivity ratios (see Table 2) between diethyl maleate and VAc: $r_{\text{diethyl maleate}} = 0.04$, $r_{\text{VAc}} = 0.17$ (ref. 36).

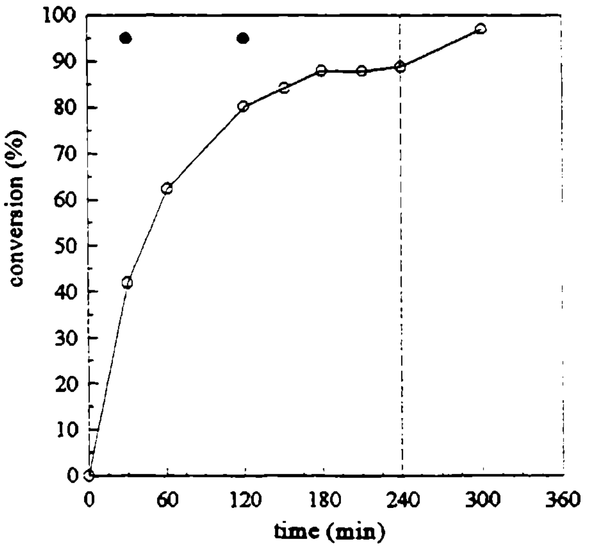

Fig. 2. Main monomer conversion (o) and M12 conversion (●) versus time in reaction 30IIM12.

III) The VAc/BA/AA system.

In this monomer system (ref. 35) BA is far more reactive than VAc, and at the end of the feeding period there will be a certain amount of VAc left even under starved conditions. In ref. 33 it was shown that M14 does not react with BA. Therefore it was expected that during the feeding time of a semi-continuos reaction with this monomer system, when there is some BA present, the maleate surfmer would not react to high conversion as it does in a system with only vinyl esters (II), and that the maleate would react with the remaining part of the VAc after stopping the feed.

Three reactions were carried out with this monomer system, two at 54 % solids with SDS and M12 and one at 30 % solids with M12 (see Figure 3).

The reaction with SDS (54IIISDS) gave a stable latex with very little macroscopic coagulum. However, the latex completely coagulated on the shelf after a few weeks. The reaction 54IIIM12 with M12, ended in total coagulation after 90 minutes of reaction. The reaction 30IIIM12 was carried out at 30% solids content and the conversion of M12 was very high from the beginning.

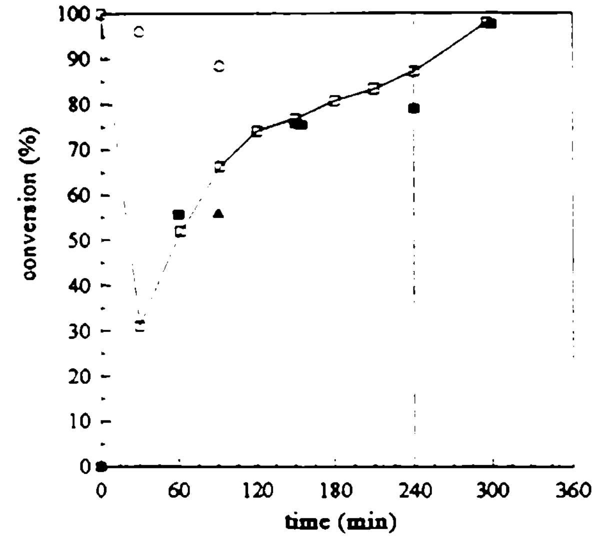

Fig. 3. Main monomer conversion and surfmer conversion versus time in reactions 54IIISDS (main monomer: ■), 54IIIM12 (main monomer ▲) and 30IIIM12 (main monomer □, M12: o).

This high conversion probably led to the observed instability. The conclusion therefore is that the maleate surfmers are too reactive, just as in the previous system, due to the presence of the vinyl esters.

IV) The MMA/BA/VAc system

In this system (ref. 35) due to the fact that VAc is by far the least reactive monomer, in semi-continuous reactions, during the period of feeding, the instantaneous conversions of both BA and MMA are quite high and that of VAc relatively low [39], which means that at the end of the feeding period the unreacted monomer will be mainly VAc. This unreacted VAc is expected to copolymerize with M12 after feeding has stopped and a high conversion of the surfmer at the end of the reaction should be found. Using a variable feed flow rate so that the instantaneous conversion of the monomers (mainly VAc) was not high at the end the conversion-time behavior found was as shown in figure 4 (see ref. 35).

