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Surfactants, polymers and their nanoparticles for personal care applications

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Synopsis

A "touch me not" plant folding up rapidly upon being attacked or microbes depositing on teeth or ocean vessels even under hostile conditions are examples in nature that provide inspiration for developing new classes of personal care release or deposition systems. In this paper, development of such systems based on polymer/surfactant colloid chemistry is explored for achieving transport and release of cosmetic and pharmaceutical molecules at desired rates at desired sites.

The successful development of products depends upon understanding and utilizing key interactions among surfactants, polymers and hybrid polymers that are relevant to personal care products. Thus, the absorbed layers or tethers on the particulates can be manipulated for desired dispersion of actives or depositions on substrate under any and all conditions.

New hybrid polymers and nanogels have been synthesized for tuning up nanodomains that can extract and deliver at will cosmetics/drugs/toxins by perturbing pH, temperature or ionic strength of the system. Particularly, hydrophobically modified polymers have features of both polymers and surfactants and due to the associative nature of the hydrophobic groups, such polymers can form intramolecular nanodomains for performing carrier functions. Nanogels developed recently include that of polyacrylamide, poly(acrylic acid) and starch nanogels modified for extraction and subsequent slow release of fragrances and overdosed toxic drugs. Binding and release processes were investigated using surface plasmon resonance and fluorescence spectroscopies, powerful techniques for monitoring short term and long term changes.

INTRODUCTION

There is an ever-increasing need for personal care products with special properties for controlled delivery and deposition of sensory attributes. Best inspiration for developing new classes of such products results from an understanding of the mechanism by which a "touch me not" plant folds up rapidly upon being assaulted, microbes deposit on surfaces. Many surfactants and polymers with appropriate modifications can be tuned to simulate such responses. In the personal care industry, surfactants are primarily used now for emulsion stabilization as well as for imparting properties that include detergency, solubilization, conditioning, thickening and emolliency. On the other hand, polymers are employed to enhance system viscosity and consistency, which in turn affect the flow and smooth delivery of the formulation. Rheology of personal care products such as shampoos and shower gels is a key property to be controlled since consumers desire shear-thinning behavior of the liquid, characterized by slow flow from the containers, absence of long threads and ease of distribution on the skin or hair. Such desirable properties are often obtained by including appropriate combinations of polymers and surfactants in formulations.

Development of new products depends upon understanding controlling interactions among surfactants, polymers and proteins in relevant media. For example, new hybrid polymers and nanogels can be designed with nanodomains that can extract and deliver at will cosmetics or drugs or extract sebaceous or toxic materials by making use of usual perturbations in pH, temperature or ionic strength of personal care systems. In this paper, development of systems based on polymer/surfactant colloid chemistry is explored for achieving transport and release of cosmetic and pharmaceutical molecules at desired rates at desired sites based on the above principles.

The effects of surfactants depend not only how much is adsorbed but also how they adsorb. A water-wetted surface that is beneficial for displacement of sebaceous and oily materials can be obtained by manipulating the orientation of the adsorbed layers. Availability of modern equipment such as analytical ultracentrifuge, fluorescence and electron spin resonance spectrophotometers offers an unprecedented opportunity for elucidating the mechanisms involved and for designing optimum reagent schemes.

In many cases, mixed surfactants perform much better than single surfactants due to synergetic effects and ability to alleviate precipitation. Also such surfactants as sugar based ones are attracting attention as they are potentially biodegradable. Adsorption of simpler single systems will be discussed here first and then increasingly complex systems will be examined steadily tending towards real systems.

SURFACTANTS

SINGLE SURFACTANTS

Various mechanisms involving a combination of the following factors have been proposed for interactions between surfactants and substrates: electrostatic attraction/repulsion, ion-exchange, hydrophobic bonding, chemisorption, hydrogen bonding and lateral chain-chain interactions. Much effort has been made to explore the adsorption effects of variables such as the type of surfactants, the chain length, polar substitution and chain branching of the surfactants, oil, polymers, solution pH, salinity and temperature.

The basic process of adsorption of surfactant can best be understood by examining the Somasundaran-Fuerstenau IV region adsorption isotherm, originally proposed for dodecyl sulfonate adsorption on a positively charged solid (1), which is illustrated in Figure 1.

Adsorption in various regions was accounted for by considering the electrostatic, hydrophobic and micellar interactions in the system. In Region I, adsorption of the negatively charged dodecylsulfonate on the positively charged surface sites takes place due to electrostatic attraction. At the onset of region II, the surfactants begin to self assemble to form solloids (surface colloids also termed hemimicelles in some cases) and

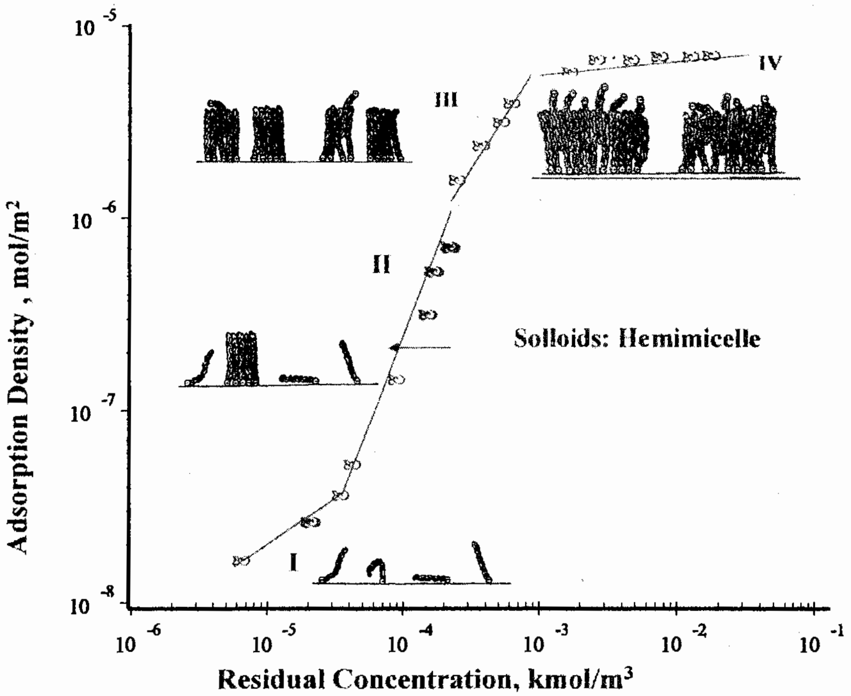

Figure 1. Schematic representation of the growth of aggregates for various regions of the adsorption isotherm.

in this region adsorption is due to electrostatic attraction between the surface sites and the oppositely charged surfactant species and lateral hydrophobic interactions between the hydrocarbon chains. Once the surface is electrically neutralized, further adsorption takes place due to chain-chain interactions alone countered by electrostatic repulsion that builds up as the surface begins to acquire now the same charge as the adsorbing surfactant species. Above the critical micelle concentration of the surfactant in Region IV, monomer activity is essentially constant and under those conditions adsorption also remains constant. It is important to note that the wettability of the surface and hence the displacement of oily material is determined by the orientation the surfactant assumes in various regions. Thus in the Region I the surface is essentially water wetted and in the Region II it will be oil wetted while in regions III and IV it would begin to become less oil wetted. It is clear the adsorption and wettability can be controlled by manipulating the structure of the surfactants.

