*Macromol. Symp.* ***2001,*** *166, 71-92*

# Interaction between Water Soluble Polymers and Surfactants

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SUMMARY: Based on literature data and some own results a short review of regularities, driving forces and mechanisms of interaction for different classes of polymers and surfactants is given. The main investigation methods of polymer-surfactant systems are described.

## Introduction

Typically, physico-chemical properties of solutions containing macromolecules and surfactants are not additive. The interaction between polymers and surfactants produces a variety of behaviours which are of intrinsic scientific interest, in addition to their potential for exploitation in industrial processes (paints, coatings, cosmetic products, tertiary oil recovery, etc.) and biology. This interaction using different methods has been studied. In this paper a short review on polymer-surfactant interaction is given that is based on literature data and some recent results obtained by the author. The material was reported at the 3d Intern. conference on polymer-solvent interactions (Beasancon, August 2000).

Interest in the properties in mixtures of polymers and surfactants in aqueous solution is quite old. For example, the formation of lipo-protein aggregates in biological fluids is well recognized more than 50 years ago. Firstly, in 40-50s protein/synthetic surfactant pairs were studied, in which the «binding» of surfactant by macromolecule is mainly due to electrical forces of attraction. The second period, in 50-60s involved mainly water-soluble synthetic nonionic polymers with charged surfactants. Different mechanisms of binding have been proposed. In 70-90s the interest has developed in charged pairs, in interaction of synthetic polyelectrolytes, including polypeptides1).

Important impact was made by Jones2) who based on the study of polyethylene oxide (PEO) and sodium dodecyl sulfate system (DDS), formalized a concept of two critical

CCC 1022-1360/00/$ 17.50+.50/0

concentrations of surfactant in polymer-surfactant systems, *$T_1$ represents the concentration at which interaction between the surfactant and polymer starts, and $T_2$ the concentration at which the polymer becomes saturated with surfactant.*

## Investigation methods

A detailed review of investigation methods of polymer-surfactant systems is given by Goddard[1)]. Below a short description of features of the commonly used methods is given.

***Surface tension.*** The main assumption of this method is that the surface tension is a sensor of the free surfactant in solution, i.e. the surface activity of the surfactant molecule considerably exceeds that of the polymer-surfactant «complex». So, this is a monitoring in the concentration changes of uncomplexed surfactants. Typically $T_1$ is less than CMC; it means that the «adsorbed» or «aggregated» state of surfactants represents a more favorable energy condition for surfactant molecules than do regular micelles. It has been shown that $T_1$ is weakly dependent on the polymer amount in solution, i.e. the «aggregate» formation is mainly the function of surfactant concentration for a particular polymer. The value of $T_2$ is directly proportional to the concentration of polymer. Using this method, the interaction between sodium dodecyl sulfate and polyethylene oxide, polypropylene oxide (PPO) or polyvinyl pyrrolidone (PVP) has been studied[1),3),4)]

***Electrical conductivity.*** There are changes in the specific conductance /concentration plots of SDS in the presence of PEO or other polymers (Fig.1). An appearance of two breakpoints is registered. The first (pre-micellar) breakpoint where the plot departs from that of SDS alone, is almost independent of the polymer concentration. The second (post-micellar) breakpoint where the plot rejoins that of SDS, varied linearly with the $C_{pol}$. Similar data have been reported in[5)-7)].

***Viscosity.*** Saito[8)] revealed a considerable increase in the viscosity of methylcellulose and PVP solutions in the presence of SDS, presumably due to a combination of electrical charging and conformational effects. An increase in the relative viscosity of PEO solutions at SDS concentrations about $T_2$ in PVP solutions at SDS content about $T_1$ or in PVAc solutions with sodium dodecyl-benzen-sulfonate (DDBS) has been observed[1),4),9)]. This is explained by an expansion of the polymer coils due to association with the charged surfactant. Fig. 2 shows an example of the dependence of reduced viscosity of PEO as a function of SDS concentration at different MM of the polymer taken from our results. A sudden increase at a concentration $T_1$ of SDS is observed which is independent of polymer

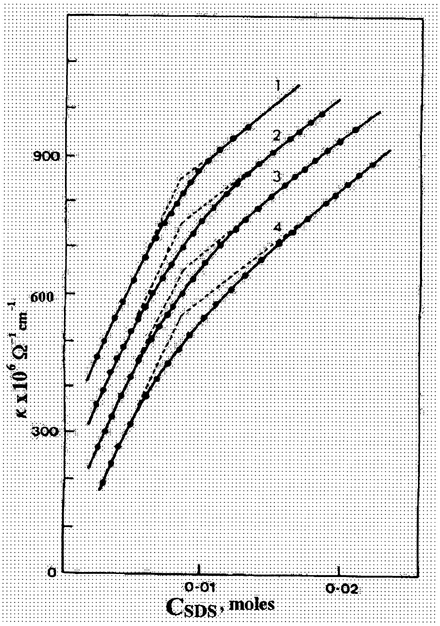

Fig. 1: Dependence of the conductivity of PEO solution on the added SDS amount 1-0.02% PEO; 2-0.04% PEO; 3-0.06% PEO; 4-.0.1% PEO

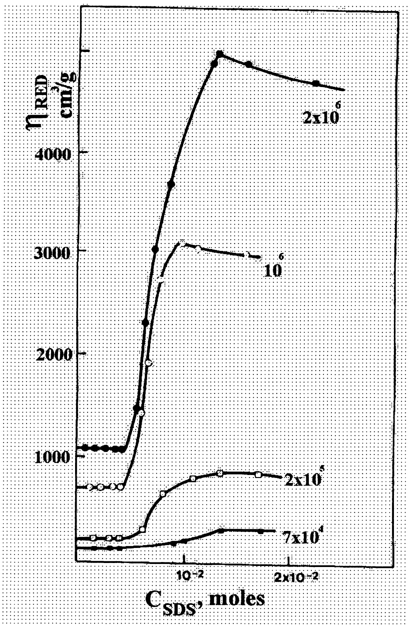

Fig. 2: Dependence of the reduced viscosity of 0.05% PEO solution on SDS concetration at different MM of the polymer (indicated)[1)]

concentration and MM. Also a levelling off at a $T_2$ concentration, which increased with polymer concentration is seen.

***Ultracentrifugation.*** Francois et al.[10)] have shown that the introduction of SDS to a solution of high-molecular PEO up to the saturation concentration $T_2$ led to progressively faster sedimentation of the polymer, i.e. a higher MM of the complex, with only one peak in the sedigram. Beyond the $T_2$ a second peak corresponding to free SDS micelle was observed. Extrapolation of the sedimentation coefficients to zero polymer concentration gives information about MM of the saturated complex and free PEO. From these data the ratio, i.e. the MM of the complex was calculated. This correspondents to 0.38 mol SDS per mole PEO at 0.1 M NaCl content.