The instantaneous conversion of the monomers was approximately 90 % at the end of the feed period. The M12 conversion after the nucleation period is relatively high, due to the fact that the charge is allowed to react in batch mode. At the end of that batch period the mixture is enriched in VAc. However, after this initial period the instantaneous conversion drops to a lower level, and at the end of the feeding period it is about 60 %. The amount of VAc (15 %) seems to high enough to allow some reaction of M12. When the feeding has been stopped, and the reaction is in batch mode with a large amount of unreacted VAc, it can be seen that the conversion of M12 starts to increase rapidly, having reached complete conversion when all main monomers have reacted.

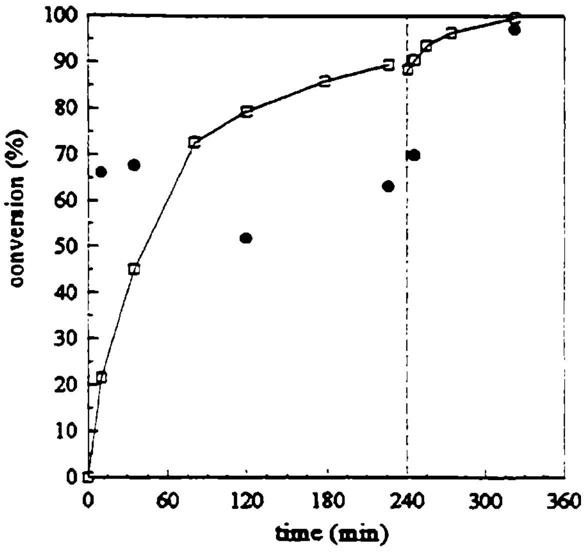

Fig. 4. Main monomer conversion and surfmer conversion versus time in reaction 30IVM12 (main monomer: □, surfmer ●).

Based on the above mentioned results it can be concluded that the reactivity of the surfmer relative to the main monomers plays an important role [35]. However, the results of various reactions with M14 in system I suggest that the level of conversion can vary significantly within the same monomer/surfmer system. Combining M14 conversion data in several reactions with monomer system I shows the interesting result [35] that the conversion of M14 is strongly dependent upon the particle diameter and reaches high levels for small particles up to 100 nm, and decreases steadily at higher particle diameters. The different M14 conversions found in various reactions could be explained by the difference in particle size. The rate of polymerization of M14 relative to the monomers decreases as a function of particle size. This result points strongly in the direction of M14 reacting at the surface, where the free, unreacted M14 will mainly be present. The locus of polymerization for the main monomers is the whole polymer particle. If the M14 only reacts in an outer shell of the particle with a set thickness, an increase in particle diameter should cause a decrease in the extent of reaction of M14, if we discard any radial radical concentration profile.

LATEX AND FILM PROPERTIES

The use of polymerizable surfactants instead of classic surfactants is only valid if there is an improvement in latex or film properties that warrants their use. Obviously the polymerizable surfactant serves best if at the end of the polymerization it resides at the particle surface, rather than being partly buried. To achieve this, in most cases both a well chosen type of polymerizable surfactant has to be used as well as a special polymerization strategy (see ref. 35). As we have seen in the above, this has probably not been achieved in any of the latices, except perhaps in latex 30IVM12. Some of the latices described above, including 30IVM12 have been analyzed with respect to mechanical stability and the corresponding films with respect to water ababsorption. To offset the results, we have not used the latices of monomer system I as mentioned above, but rather we have synthetized two new latices with the objective to have two very similar latices, only differing in the nature of the surfactant groups at the surface: one latex with the unbound SDS (35ISDS), and the second latex with the SDS replaced by M14, all bound to the particle surface. The latter latex was prepared by replacing the initially used SDS with M14 using dialysis, followed by addition of KPS and a 70:30 mixture of VAc and VEOVA10 which react very well with M14. This procedure ensures the inmobilization of the M14 groups at the particle surface (35IM14).

In addition to the latex mechanical stability and water ababsorption of the film, in this case also the exhudation of the surfactant to the film surface was investigated with attenuated total reflectance (ATR) -FTIR spectroscopy.