SURFACTANT STRUCTURAL EFFECTS

Based on a full knowledge of the role of the structure of the surfactants in determining adsorption, new surfactants can be designed for minimum adsorption as well as low interfacial tension and excellent salt tolerance for emulsification and salt tolerance. The effects on adsorption of some structural variations of surfactants have been extensively studied (2):

1) Increase in the chain length of the alkyl groups increases the adsorption by orders of magnitude,

2) Incorporation of a phenyl group into the surfactant increases the effective chain length by 3 to 4 methylene groups and hence the adsorption,

3) The position of the branching of the sulfonate has a measurable effect on adsorption,

due to the difficulties in the packing of the surfactant species in the two-dimensional colloidal aggregates;

4) Alkyl substitutions on the aromatic ring of the alkylaryl asulfonates decreases the adsorption.

Even the apparently minor change in the position of the sulfonate and the methyl groups on the aromatic ring of the alkylaryl sulfonate has a ten-fold effect on adsorption as well as the degree of wettability of the adsorbed layer (3).

MIXED SURFACTANTS

Mixtures of surfactants normally yield improved solution and interfacial properties as compared to that of the individual components. It is to be noted that commercial surfactants are invariably mixtures of surfactants. Adsorption of surfactant mixtures can be synergistic or competitive and can be manipulated better for practical applications than the adsorption of single surfactants. For example, our work has shown that the non-ionic surfactant $C_{12}EO_8$ does not adsorb on solids, but in the presence of an anionic surfactant, synergetic adsorption of it can be obtained (4). In addition, the adsorption of the anionic surfactant is facilitated on a similarly charged substrates when co-adsorbed from a mixture containing the non-ionic ones, interaction between the hydrocarbon chains of the surfactants being the driving force. Adsorption of the anionic sodium dodecyl sulfate (SDS) and the nonionic octaethylene glycol mono n-dodecyl ether ($C_{12}EO_8$) from their mixtures revealed many interesting points. For example, while at pH 5, the adsorption of the nonionic $C_{12}EO_8$ was markedly enhanced by the presence of the anionic dodecyl sulfate suggesting cooperative adsorption through lateral interaction between the hydrocarbon chains, at pH 10 its adsorption was suppressed.

The phenomenon of mixed micellization of ionic and non-ionic surfactants in homogeneous solutions has been addressed in the past where models based on electrostatic principles or regular solution theory showed deviations from ideal behavior. However, the regular solution theory can be modified to model interactions between similar and dissimilar surfactants in the bulk solution, and obtain interaction parameters, which enable the prediction of synergism or competition for mixtures.

The micellization behavior of cationic-nonionic hydrocarbon surfactant mixtures has been studied using the ultrafiltration technique, and the data suggest coexistence of mixed micelles (Figure 2) (5). The importance of such coexistence in guiding colloidal behavior of the micellar solutions should be noted. The results suggested that the micellization behavior can be divided into three regions. In region I, the surfactant concentration is low and only monomers exist. In region II, surfactants begin to form aggregates. And in region III, two types of coexisting mixed micelles are proposed to be present in the system. Recently we have proven the presence of region III, i.e. coexistence of two micelles in the same system using analytical ultracentrifugation (Figure 3). Co-existence of such multispecies has intact practical implications in both system stability and efficacy.

NOVEL SURFACTANTS

Based on the available information on the effect of surfactant structure on adsorption and environmental considerations, many new interesting surfactants have appeared on the

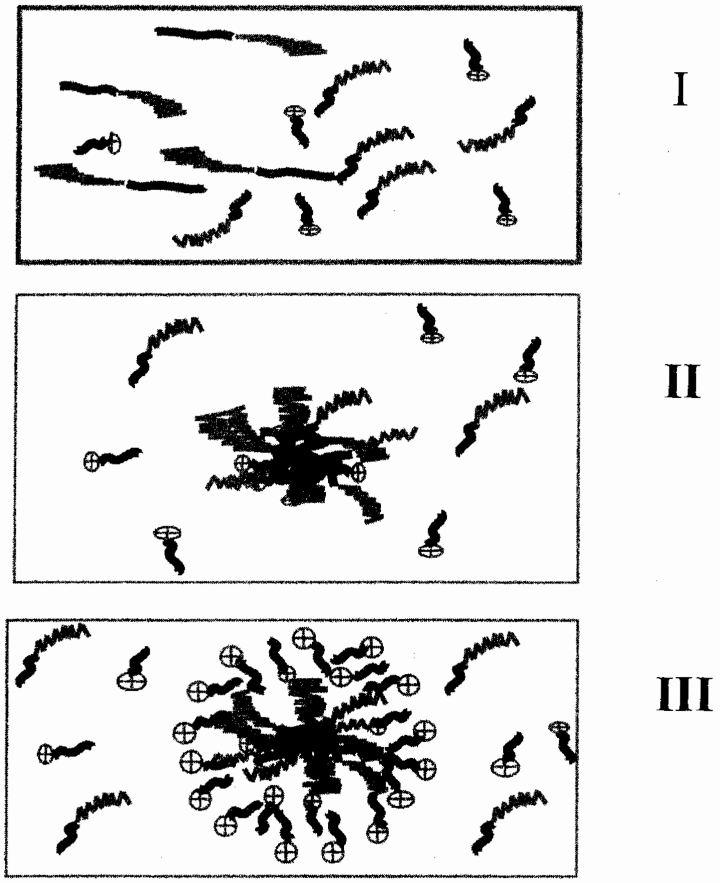

Figure 2. Schematic model for a binary surfactant system: region I, no micelles in the mixed solution; region II, one type of mixed micelles formed; region III, two types of coexisting mixed micelles formed.