***Cloud point and solubility.*** A "polyelectrolyte effect" is the enhancement of the polymer solubility in water when it associates with ionic surfactant. The solubility of uncharged polymers is due to the presence of polar groups that hydrate in water. This hydration can diminish with temperature and the critical balance governing solubility can be upset at a specific temperature ("cloud point") at which the polymer precipitates from solution. If polymer acquires charges by adsorption of charged surfactants, enhanced solubility or elevation in the cloud point is observed$^{1)}$. For example, the cloud point of hydrolysed polyvinylacetate (PVAc) is raised $20^0$ C in the presence of 0.01% dodecylbenzene sulfonate$^{9)}$. The cloud point of PPO of MM 1,025 and 2,000 is raised by addition of $2x10^{-2}$ M SDS from $40^0$ and $20^0$ C to $90^0$ $C^{11)}$.

***Gel filtration.*** Advantages of the gel filtration to obtain information on the binding of surfactant to polymers are$^{1)}$: (1) it is rapid, (2) does not require the addition of electrolyte as in the dialysis method. The eluation volumes from the column with Sephadex G100 in PEO/SDS systems increased in the order: complex < micelles < single surfactant ions that corresponds to decreasing molecular volumes. Complex formation was observed to occur above PEO concentration ($T_1$) of SDS of $4x10^{-3}$ $M^{1)}$.

***Adsorption on solids.*** Sometimes the preadsorbed surfactant enhances the adsorption of polymer and vica versa as it has been shown for PVA/DDBS and PVA/CTAB pairs on silica$^{9)}$ or for strongly interacting pairs of PVP/SDS on titania$^{12)}$ as the concentration of SDS was below $4x10^{-4}$ M, i.e. below $T_1$. To explain these results authors invoked the formation a type of surface complex between PVP and SDS at bulk concentration of surfactant below $10^{-3}$ M. The formation in solution of higher SDS concentration of "conventional" PVP/SDS complexes resulted in lowered adsorption of both compounds since the complexes are relatively surface inactive$^{1)}$.

***Dialysis equilibrium.*** It is a traditional method, which was used in early works for proteins, later for PVP/SDS and other systems$^{13)}$. The uptake of surfactant by the polymer in the inner compartment of the dialysis cell is observed that is the evidence of binding of the surfactant by polymer. The rise in uptake occurs at a concentration close to that observed as $T_1$ and the curve is levelled off at the approaching the equilibrium concentration to CMC. Dialysis measurements are carried out in the presence of salt, typically 0.1 M NaCl or KCl to minimize Donnan membrane effects. In consequence both $T_1$ and CMC are depressed but the salt elevated the binding ratio up to 0.9 for $C_{12}$ homolog. Similar behaviour was observed for PEO/SDS system as well, with limiting binding ratio in 0.1 M NaCl solution up to 0.4 mol SDS per mol of PEO repeated unit$^{1)}$.

***Use of ion specific electrodes.*** Membrane electrodes specific for dodecyl sulfate and other surfactants have been used for studying the PVP/Sodium alkyl sulfate$^{14)}$ and other$^{15)}$ systems. A plot of *emf* against the logarithm of surfactant concentration is linear and showes a change at the CMC. In the presence of polymer two new slope change points are revealed consistent with $T_1$ and $T_2$. The deduced saturation binding ratio of SDS to PVP of 0.34 is found, and it is independent of the MM of the PVP in the range of 10,000-340,000. Another method to obtain information about the binding of an anionic surfactant to neutral polymer like PVA or PEO is to follow the change in counterion (eg. $Na^+$) activity during binding, using an electrode specific to this ion16).

***Solubilization of dyes.*** A number of water-soluble polymers can enhance the capacity of various surfactants to solubilize the oil-soluble materials like dye Yellow OB17). The solubilization capacity towards the dye Orange OT of PEO/SDS mixtures is much higher than that of "pure" micelles. Good agreement exists between the point of initiation of solubilization and $T_1$ value derived from conductivity and other data. The effect of PVP on the solubilization concentration toward Orange OT as a fuction of sodium alkylsulfates content of different chain length has been studied. It has been shown that the $T_1$ values are less than corresponding CMCs. These results provide indication that the bound surfactant must exist in some kind of cluster and there is a similarity between the process of "binding" and micellization.

***Fluorescent probes.*** By this technique one can obtain a measure of the effective polarity of that portion of the micelle where the fluorescer is located. The most widely used probe is pyrene, this measure for pyrene is provided by the ratio of the 1st and 3rd fluorescent peaks. Dependence of the flourescence parameter $I_I/I_{III}$ of pyrene on the SDS concentration in the presence of different amount of PVP shows an appearance of a plateau and two transition concentrations by the two ends of the plateau. They are the beginning and end of the interaction zone between polymer and surfactant. The first transition has about the same value as $T_1$ observed by other methods, and the length of the plateau increases with polymer concentration yielding a binding ratio of 0.3 mol SDS per mol of repeated unit of PVP, consistent with data obtained by other methods18). Similar results have been obtained for PEO/SDS and PVP/SDS systems19). At certain conditions the method can provide information about the SDS clusters which form in the presence of PVP or PEO. Zana et al.19) have found about 20-50 monomers in the $T_1$-$T_2$ concentration range, these values are less than 60-80 monomers for regular SDS micelles. The cluster size increases in the $T_1$-$T_2$ concentration range. The clusters which form first, i.e. at SDS concentration near $T_1$ are quite small (about 20 monomers). Beyond $T_2$ there is an increase in size of SDS aggregates due to increasing dominance of regular SDS micelles19).Kogej and Skerjanc[20)] have used this method for studying the aggregation of alkyltrimethylammonium bromides induced by sodium polystyrenesulfonate.

***Fast kinetics measurements.*** There are two characteristic relaxation times of micelle formation - a short one $\tau_1$ corresponding to the exchange of a surfactant monomer with a preformed aggregate (microseconds), and a longer one corresponding to micelle formation/disintergration, measured in milliseconds. Authors[21)] using ultrasonic measurements for PVP/octylsulfate system revealed the existance of a premicellar zone in which relaxation rates ($1/\tau_1$ ) were 10-fold greater than that at CMC of the surfactant alone, for which no premicellar relaxations were observed. For both PVP/SDS and PEO/SDS systems, relaxation rates were substantially higher in the presence of polymer. By determining the temperature dependence of $\tau_2$ , activation energy can be obtained for the surfactant aggregation/deaggregation process. In the concentration region where the aggregated surfactant is associated with polymer, the activation energy was reduced by two-thirds compared with the value in the polymer-free system. It means that the aggregation of surfactants on the polymer chain is faster than between single ions[1)].