MECHANICAL STABILITY

Table 6 shows the amount of coagulum after the mechanical stability test of some latices.

The results were interpreted taking into account the surfactant distributions.

System I, 35ISDS and 35IM14

In this case the small amount of coagulum indicates a good stability of both latices, but the one prepared with the surfmer is better. This is in accordance that the observations of Greene and Sheetz [26] that when the charges are immobilized on the latex surface, deabsorption is highly improbable and the latices are more stable.

Table 6

Properties and mechanical stability[a] of the latices tested

System	reaction code	Surfactant (1% w)	solids content(%)	particle size (nm)	coagulum (w%)[b]
I	35IM14	M14	35	164	1.5
	35ISDS	SDS	35	153	3.3
II	30IIM12	M12	30	128	10.4
	B5	DDBS[c]	30	127	25.4
III	30IIIM12	M12	30	109	28.3
	30IIISDS	SDS	30	76.2	8.9
IV	30IVM12	M12	30	114	30.7
	30IVSDS	SDS	30	236	11.2

[a] 12,000 rpm, 5 minutes. [b] w% based on solid content.
[c] In this case a non-ionic surfactant was used in conjunction with dodecyl benzene sulfonate (DDBS).

System II (VAc/VEOVA10/AA - 69/30/1)

The high amount of coagulum could be due to the fact that the surfmer has an elevated conversion from the beginning of reaction (Fig. 2), i.e., it is likely that a high proportion is buried inside the particle. Greene *et al* [26], found that the amount of coagulum formed after a mechanical test decreased with increasing surface coverage and due to the fact that when the surfmers are bound in parts of the particle other than the surface, the stabilization is not achieved until an optimum coverage is reached.

System III (BA/VAc/AA - 20/79/1) and system IV (MMA/BA/VAc - 50/35/15)

In systems III and IV the situation is more complex. The latices with SDS obviously have all the surfactant on the particle surface. On the other hand the latex with M12 in system III probably has few surfactant groups on the surface due to burying. Reaction 30IVM12 was carried out so as to obtain a latex with most M12 bound to the surface, by maintaining a low surfmer conversion during the feeding period (ref. 35) However, the remaining amount of M12 at the end of the feeding period reacts very rapidly with VAc, possibly leading to copolymer chain which are very rich in M12 (1:1). This means that although the problem of burying surfactant groups is (partly) circumvented, it is possible that the 1:1 polymer formed at the end does not stabilize the particles as effectively as free M12 or M12 bound more homogeneously to the particle surface. This a matter for further investigations. The stability results suggest the present situation (1:1 polymer) is not good. Perhaps the reactivity of the remaining main monomer needs to be higher than 0 (as in this case).

WATER ABABSORPTION

Figure 5 shows the water ababsorption of films prepared from latices discussed here. It can be seen that in general films with surfmers have a lower final water absorption than films with SDS.

In system I, we had an example where there was not much difference in the initial stage, between M14 and SDS (although $X_{\text{final, M14}}$ was not very high (64%)), but the final water absorption is lower in the latex with M14. So it seems that there is a general improvement in water absorption. Comparing films cast from the different systems (prepared with surfmers), we observe that the final water uptake is similar for systems I, II and III (about 45 % after 30 days) and lower for system IV (33 % after 30 days). These differences are due to the presence of the more hydrophilic AA monomer in the first three systems.

SURFACTANT MIGRATION

The latex from reaction 35IM14 and its counterpart with SDS, were cast on glass and peeled off, to study surfactant migration to the interfaces, using FTIR-ATR spectroscopy.

Figure 6 shows the spectra in the low wavenumber region where the bending modes of the $-SO_3$ or the $-OSO_3$ groups appear.

It can be seen that in the SDS latex, the spectrum of film-air (F-A) interface shows a somewhat different pattern than the transmission spectrum (bulk), indicating that there is surfactant migration during coalescence. The relative intensities of band of 635 cm^{-1} due to SDS and that of ca. 620 cm^{-1},due to the polymer, indicates an exhudation of SDS to the film-air interface.