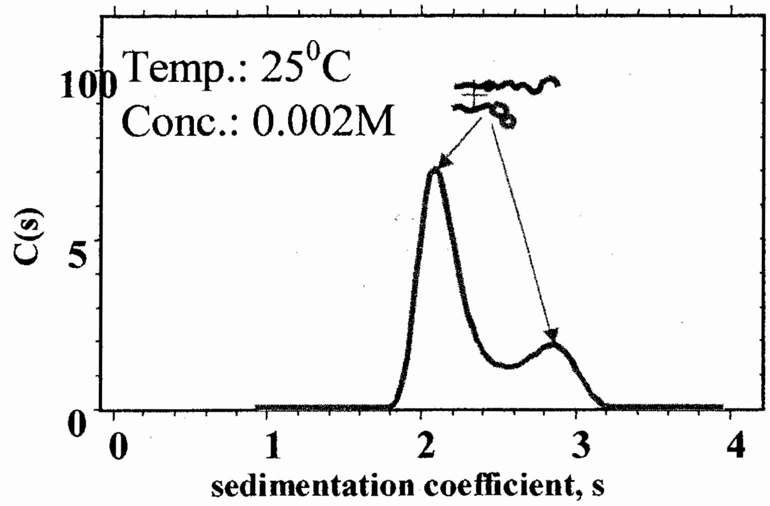

Figure 3. Analytical ultracentrifuge of mixed surfactants: coexistence of two micelles.

horizon and some of the most promising ones include alkyl polyglucosides, alkyl pyrrolidones and the Gemini types. The polyglucosides are attracting attention because of their high surface activity, salt tolerance and environmental compatibility. They are manufactured from natural products and are biodegradable making them environmentally advantageous. Also their bulky head group can lead to useful aggregation features.

in solution and at the substrate/solution interface. Its surface tension behavior in salt solutions shows some unexpected behavior. It is highly surface active even at very low dosages and under high salinity conditions and shows excellent tolerance towards detrimental species such as calcium. As a nonionic surfactant, sugar-based surfactants can also be expected to interact with anionics and enhance the activity of both components. Adsorption and solution properties of Gemini surfactants, with two hydrophobic chains and two hydrophilic head groups, also make them potential candidates as cosurfactants. With the possibility of bilayer formation of Gemini surfactants at solid/liquid interfaces, substrates can be made water wetted through proper surfactant packing on the solution/rock interface, which would be beneficial for the displacement of oily materials from the pores of hair and skin.

LIPOSOME/SURFACTANT INTERACTIONS

Liposomes are proven delivery agents. Their stability and efficacy depend on the structure of their constituents as well as interactions with proteins, carbohydrates, cholesterols and such components of biosystems. Even simple combinations of the relevant species in liposomes and the above components show new and interesting effects. Thus, when a surfactant such as dodecyl sulfonate is added to a liposome made up of phosphatidyl choline and phosphatidic acid, initially the size of the liposome increases and subsequently it is solubilized (6). Furthermore, while the addition of cholesterol stabilizes liposomes, proteins destabilize them; the reasons for this effect are still far from evident (7). Electron spin resonance studies have shown the polarity and viscosity of liposomes to change to that of micelles of dodecyl sulfonate at sufficiently high concentrations of the surfactant (Figure 4a).

These results suggest that liposome stabilization by dodecyl sulfonate involves the adsorption of sulfonate on them, leading to an increase in size, and their subsequent

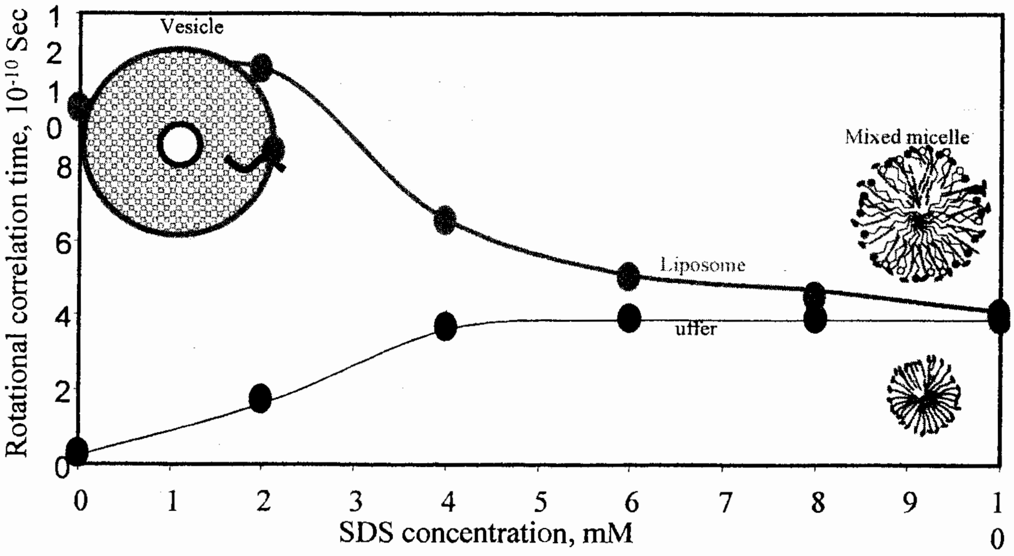

Figure 4a. Change in rotational correlation time of 5-doxyl stearic acid due to interactions with SDS. Buffer: increased correlation time (T)—transfer into SDS micelle. Liposome: decreased T—transfer into less rigid mixed micelle.

disintegration into mixed micelles composed of liposome components and dodecyl sulfonate, resulting in a drastic decrease in size (Figure 4b).

The actual processes by which such disintegration takes place are not known. Some preliminary results suggest that phosphatidic acid would exit first, leading to the weakening of the liposome structure and its dissolution. Similarly, the mechanisms by which species such as cholesterol stabilize liposomes and proteins destabilize them are also not known.

POLYMERS

Polymers are widely used currently in personal and home care products for a variety of purposes such as dispersion/flocculation, deposition/coating, adhesion, rheology, and insulation. Among the properties that affect their performance are adsorption and conformation, which in turn are determined by molecular weight, polydispersity, and functionalization, particularly with ionic and hydrophobic groups. Polymers with high molecular weight are usually employed as flocculants while those with low weight serve as dispersants. Recently, however, it was discovered that low molecular weight "dispersants" can act as flocculants if used in ultra low dosages (8).

While normally adsorption increases with molecular weight the opposite was the case with the adsorption of polystyrene sulfonate on hematite under low ionic strength conditions. It was proposed that this preferential adsorption of low molecular weight species on hematite is due to the ability of the smaller anionic molecules to diffuse to the surface faster than the larger ones and then keep similarly charged larger ones away by means of electrostatic repulsion by the adsorbed anionic species. When the ionic strength is higher, the electrostatic repulsion is minimized, allowing the larger species to get to the surface and even displace the smaller ones. Higher adsorption of the low-molecular-weight species was observed also in the case of the adsorption of polyacrylates on porous alumina where pores are relatively inaccessible to the larger molecules (9). Also under conditions of *similar* adsorption density, flocculation or dispersion of a suspension can be