***Nuclear magnetic resonance.*** Muller and Johnson[22)] have measured the chemical shift of F in PEO/$F_3$SDS system. It has been shown that at certain concentration ($T_1$) lower than the CMC of the surfactant, a slope of the plot of chemical shift versus surfactant concentration changes. At a second concentration ($T_2$) the slope again changes becoming close to that of polymer-free micellar solutions. $T_1$ was independent of polymer concentration, while $T_2$ increased with it. Cabane[23)] measured the chemical shift of $C^{13}$ of various carbons in PEO/SDS mixtures. No shifts were observed for carbons $C_4$ through $C_{12}$ but substantial shifts occured for the carbon closest to the sulfate headgroup of SDS ($C_1$) and $C_2$ and $C_3$. This means that these carbon atoms encounter different environment in polymer/aggregate state, namely EO groups replace water in the outer region of the "micelles", i.e the zone comprising the headgroup and first few carbons. The aggregates are complexes in which the polymer chains wrapped around the micelles, and only a fraction of the polymer units are in contact with the micellized surfactant and the rest is in the form of loops[1),23)].

***Small-angle neutron scattering (SANS).*** This method explores the large difference in scattering length density of H and D atoms to neutrons while in the mixture of two solutes one solute is obtained in hydrogenous form and the other one in deuterated form. Authors[24)] studied PEO/SDS mixtures of different composition and concentration, in NaBr solutions with various ionic strengths. At stoichiometric composition, i.e. along $T_2$ line, SDS clusters adsorbed on the PEO resemble a string of beads, the distance of beads changed from 9 to 6 nm with increasing the salt content from 0 to 0.8 M. EO monomers of pure PEO repel each other more than they are associated with SDS. The saturated macro-aggregate formed from PEO of MM 135,000 contains about 27 micelles, i.e there is 1 micelle for every 114 monomer units of PEO1),24).

***Electron spin resonance (ESR).*** Shirahama et al.25) have studied the ESR spectra of hydrophobic spin probe in simple micellar solutions of SDS and in solutions where SDS were present in complexes with PVP or PEO. In the presence of polymers the line width of a peak was found to be narrower that was identified as a greater level of separation of the spin proble molecules, i.e. the SDS aggregates in which the probes are solubilized are smaller in the presence of polymers. The faster $T_2$ rates of nitroxide radicals in SDS/PVP complexes are interpreted as the formation of less compact smaller aggregates of SDS in complex as compared to regular SDS micelles1).

***Electrophoresis.*** Shirahama and others (see in1)) have found that complexes of PVP/SDS and PVAc/SDS have a substantial negative charge and their electrophoretic mobility was independent of the MM of PVP in the range of 25,000-700,000. The authors invoked a «necklace» model for complex in which the «beads» are SDS clusters along the polymer «string» or chain. The individual clusters, i.e. charge centers, control the mobility of the complex. The measured electrophoretic mobility of complexes reached about 2/3 of the value characteristic for free SDS micelles. I have also used this method for studying the interaction between surfactants and oppositely charged polyelectrolytes (see below).

***A new potentiometric method*** has been developed for the determination of the aggregation number of ionic surfactants in polymer (PVP)-surfactant (NaDDS) complexes by Gilanyi and Varga26) . The method is based on the comparison of the measured mean activity of an inert electrode added in trace amount to the system to that calculated from the distribution of ions in the macro-ionic system.

***Solubility characteristics.*** At low concentrations of the added surfactant the polymer solution remains clear but the binding of surfactant to the macromolecule starts to occur in this region. The continues addition of surfactants to a polyelectrolyte of opposite charge results in the appearance of precipitation. The maximum precipitation often takes place at stoichiometric 1:1 complex based on charge neutralization. Addition of excess surfactant results in complete clarification of the solution as the complex is resolubilized. Many factors affect these phenomena like charge density of the polymer, chain branching, length of the surfactant alkyl group, hydrophility of headgroups, etc. As an example, Fig. 3 shows our data on the change of the transmittance of a cationic polyelectrolyte (copolymer of acrylamide with ammonium salt of alkyl acrylates) solution in the presence of increasing amount of sodium dodecyl benzene sulfate. The formation of non-soluble complexes at surfactant concentration 5-15 mg/100 ml has been observed. Also a good agreement between viscosity and solubility data is seen.

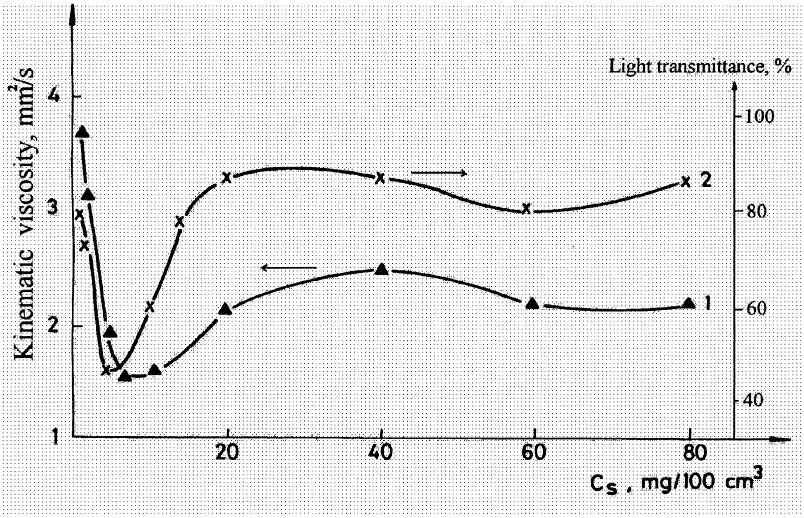

Fig. 3: Dependence of the viscosity and light transmittance of 0.04% cationic copolymer solution on the DDBS concentration in the system, see text (own data)

## Factors influencing the association ofsurfactants with nonionic polymers

***Temperature.*** An increase the temperature makes the association less favorable, as evidenced by an increase in $T_1$. This is similar to the behaviour of ionic surfactants that change in the same way.

***Salt.*** The addition of electrolytes generally depresses the $T_1$ values, i.e. promotes the formation of surfactant-polymer complexes. The slope of logSDS vs. log sodium ion concentration in the SDS/PVP system is the same as the dependence of the CMC on sodium ion concentration[27)] . Addition of salt also increases the binding ratio, i.e. extends the $T_1$ to $T_2$ range. For example, addition of 0.1 M NaCl increases the ratio to 0.9 mol SDS per mol of PVP repeated units from 0.3 observed in water. Similarly, the addition of 0.4 M NaBr increases the binding ratio of SDS per mol of PEO units to 0.85 from 0.25 in water (data from [1)]). Saito and Kitamura[28)] concluded that structure-breaking counterions (cations) tend to increase the association of surfactant anion to polymer, and structure-making cations do the reverse.