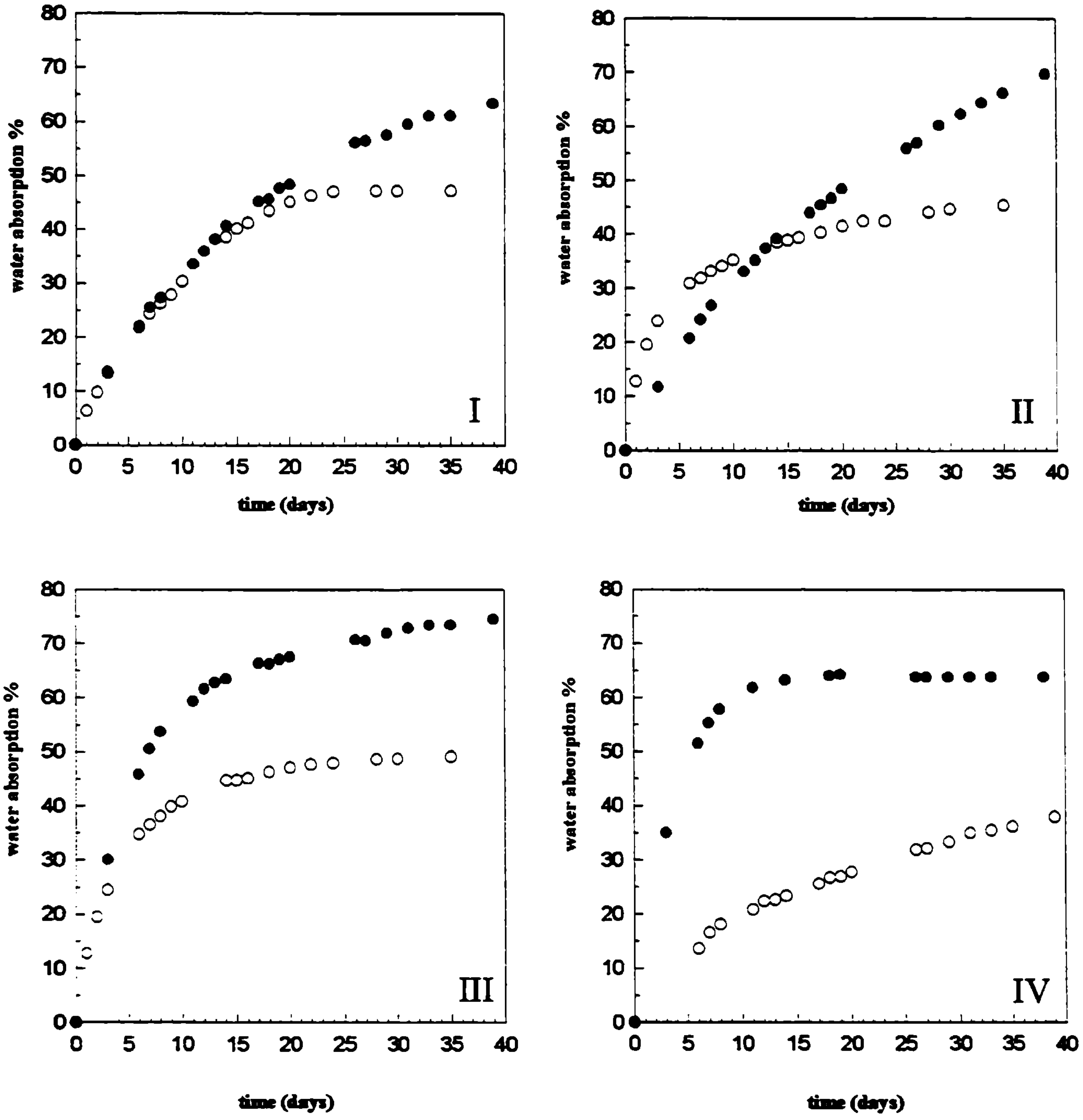

Fig. 5. Water absorption vs. time of latices from systems I to IV. Open circles with surfmer and closed circles with SDS.