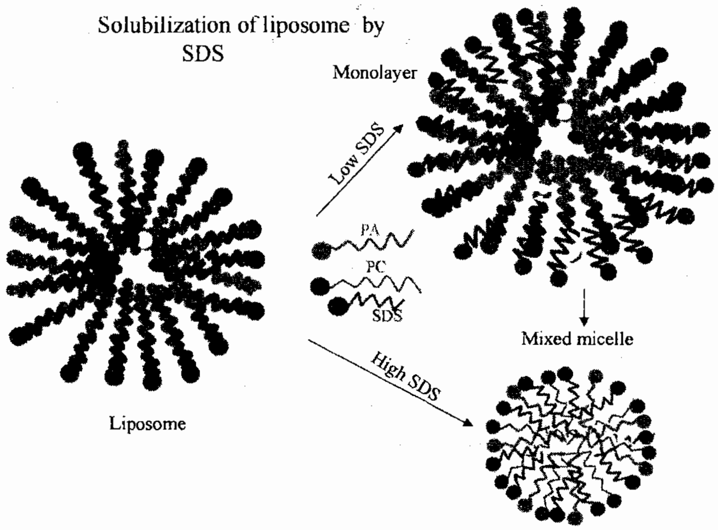

Figure 4b. Depiction of solubilization of liposomes under low and high SDS concentrations.

obtained depending on the experimental path. For example, superior flotation is obtained by pH shift to higher values than under fixed pH conditions (10) (Figure 5).

When more than one polymer is used, the sequence of addition can also determine the state of dispersion (11–14).

POLYMER/SURFACTANT COMBINATIONS

Adsorption properties of surfactants and polymers can be affected markedly by the presence of one another and this in turn can affect the wettability of the surfaces. This is illustrated by the fact that an essentially oil wetted surface with adsorbed dodecylamine can be converted to a water wetted one by the addition of a cationic polymer (acrylamide-methacrylamidopropyltrimethyl-ammonium chloride copolymer) without any change in adsorption density of the amine itself. On the basis of these results, the molecular model depicted in Figure 6 was proposed for the polymer-surfactant layer on the substrate for the water wettability (15). In accord with this model, adsorption of anionic dodecylsulfonate was activated by the cationic polymer resulting in an oil-wetted surface.

HYDROPHOBIC POLYMERS

One of the major developments in the area of water soluble polymers is the introduction of polymeric surfactants with hydrophobic groups attached to the polymer backbone. Unusual rheological properties which result from the association of hydrophobic groups are the main attractive feature of these polymers. Hydrophobically modified (hybrid) polymers, also known as polysoaps have the advantage that they have features of both polymers and surfactants and due to the associative nature of the hydrophobic groups, hybrid polymers can form intramolecular nanodomains at all concentrations and enhance viscosity above a certain concentration (16). Figure 7 shows the reduced viscosity for hydroxy ethyl cellulose (HEC) and its hydrophobically modified analogue (HMHEC) solutions at a fixed concentration of 1000 ppm as a function of added $C_{12}EO_8$. In contrast to the viscosity of HEC solution that is unaltered by the addition of surfactant. The reduced viscosity of HMHEC gradually increases with surfactant concentration and

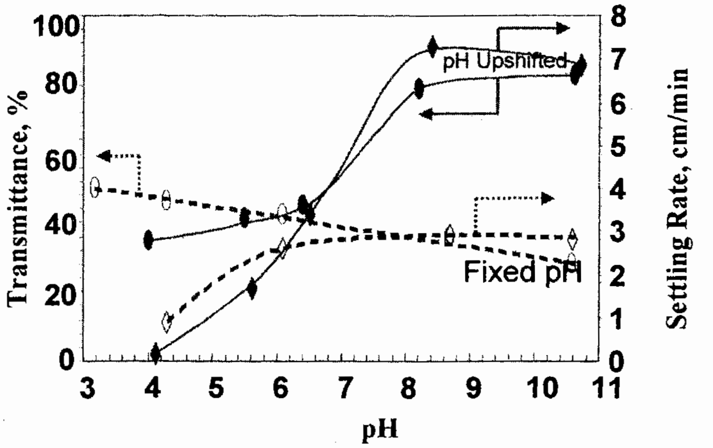

Figure 5. Effect of pH on PAA conformation and flocculation responses of alumina suspension with PAA.

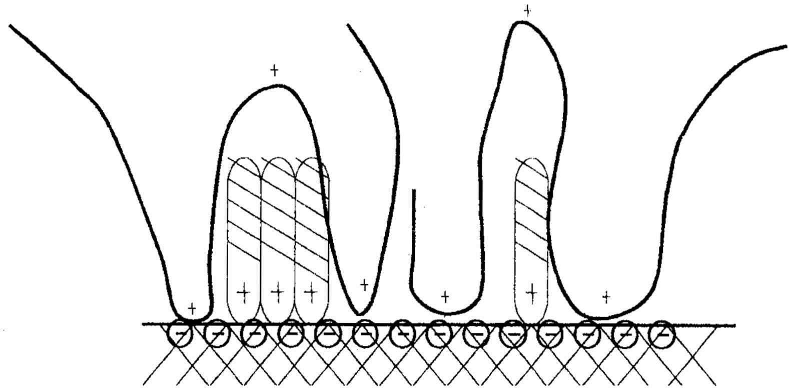

Figure 6. Schematic representation of cationic polymer-dodecylamine layer on quartz.

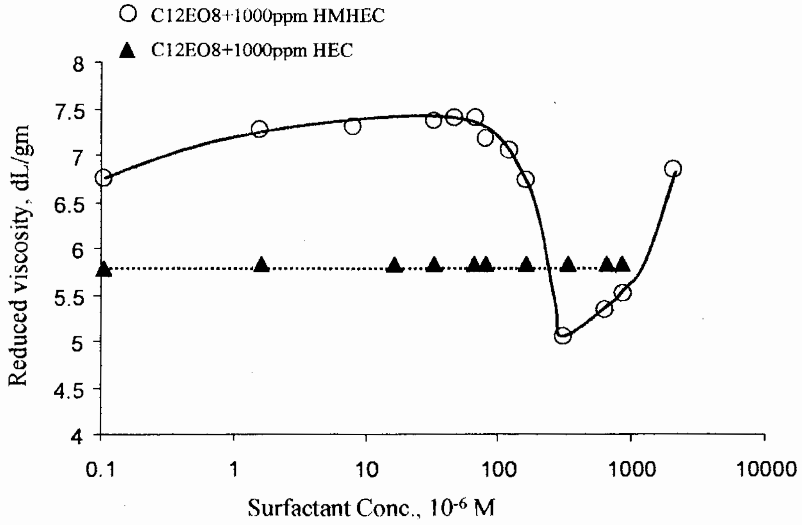

Figure 7. The reduced viscosity of HEC and HMHEC solutions (1000 ppm) as a function of added $C_{12}EO_8$.