***Surfactant chain length.*** In homologous series, the initial binding concentration $T_1$ decreases with increasing chain length of the alkyl sulfate[1),5)]. A linear relation between $\log T_1$ and n-number of alkyl chain carbons exists like for the CMC. It has been found[29)] that the free energy change per $CH_2$ group on transferring the surfactant (SDS) from the non-associated state in water to the complex with PVP is about –1.1 kT that is comparable to the value for the analogous transfer of the surfactant to a micelle.

***Surfactant structure (nature).*** Typically the interaction between uncharged polymers is more favorable with anionic surfactants than with cationic surfactants. The interaction between a polymer and a cationic surfactant can be promoted when a strongly interacting counterion is present. For example, dodecyl ammonium chloride interacts weakly with PVAc compared to strong interaction of dodecyl ammonium thiocyanate to this polymer[30)]. Similar results were obtained with PVP, PEO and PVA using different methods. This demonstrates that the "right" headgroup of the cationic surfactant is a requirement for good association.

PEO, PVP and PVA are identified as uncharged polymers possessing the ability to form complexes with charged surfactants. The lack of activity in this respect of other polymers like hydroxyethylcelluloze (HEC) or dextran may be due to insufficient flexibility of the macromolecular chain[1)].

No interaction or weak interactions between non-ionic polymers and surfactants have been found. Small changes in cloud point of non-ionic surfactants or in solubilization of dyes in the presence of uncharged polymers are explained by weak hydrophobic interactions or by the joint effect of components on the activity of the solvent. The interaction between nonylphenol polyethylene glycol and PEO is explained by the affinity of the aromatic phenol to PEO[11)].

***Molecular mass of polymer.*** A minimum MM of polymer is required to ensure "complete" interaction with the surfactant. Several authors have determined this molecular mass for PEO and PVP to be about 4,000. Below MM approximately 1,500 the interactions with these polymers are restricted[1)].

***Amount of polymer.*** The value of $T_1$ is insensitive to polymer concentration while $T_2$ increases linearly with it, as it was demonstrated in most of studies devoted to interaction of surfactants with nonionic polymers (see as example[1),25)] ).

***Polymer hydrophobicity.*** The "activity" of nonionic polymers toward surfactants can be enhanced sometimes by introducing hydrophobic sites (example: methyl-ethyl celluloze vs. hydroxyethyl celluloze or polypropylene oxide vs. ethyleneoxide, etc.) The "activity" of polymers does seem to correlate with a kind of "HLB" index. For anionic surfactants the list of polymers of increasing reactivity is given by Breuer and Robb$^{1)}$ :

PVA < PEO < MeC < PVAc < PPO ~ PVP

and for cationic surfactants:

PVP < PEO < PVA < MeC < PVAc < PPO

The influence of macromolecular flexibility is demostrated also by the relatively strong interaction od SDS with amylose (which undergo a helix-coil transition) and weak interaction of SDS with amylopectin (which does not).

## Interaction models

The Smith and Muller's model$^{1),31)}$ explaining the results of binding SDS to PEO, is based on assumptions: (1) each polymer molecule consists of a number of "effective segments" of mass $M_s$ and total concentration P that act independently, where $M_s$ is the minimum molecular mass of the polymer for interaction; (2) each segment is able to bind a cluster of $n$ surfactant anions, $D^-$, in a single step, so the binding equilibrium is

$$P + nD^- = PDn^{n-}$$

with equilibrium constant $K = [PDn^{n-}]/[P][D^-]^n$

K is obtained from the half saturation condition

$$K = [D^-]_{1/2}^{-n}$$

Assuming trial values of $n$ and using experimental values of other parameters, the experimental isotherms can be calculated$^{1)}$. The best fit yields the parameters $M_s$, $n$ *and* $K$. Values of $n = 15$ and $M_s$ of 1,830 were obtained, which explains the experimental finding that PEO with M=1,500 is ineffective to bind SDS, and the NMR data that every "bound" surfactant molecule experienced the same environment$^{1)}$.

The free energy of binding is

$$\Delta G^o = - RT\ln K^{1/2}$$

The value obtained for this system is -5.07 kcal/mol, which is close to that of micelle formation for this surfactant. This is an evidence that the surfactant binding to polymer and micellization are related processes.

The model has been developed by Gilanyi and Wolfram32) who took into consideration both complex formation and micelle formation in the mass balance equation. The authors allowed in addition for a different degree of binding of the surfactant counterions by considering the degree of ionic dissociation of the bound-surfactant aggregate. The free energy of transfer of surfactant ($K^+D^-$) from solution to the bound state in complex, is

$$\Delta G^o = - RT\ln [D^-] + RT (1-\alpha) \ln [K^+] - (RT[\text{complex}])/([P_0]-[\text{complex}])$$

where $[P_0]$ is the total initial concentration of "active" polymer sites.

Shirahama33) has shown that the binding of SDS to PEO fits the Langmuir adsorption equation in form provided that the binding was accompanied by cluster formation of the surfactant molecules ($n \approx 20$ monomers). The equation has the form

$$\theta = KC^n / (1+C^n)$$

where $\theta$ is the degree of binding, $n$ is an empirical exponent, $C$ is the equilibrium concentration of bound species, and K is a constant (Hill constant).

Nagarjan34) has developed a theoretical model similar to that of Gilanyi, with assumptions: (1) the surfactants solution contains both free micelles and "micelles" bound to polymer molecule, (2) the total surfactant concentration $X_t$ is partionated into single dispersed surfactant $X_1$, surfactant in free micelles $X_f$ and surfactant bound to aggregates $X_b$. The mass balance equation is

$$X_t = X_1 + g_f (K_f K_1)^{g_f} + g_b\, n\, X_p [(K_b X_1)^{g_b} / ( 1 +[K_b X_1)^{g_b} ])$$

here the second and third terms represent $X_f$ and $X_b$, respectively, $g_f$ is the average aggregation number of the free micelles, $K_f$ is the equilibrium constant for their formation. Each polymer molecule has $n$ binding sites for surfactant aggregates of averege size $g_b$, $K_b$ is the intrinsic-equilibrium constant for the binding of the surfactant to the polymer, $X_p$ is the total concentration of macromolecules in solution. The calculated relations between $X_1$ and $X_t$ for different polymer concentrations are in good agreement with Gilanyi and Wofram32) experimental results for the PEO/SDS system.