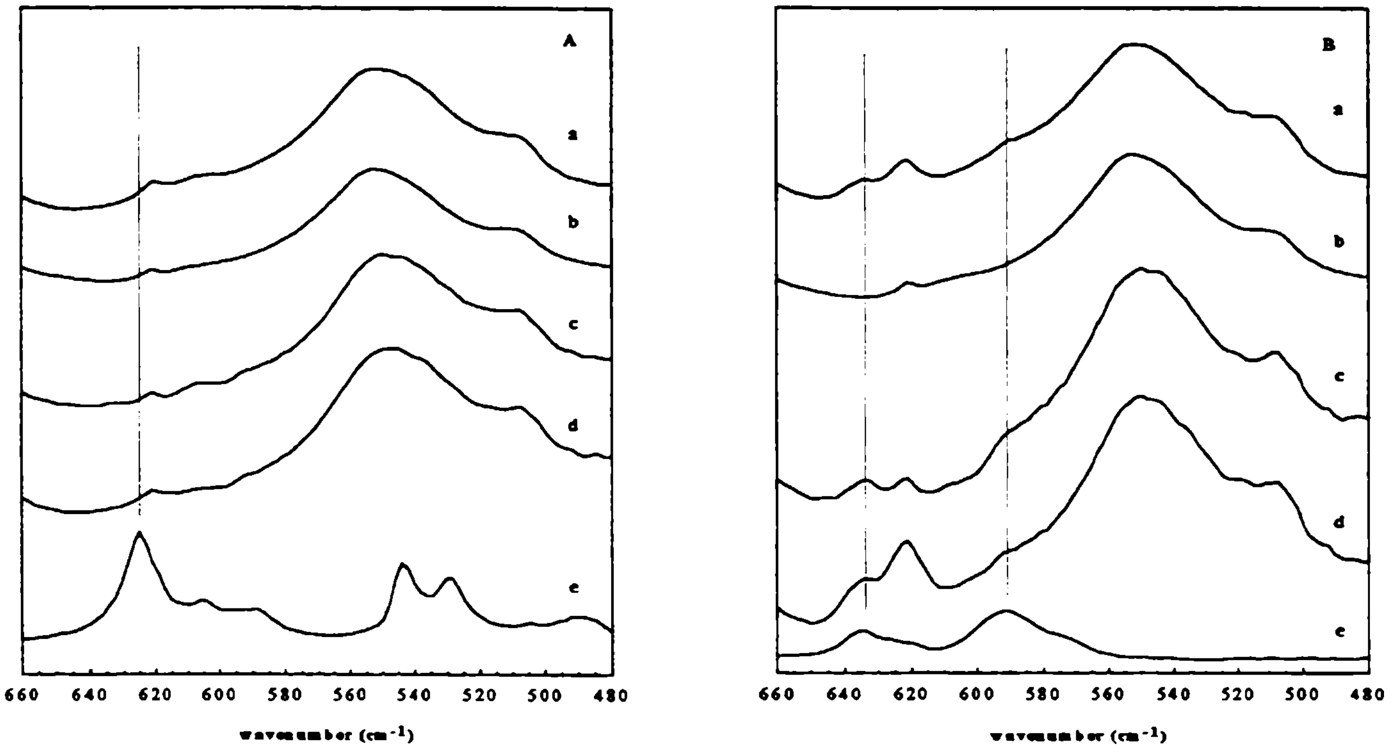

Fig. 6. FTIR spectra in the low wavenumber region of latices cast from 35IM14 (A), 35ISDS (B) and surfactants. Film transmission (a), film transmission of latex without surfactant (b), ATR of film-air interface (c), ATR of film-substrate interface (d) and pure surfactant (e).

In the case of films cast from 30IM14, no difference between transmission (bulk), F-A or F-S interfaces is observed, indicating that due to the surfmer is chemically bounded, the migration is prevented. However, it has to be pointed out that between both surfactants there are differences in molecular weight, in polarity and consequently in compatibility with the polymer. These should contribute to a lower migration of M14 in comparison with SDS. Anyway, it can conclude that the use of a surfmer hinder the surfactant migration.

CONCLUSIONS

It can concluded clearly that water ababsorption is improved by using reactive surfactants. At the same time it can be conclude that exhudation of surfactant to the film surface can be prevented. The mechanical stability of the latex can be improved as well, although this requires all of the surfactant to be bound to the latex particle surface, but possibly not in highly enriched polymer chains. This can only be achieved by using what was coined as "optimum surface behavior" in a previous publication [35], where ways of avoiding burying of surfactant groups, but ensuring 100% incorporation, are suggested. This optimum behavior was "attained" in reaction 35IM14.

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