then decreases in the vicinity of the critical micelle concentration. Minimum viscosity is observed at a surfactant concentration of $3.26 * 10^{-4}$ mol/l. Above this concentration the viscosity again increases and approaches the value of pure aqueous solution at a surfactant concentration of $2.04 * 10^{-3}$ mol/l. Since the solvent power of the water is not greatly affected by the presence of the surfactant, the changes in the reduced viscosity can be considered to be due to the changes in the hydrodynamic volume of the polymer molecule and the polymer-polymer interactions. In the dilute polymer concentration region, the changes in the hydrodynamic volume are more significant than inter-polymer interactions and the variation in viscosity reflects the structural changes of the polymer. The low viscosity is the result of the compact polymer structure stabilized through the intra-molecular association of the hydrophobic groups on the polymer. Hence, the initial increase in viscosity can be attributed mainly to chain expansion due to the surfactant binding on polymer and the resultant less compact structure. In the region of the c.m.c. of the surfactant, the bound surfactant molecules on the same chain associate to form a highly compact structure. The minimum obtained in Figure 6 is the result of this intramolecular (associated) polymer structure and the surfactant concentration ($3.26.10^{-4}$ mol/l, $C_{12}EO_8$) here corresponds to the onset of free micelles in the system. Further increase in the viscosity in the micellar range may be due to the dissolution of the hydrophobic groups in micelles which reduce their association or the

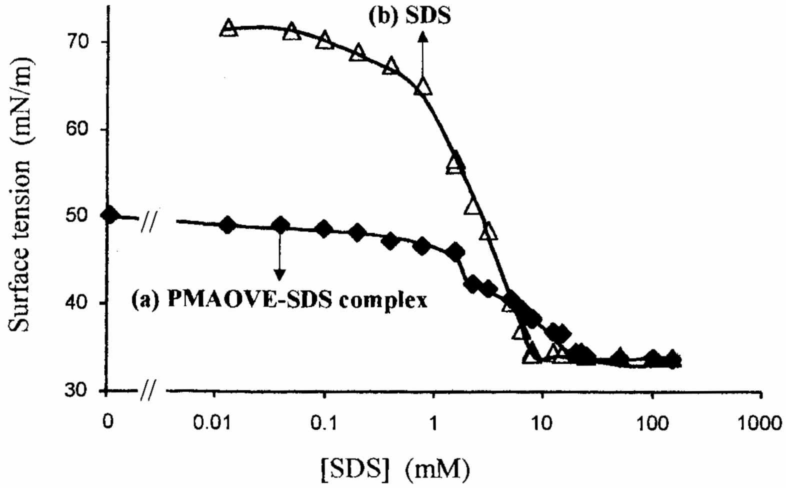

Figure 8(A). Surface tension of aqueous solutions of sodium dodecyl sulfate in the absence (b) and in the presence (a) of 0.1% (wt/wt) PMAOVE as a function of SDS concentration. S.D. = ±2%.

bridging of the polymer chain through micelles. The constant viscosity observed for the HEC-$C_{12}EO_8$ system implies a low degree of binding of the polymer with the individual surfactant molecules or its micelles.

Similarly poly(maleic acid/octyl vinyl ether) (PMAOVE) was found to interact with sodium dodecyl sulfate (SDS) by Deo et al. (17), to yield enhanced viscosity and reduced surface tension. This has been attributed to the coexistence of the mixed micelles of PMAOVE and SDS. This behavior as shown in Figure 8(A) and (B) is promising for the use of PMAOVE as thickener in hair styling gels.

The ability of the hydrophobically modified polymers to form nanodomains can be utilized also for the release of organic sensory attributes. Thus, the system poly(maleic acid/octyl vinyl ether) (PMAOVE) forms hydrophobic nanodomains that can solubilize and release organic molecules by changes in pH or salinity. Effect of dilution and pH on such release is shown in Figures 9(A) and (B). These figures show that hydrophobically modified polymers uncoil on dilution or on increase in the pH of the medium and release the trapped hydrophobes.

Interestingly, such polymers can also release entrapped material upon deposition on solids. Figure 10 shows results obtained when PMAOVE is deposited on alumina particles. It can be seen that organics entrapped is less when the PMAOVE is in contact with the solid than when it is in micelles above 200 ppm. Evidently, the hydrophobic polymeric entanglements loosen up on coming in contact with a surface and facilitates the release of entrapped moieties.

The potential use of hybrid polymer for formulation of personal care products is illustrated in Figure 11 which shows that in the presence of a polar solvent the hybrid polymers will form hydrophobic domains inside which hydrophobic attributes can be incorporated and used as such or can be centrifuged and freeze dried for the end use.

SUGAR BASED POLYMERS

Sugar based polymers and surfactants play a vital role in cosmetic formulation technology. They can act as rheology modifier, suspending agent and hair conditioner. In the cosmetic industry, cationic guar is used as a skin protection agent and as conditioner in

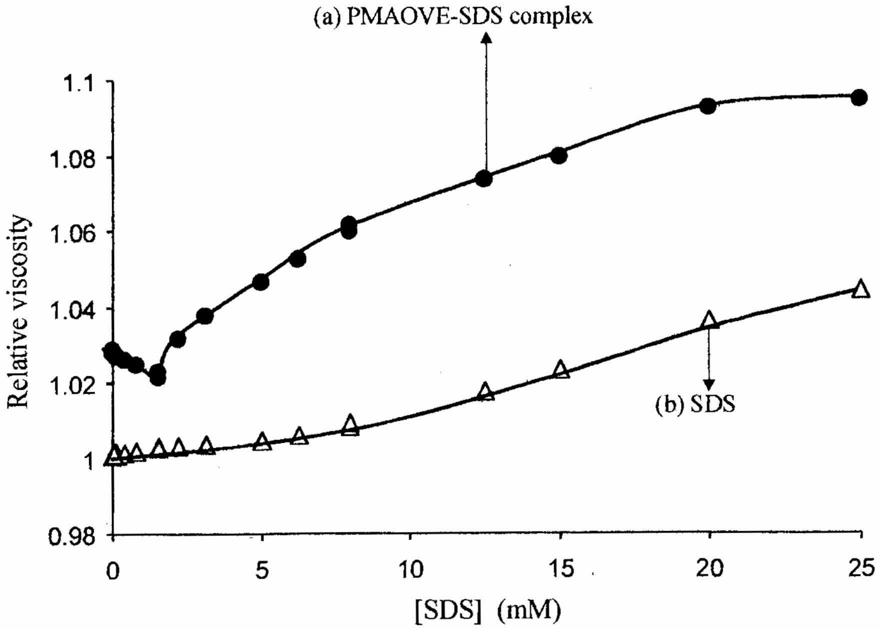

Figure 8(B). Relative viscosity of aqueous solutions of sodium dodecyl sulfate in the absence (b) and in the presence (a) of 0.1% (wt/wt) PMAOVE as a function of SDS concentration. S.D. = ±2%.