## Driving forces

The driving force of self-association or micellization of surfactants in water is a reduction of the hydrocarbon/water contact area of the alkyl chains of dissolved surfactants. The process of micellization of ionic surfactants is a balance between several forces favoring and resisiting aggregation(1). The latter is due to the crowding together of the ionic headgroups in the periphery of the micelle. The high charge density in this zone favors the tight binding of counterions which diminishes the electrical potential and headgroup repulsion. A variety of explanations of the force underlying the binding of DDS micelles to PEO (the most commonly studied system) is given:

- a positive charge on PEO can arise from partial protonation of ether oxygens(4) ;
- hydrated part of the SDS molecule is bound to the polymer and there is an electrostatic interaction of the PEO with polar groups of SDS(24);
- „the comples comes from the interaction between ionic headgroup of the surfactant and ethylene oxide group of the PEO” (5);
- „the $-CH_2$ – groups of PEO tend to be bound within the aliphatic part of micelles”, i.e. there is a dominance of hydrophobic interactions(10)
- the binding of PEO to SDS is mediated in part by cation, PEO binds $Li^+ > Na^+ > NH_4$ ; a favorable interaction of cations with PEO results in a tendency for the polymer chain to reside in the micelles’ vicinity(35)

While adding a surfactant to a water-soluble polymer with alternating hydrophilic and hydrophobic segments with sufficient flexibility, one can imagine a configuration allowing ion-dipole association between the dipole of the hydrophilic group and ionic headgroup of the surfactant as well as contact between hydrophobic segments of the polymer and the “exposed” hydrocarbon areas of the micelle. This diminishes the extension of these exposed areas and results in screening the electrical charges. This is a structure in which aggregated surfactant is surrounded by macromolecule in a “loopy” configuration (Fig.4).

This picture well describes the properties of PEO/SDS and PVP/SDS systems, with experimentally determined approximately three monomer units of macromolecule per molecule of aggregated SDS. Consequences from this arrangement(1): (1) a more favorable energy of association as manifasted in lowered CMC (i.e. $T_1$ <CMC); (2) increased ionic dissociation of aggregates; (3) an altered environment of the $CH_2$ groups of the surfactant

near the headgroup (as demonstrated by NMR data)

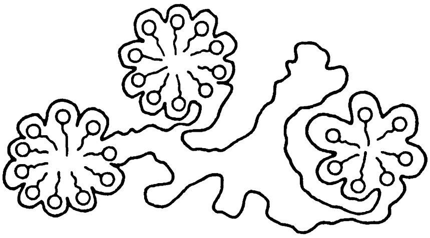

Fig.4: Schemetic diagram of polymer-surfactant complex1) given by Nagarjan (1982)

Since the balance of forces leading to surfactant aggregation is changed in the presence of the polymer, so the aggregation number also changes. From this picture also follows that certain polar groups in polymer are more favorable for interaction than others, that backbone flexibility is a favorable factor, that there is a minimum molecular mass required for reacting with the surfactant cluster, and that a high-molecular mass polymer can loop around several surfactant clusters forming a necklace structure. The higher hydrophobicity lowers the molecular-mass limit for interaction1).

The increase of "activity" with polymer hydrophobicity in Breuer and Robb series is due to the reduction of the polymer hydrophobic segment/water interfacial area by contacting such areas with exposed hydrophobic areas of developing surfactant aggregates. In harmony with this picture, polymers with a very low level of hydrophobicity, e.g. dextran or HEC, would have little interaction tendency with surfactants as has indeed been observed (see more in1)).

## Polyelectrolyte-oppositely charged surfactant systems

There is a strong association between surfactant and polymer ions mainly due to the mutual action of electrostatic and hydrophobic forces between surfactant ions and the polyion and between bond surfactant ions.

Many similarities exist between binding of surfactants to polyions and micelle formation in polymer-free solutions: self-aggregation of surfactants into micelles at well-defined critical micellization concentration (*cmc)*, likewise, in the presence of polymer micelle-like aggregates start to form along the polymer chain at a *critical aggregation concentration (cac)*

*Cac* is always lower than the *cmc* of the corresponding surfactant, especially for polyelectrolytes (PE) with flexible backbone and high linear charge densities. *Cac* depends on the surfactant chain length, on the ionic strength of the solution as well as on the hydrophobicity and flexibility of the polymer.

**Main methods employed** for studying the polyelectrolyte-surfactant interactions are: surface tension measurements, solubility of PE-surfactant complexes, fluorescence emission spectroscopy, viscosity and density measurements, determination of transport numbers of polyions, electrophoresis, light scattering, dialysis, rheology, etc. Some of these methods are described above.

## Laws and mechanisms

Main factors governing the binding process of the surfactant and polymer ions are: (1) the polymer charge density parameter determined by the average linear charge separation on the PE backbone, (2) the hydrophobic character of the PE chain. Below the short description of major factors influencing the interaction is given.

***Nature of the polyelectrolyte.*** Usually the binding affinity varies considerably with nature of polyanion/polycation1),36),37). For example, the binding constants of dodecyl trimethyl ammonium ion ($DTA^+$) decreases by 2 orders of magnitude ( from 200 to 1.8) in raw:

> Polystyrenesulfonate(PSS) > sodium dextran sulfate (DexS) > polyacrylic acid (PAA) > alginate > pectate > sodium carboxymethyl celluloze (NaCMC)

PSS is the most hydrophobic and also relatively flexible polyelectrolyte36). Very strong interaction of alkyl-trimethyl-ammonium bromides with highly charged NaPSS is shown by Kogej and Skerjanc38),39). The reason for that is the fact that a flexible polymer can better wrap around the surfactant molecule.

***Charge density of polyelectrolyte.*** As illustration (Fig. 5) the dependence of the amount of binding $\beta$ in the plateau region of binding on the degree of ionization in cetylpyridinium cation/polyacrylic acid system is shown[40)]. It is seen that the amount of binding increases with the degree of ionization of polyacrylic acid, indicating the important role of charge density parameter.

For weak polyelectrolytes like hyaluronate, pectate, alginate, poly(methacrylate) higher *cac* values were measured and the difference between *cac* and *cmc* is much smaller.

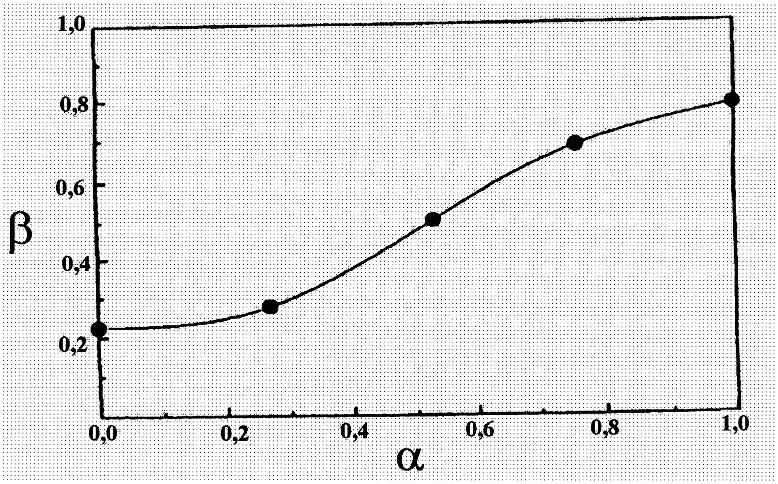

Fig.5: Dependence of the amount of binding in the plateau region of binding in CPyBr/PAA system on the degree of ionization of polyacrylic acid[40)]

It has been shown[41)] that complex formation between weak sodium polyacrylate and cationic mixed micelles of hexadecyltrimethyl - ammonium chloride/dodecylhexaoxyethylene glycol monoether is driven by electrostatic forces and it is controlled by three variables: the polymer linear charge density (ξ), the micelle surface charge density (σ) and the ionic strength or Debye-Huckel parameter (κ). The critical mole fraction of CATC corresponding the polymer-micelle formation, $Y_c$, varies inversely with pH, in the range of $0.80<\alpha<1.0$. At these pH $\sigma_c \times \xi \times \kappa^{-1}$ = const , suggesting the PE-surfactant interaction is controlled by electrostatic forces. The interaction at low pH (<4.0, $\alpha$=0.1) is dominated by H-bonding. An additional factor in PAA-CTAC/$C_{12}E_8$ complexation is the role of the PAA counterion.

***Effect of salt.*** Addition of salts increases the steepness of isotherms, i.e. the "cooperativity" of binding but decreases the affinity of binding due to shielding the electrical charges both of polyelectrolyte and surfactant (Fig. 6);

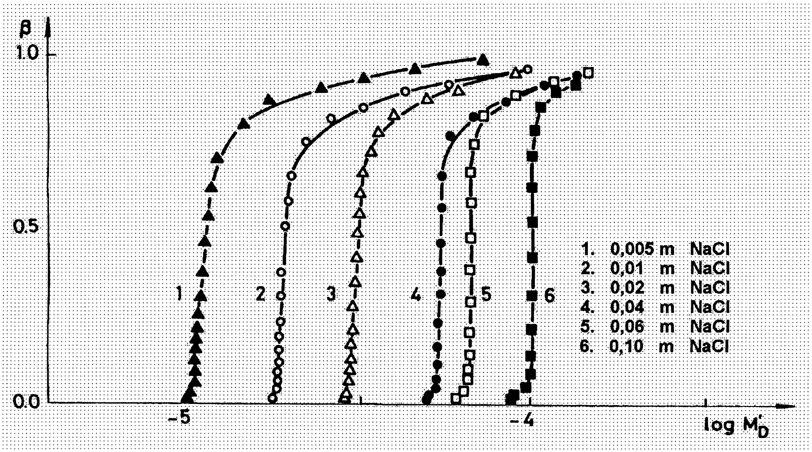

Fig. 6: Binding isotherms for sodium dextran sulfate (5x10$^{-4}$ M)-dodecylpyridinium chloride-NaCl systems[43)]

An increase in the valency of the counterions (cations) causes an increase in the concentration for binding of DTAB to NaPSS or NaDexS[42)] and other systems[1)]

***Effect of the surfactant chain length.*** Typically an increase in the surfactants chain length favors the interaction between the polyelectrolyte and surfactant. As illustration on Fig.7 the dependence of the degree of binding of alkylpyridinium bromides to NaPSS on the number of C atoms in the hydrocarbon chain of surfactant[42)] is presented.

The experimental data on polyelectrolytes-charged surfactant interactions can be summarized as follows[38)-40),43)]:

(1) log *cac* exhibits the same dependence as does the log *cmc*; between $C_{12}$ and $C_{16}$ it decreases linearly with increasing the hydrophobicity of the surfactant; (2) the shorter the chain, the weaker the interaction between surfactant ions and PE which gives rise to larger *cac*; (3) *cac* is considerably lower than *cmc*, about 1800 times for $C_{12}$ in water and only 10 times for $C_{18}$ in 0.01 M NaBr; (4) the *cmc/cac* ratio is a measure of the strength of interaction between surfactant and PE. The polyelectrolyte-induced micelle is much more stable than the free micelle of surfactant.

The free energy of binding increases with the chain length of surfactant as it is shown for the binding of alkylpyridinium bromides ($C_{11}$, $C_{12}$, $C_{13}$ and $C_{14}$) to SdexS (1.29 kT per $CH_2$), PAA (1.19 kT per $CH_2$), etc.[1), 44)]

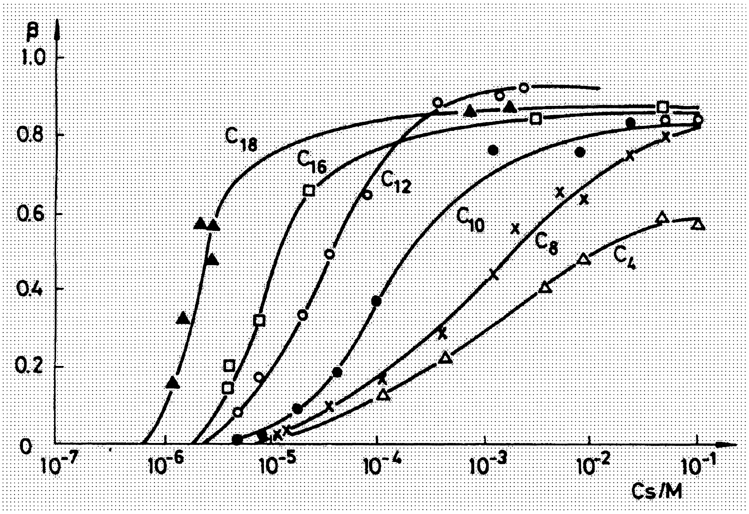

Fig.7. Dependence of the degree of binding of AlkPyBr to NaPSS on the surfactant concentration at different chain length of the surfactant[43)]

***The surfactant headgroup nature*** also affects the binding; for example, alkylpyridinum surfactants are bound more strongly because of the extra hydropobicity of the pyridinium group. Also the steric hidrance effect of the big trimethylammonium ($TMA^+$ ) group may play a role: at equivalent chain length the alkylpyridinium surfactants are bound to polyacrylate more strongly compared to alkyltrimethylammonium bromides[45)].