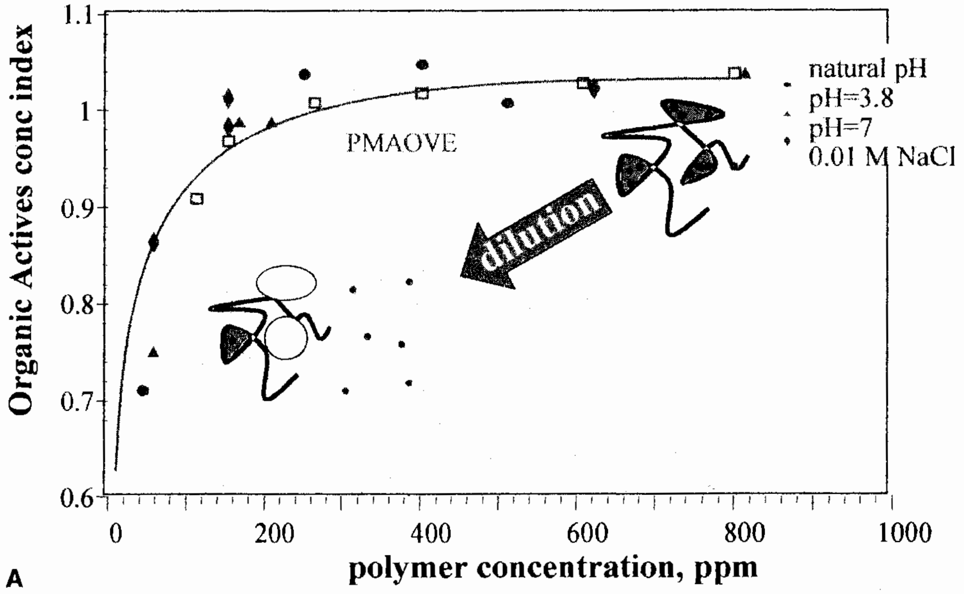

Figure 9(A). Effect of dilution on the uncoiling of PMAOVE for the release of organic actives.

shampoos (18). We are exploring the relationship between the performance of the polysaccharides and their structure including functionality. We have investigated the interaction of sugar-based polymers with different surfaces. The polysaccharides under consideration are hydroxyethylcellulose, hydrophobically modified hydroxyethylcellulose, guar gum, cassia gum and locust bean gum. Computer modeling of these polymers in water (Figure 12) shows that the conformation of these polymers differs from each other, depending on the structure of the sugar unit.

Differences in their structure, particularly the helical structure can be used to obtain desired rheological as well as loading properties among these sugar-based polymers.

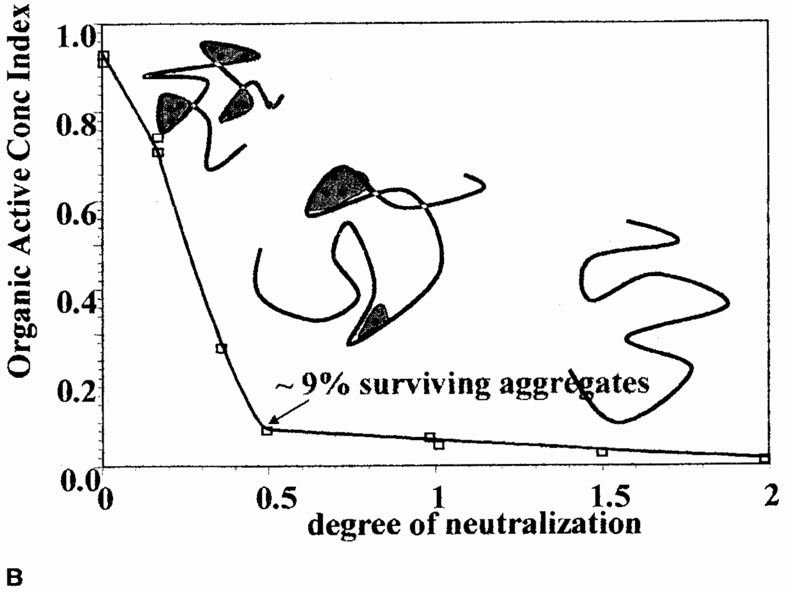

Figure 9(B). Effect of pH of the medium on the uncoiling of PMAOVE for the release of organic actives.

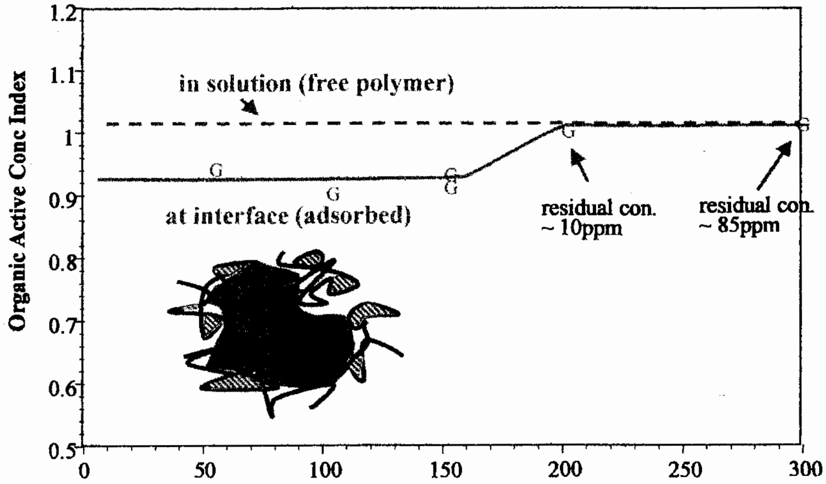

Figure 10. Uncoiling of hydrophobic domain in contact with a surface.

NANOGELS AS ENCAPSULATING AGENT

Water soluble, lightly cross-linked polymers can also act as a thickening agent. Molecular weight distribution, cross-linking type and density largely determine rheological performance in this case (19). Cross-linked poly(acrylic acid) and its copolymers have been considered to be the most preeminent thickening resins. If these crosslinked polymers are reduced to nano or micron size particles, apart from being used as thickeners they can also be used as vehicles for the release of cosmetic attributes such as fragrances and antimicrobial agents at a rate and duration designed to accomplish the intended effect. Other than fragrances, sunscreen, sebum oil absorber and anti aging compounds can also be formulated in controlled release systems. The release from these formulations is usually triggered by shear force (rubbing), temperature, pH etc.