## Surfactant binding studies

Direct binding studies of surfactants by a variety of polyelectrolytes have been carried out using dialysis, ion-selective electrodes, analytical determinations or electrical conductance measurements. Excellent illustration of typical binding isotherms are isotherms for sodium dextran sulfate- dodecylpyridinium chloride-NaCl system[44)], Fig. 6.

The main conclusions from binding studies of this systrem as well as of cationic cellulose/SDS[46)] and other systems[1)] are :

- binding occurs at very low concentration of SDS, at 1/20th of the CMC, the degree of binding β reached the value of 0.8 (β=1 corresponds to 1 bound SDS ion for each ammonium group of the polymer);

- salt adding increases the steepness of isotherms but decreases the affinity of binding,
- precipitation was encountered at $\beta=1$;
- the degree of binding increases in the precipitation zone, and in the resolubilization zone rises to value of ~ 3 which is in the vicinity of the regular CMC of the surfactant;
- binding in the initial part of the isotherm follows the Langmuir equation.

## Electrophoresis of polyelectrolyte-surfactant systems

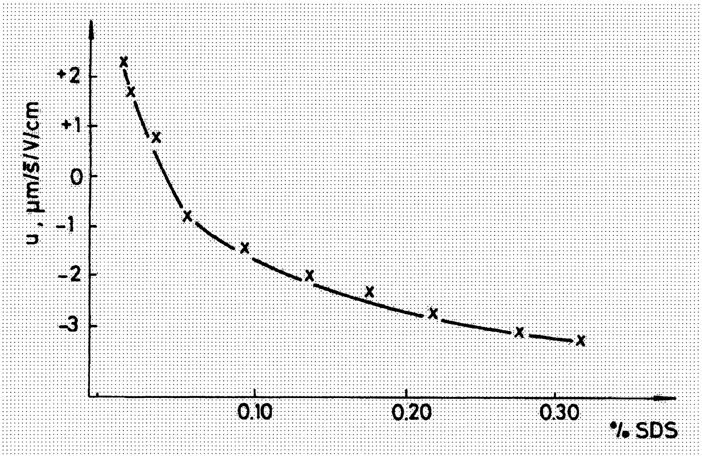

Fig.8: Electrophoretic mobility of complexes formed by alkylacrylate ammonium chloride-acrylamide copolymer (0.2%) with sodium dodecylsulfate vs. SDS percent in the system (own data)

Formation of complexes between polyelectrolytes and oppositely charged surfactants is also proved in our electrophoretic experiments on precipitates separated from cationic PE solutions containing different amount of sodium dodecylsulfate (Fig. 8). Below the stoichiometric SDS concentration the particles have a positive charge, and above it a negative charge due to overcompensation of the PE charge as a result of surfactant excess adsorption. Near the stoichiometric ratio, the particles have zero or a little charge;see also[1)]

## Binding models

As stated above, the binding is characterized by two main processes: (1) electrostatic interaction of oppositely charged ions of surfactant and fixed ions on the polyelectrolye;

i.e. electrostatic salt formation (*initiation process)* and (2*)* hydrophobic interaction between adjacently bound surfactant molecules, which stabilizes the aggregate *(cooperative process).*

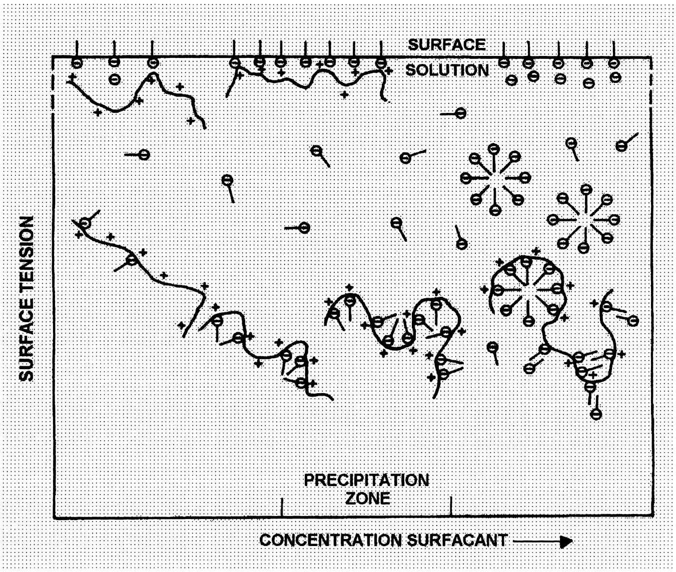

Fig.9: Conditions in bulk and solution surface containing a polycation and anionic surfactant. Simple counter-ions are depicted only in surface zone 1)

Fig. 9 gives a schematic picture of interaction between a charged surfactant and oppositely charged polyelectrolyte taken from the Goddard paper 1)

The model of cooperative adsorption of surfactant molecules onto polymer including the nearest neighbor interaction is developed by Shirahama et al[46)]:

$$K= [u(C_{1/2})]^{-1}$$

K is the constant for binding to an isolated site on the polymer, u is a cooperativity parameter characterizing the interaction between adjacently bound surfactants calculated from the slope of the binding isotherms at the half-bound point, i.e. at $\beta=0.5$ (degree of binding = molar ratio of bound surfactant to total ionic group in PE gel or solution)

$$(d\beta/d \ln C)_{0.5} = \sqrt{u}/4$$

The model applies to the region of isotherm ($\beta<0.5$) where the binding does not alter the Stern ($\psi$)-potential of the polyelectrolyte.

It has been shown for decylpyridinium bromide-PVS system that the cooperativity parameter u is unchanged as the salt is added, and K drops as the salt concentration increased, because of shielding the ions1),46)

From the u and $\beta$ values, the averege cluster size of bound surfactant *m*, can be estimated1)

$$m= 2\beta(u-1)/[\{4\beta(1-\beta)\,(u-1)+1\}^{1/2} - 1]$$

For example, the average cluster size of bound decyl sulphate ions to poly-L-Lysine is ranging from 34 to 101 while the binding ratio increased from 0.1 to 0.5 for $u=10^4$ .

## Binding of surfactant to polyelectrolyte network

This process somewhat differs from that characteristic for linear polymers. The main features of binding the surfactant to crosslinked PE are48)-50): the presence of cross-linkage enhances the initiation process of binding; the initiation of binding to a network occurs at surfactant concentration an order of magnitude lower than that for linear PE48) .