New nanogels developed recently by reverse microemulsion polymerization include polyacrylamide, poly(acrylic acid) and starch nanogels modified for extraction and sub-

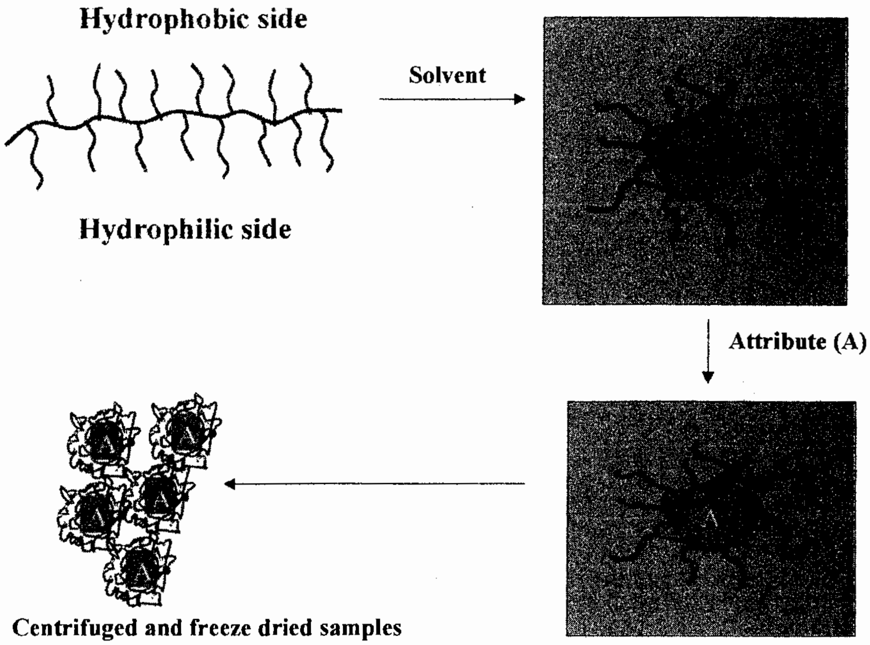

Figure 11. Use of hybrid polymer for encapsulation of cosmetic attributes.

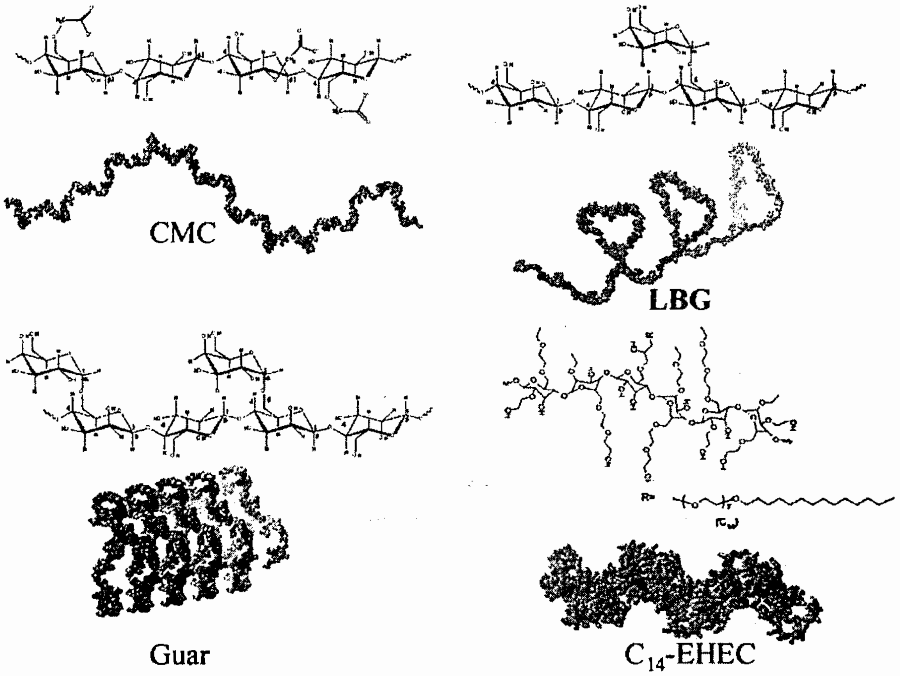

Figure 12. Orientation of carboxymethyl cellulose (CMC), locust bean gum (LBG); guar and hydrophobically modified hexaethyl cellulose (C_{14}-EHEC) in water.

sequent slow release of fragrances and overdosed toxic drugs. Our AFM study (Figure 13) revealed that the dry particle size of the polyacrylamide nanogels is 40 nm and on swelling the size increases to 140 nm, giving the nanogels capability to contain and release materials.

The potential of poly(acrylamide) and starch nanogels to extract vanillin was recently evaluated. We have also examined the extraction and release properties of the linalyl

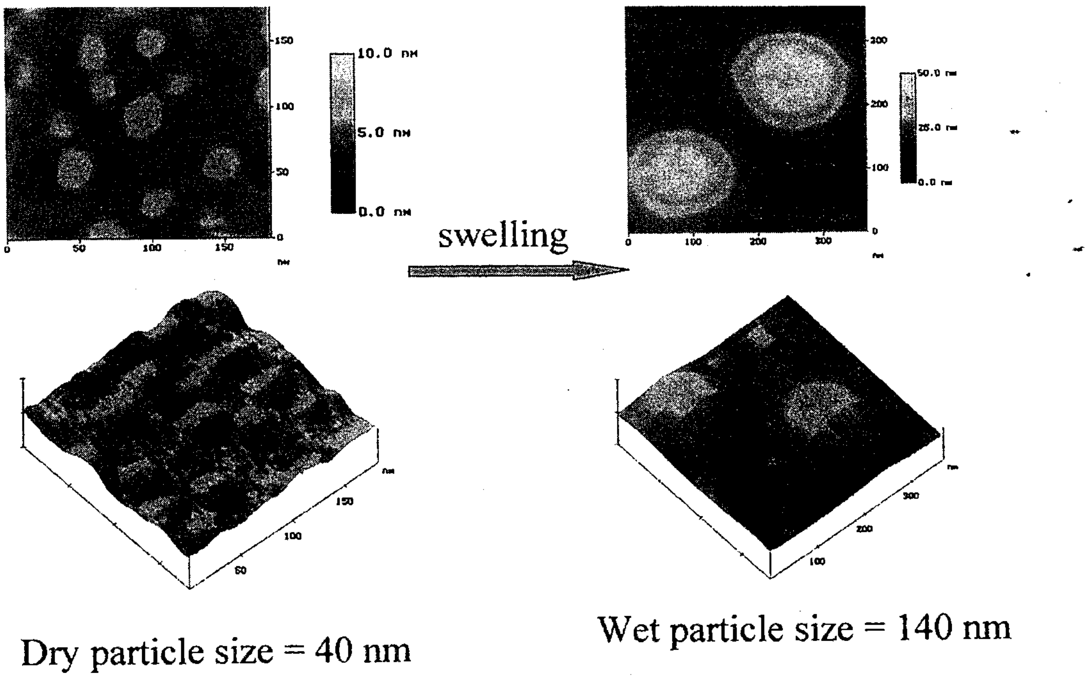

Figure 13. AFM image of dry polyacrylamide nanogels (40 nm) and wet polyacrylamide nanogels (140 nm).

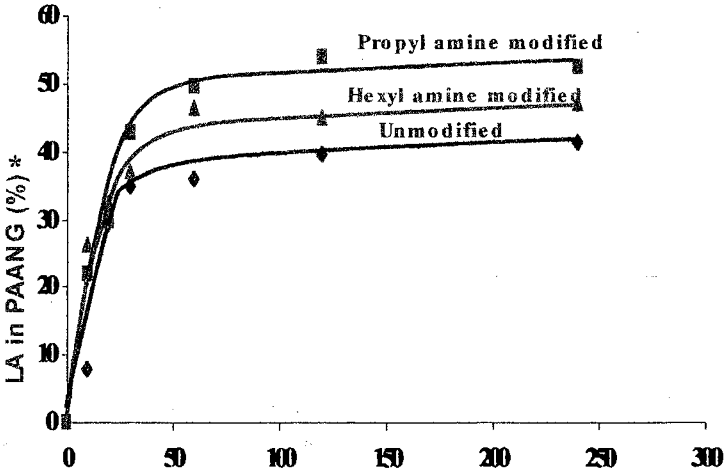

Figure 14. Extraction of linalyl acetate (LA) by poly(acrylic acid) nanogels (PAANG) in methanol. Conditions for extraction: PAANG: 10 mg; LA: 10 µL; methanol: 10 mL.

acetate fragrance from poly(acrylic acid) and hydrophobically modified poly(acrylic acid) nanogels. As shown in Figure 14, hydrophobically modified poly(acrylic acid) nanogels extracted 50% linalyl acetate (LA) in 4 hours whereas the unmodified one could extract 45% linalyl acetate in 4 hours.

At pH 7, unmodified poly(acrylic acid) nanogels release more fragrance as compared to the modified nanogels (Figure 15). This suggests that appropriate modification is required for optimum carrier and delivery properties.

Clearly, it is important to have a knowledge of the mechanisms controlling the rate of extraction and release. Towards this purpose, a technique based on surface plasmon resonance technique has been successfully developed recently for monitoring both short

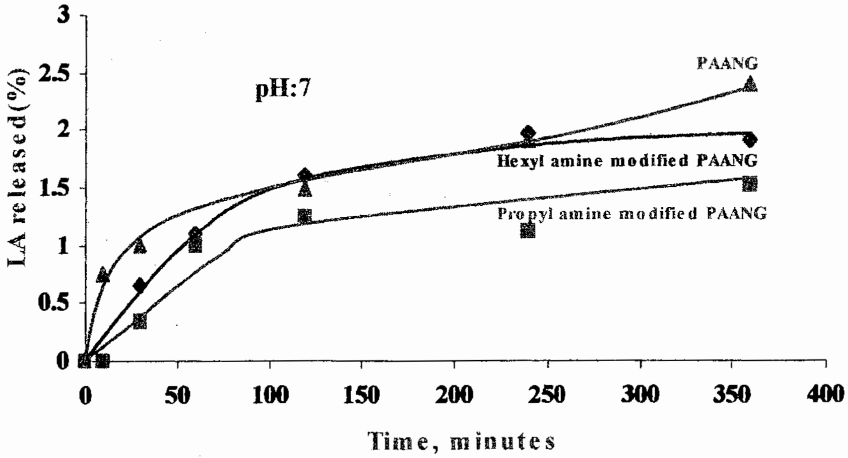

Figure 15. Release of linalyl acetate (LA) from unmodified and hydrophobically modified poly(acrylic acid) nanogels (PAANG) in water. Conditions for extraction: LA incorporated PAANG: 10 mg; water: 10 mL.

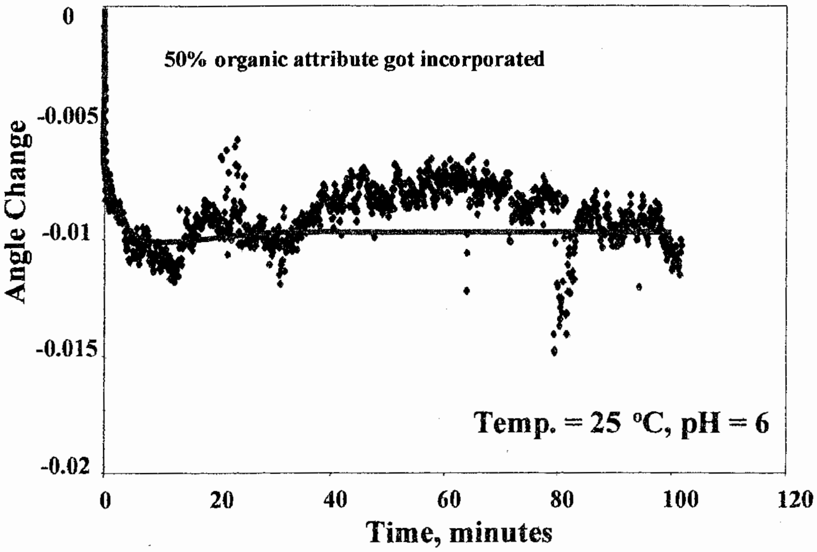

Figure 16. Interaction of organic attribute with polyacrylamide nanogels as studied by surface plasmon resonance (SPR) technique.

term and long term dynamics (20). Figure 16 shows that release of 50% of organic attribute from polyacrylamide nanogels could be detected in 100 minutes using this technique.

ZWITTER IONIC LATEX PARTICLES

Deposition provides good conditioning properties to the hair. Properties such as combability, flyway and curl retention are affected by deposition of polymers on hair strands. Based on the consideration that nano or micro particles with different type of tethers can deposit on surfaces if there are at least some tethers that are complimentary to some sites on the substrate, we examined negative overall zwitterionic latex particles for deposition on negative surfaces. Deposition of anionic, cationic and zwitterionic latex particles on a negatively charged surface was studied as a function of deposition time, pH and particle concentration. It was discovered that zwitterionic particles deposit better than all the others even under hostile conditions (21).

CONCLUDING REMARKS

It is clear that research involving synthesis and characterization of hydrophobically modified polymers, sugar-based polymers and polymeric nanogels and study of their interactions with surfactants and relevant biosurfaces hold considerable promise for developing better personal care products. This will depend primarily on a full understanding of the relationship between the structure and performance of surface-active molecules and particles. We have demonstrated that hydrophobically modified polymers and polyacrylamide and poly(acrylic acid) nanogels can be used to encapsulate attribute molecules and then release upon dilution. The nanogels can be included as one of the ingredients in shampoo or conditioner formulations. In this type of formulation, the nanogels, owing to their small size can achieve good dispersion in the formulation, imparting thickening property to the product and at the same time, deliver pleasant odor of the fragrance over a long period of time.

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