From data presented on Fig. 10 and in48)-50) follows that: (1) the cross-linkage of PE favors the surfactant binding: the larger the cross-linking density, the larger the stability constant; (2) the K for linear polymer strongly deviates from the curve for gels, i.e. the process of binding of the network distincts from that for linear-PAMPS; (3) enthalpy and entropy of the binding calculated from the T-dependene of K are positive, they indicate the contribution of hydrophobic interactions. There are different reasons for such a behaviour:

- the binding constant $K_0$ increases slightly with an increase in degree of cross-linkage (DCL), and the $K_0$ for linear PE is 2 orders of magnitude smaller than that for gel. These results can be explained by increased charge density of the network: the sulfonate charge density in the gel with DCL 4.5% is $98 \times 10^{-3}$ M, for polymer solution only $3 \times 10^{-3}$ M;
- the initiation process of the binding is dominated by long-range electrostatic forces; there exists deep electrostatic potential wells at cross-linking points with electrostatic

field up to $10^8$ V/m. The high potential results in an increased local concentration of the surfactant in the network domain.

An increase in cross-linkage decreases the $C_{min}$ at which the binding starts and increases the maximum β value, approaching 1.0[49)]

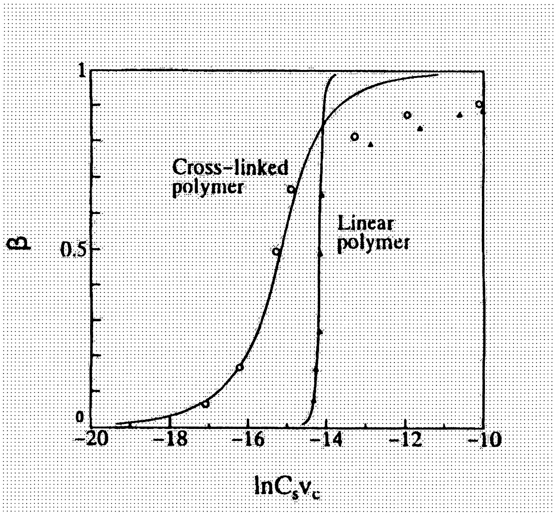

Fig. 10: Binding isotherms of dodecylpyryridinium chloride with linear and cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid). Open circles: cross-linked polymer, triangulars: linear polymer. Experimental data of Gong and Osada[47)]

This study has been performed with support of the Hungarian Fund for Fundamental Researches (OTKA), Grant T 029033; this support is acknowledged.

## References

1. E.D. Goddard, *Colloids a. Surfaces*, **19,** 255 (1986)
2 . M. Jones, *J.Colloid Interf. Sci*, **23**, 36 (1967)
3. H. Lange, *Koll.Z.-Z.Polymere,* **243,** 101 (1971)
4. M. Schwuger, *J. Colloid Interf. Sci*, **43,** 49 (1973)
5. Y. Moroi, H. Akisada, M. Saito, R. Matuura, *J. Colloid Interf. Sci.* **61**, 233 (1977)
6. N. W. Fadnavis, J.B. Engelberts, *J. Am. Chem.Soc.*, **106**, 2636 (1984)
7. I. Garcia-Mateos, et.al. *J. Colloid Interf. Sci.,* **194,** 356 (1997)
8. S. Saito, *Kolloid Z.*, **154**, 19 (1957)
9. Th.F. Tadros, *J. Colloid Interf. Sci.*, **46**, 528 (1974)
10. J. Francois, J. Dayantis, J. Sabbadin, ***Eur. Polym. J.*** **21,** 165 (1985)
11. M.Yu. Pletnev, A.A. Trapeznikov, *Kolloidn. Zhurn.* **40**, 948 (1978)

12. C. Ma, *Colloids Surfaces*, **16**, 185 (1985)
13. M.L.Fishman, F.R. Eirich, *J. Phys. Chem.*,**75**, 3135 (1971)
14. G.C. Kresheck, I.Constantinidis, *Anal. Chem,* **56,** 152 (1984)
15. A.Ya. Tretyakova, A.V. Bilalov, V.P. Barabanov, *Polymer Science*, **34**, 425 (1992)
16. T. Gilanyi, E. Wolfram, *Colloids Surfaces,* **3,** 181 (1981)
17. S.Saito, *Kolloid Z.,* **158**, 120 (1958)
18. N.J. Turro, B.H. Baretz, P.L. Kuo, *Macromolecules,* **17**, 1321 (1984)
19. R. Zana, P. Lianos, J. Lang, *J. Phys. Chem.*, **89**, 41 (1985)
20. K. Kogej, J.Skerjanc, *Langmuir*, **15**, 4251 (1999)
21. D.M. Bloor, E. Wyn-Jones, *J. Chem.Soc. Faraday Trans.* **2, 78**, 657 (1982)
22. N. Muller, T.W. Johnson, *J. Phys. Chem.*, **73**, 2042 (1969)
23. B. Cabane, *J. Phys.Chem.*, **81**, 1639 (1977)
24. B.Cabane, R. Duplessix, *Colloids Surfaces*, **13,** 19 (1985)
25. K. Shirahama, M. Tohdo, M. Murahashi, *J. Colloid Interface Sci.*, **86**, 283 (1982)
26. T. Gilanyi, I.Varga, *Magyar Kemiai Folyoirat (Hung. Chem. J.),* **105**, 90 (1999)
27. M.Murata, H. Arai, *J. Colloid Interface Sci.*, **44**, 475 (1973)
28. S. Saito, K. Kitamura, *J. Colloid Intreface Sci.*, **35**, 346 (1971)
29. H. Arai, M. Murata, K. Shinoda, *J. Colloid Interface Sci.*, **37**, 223 (1971)
30. S. Saito, M. Yukawa, *J. Colloid Interface Sci.*, **30**, 211 (1969)
31. M.L. Smith, N. Muller, *J. Colloid Interface Sci.*, **52**, 450 (1975)
32. T. Gilanyi, E. Wofram, *Colloids Surfaces,* **3,**181 (1981)
33. K. Shirahama, *Colloid Polymer Sci.*, **252,** 978 (1974)
34. R. Nagarjan, *Colloids Surfaces,* **13**, 1 (1985)
35. P.L Dubin, J. Gruber, J. Xia, H. Zhang, *J. Colloid Interf. Sci.,* **148,** 35 (1992)
36. K. Hayakawa, A. L. Ayub, J.T.C. Kwak, *Colloids Surfaces,* **4,** 389 (1982)
37. K. Hayakawa, J.P. Santerre, J.C.T. Kwak, *Macromolecules,* **16,** 1642 (1983)
38. K. Kogej, J. Skerjanc, *J.Phys.Chem.*, **93,** 7913 (1989)
39. K. Kogej, J. Skerjanc, *Acta Chim. Slov.* **46 (4),** 481 (1999)
40. K. Kogej, J. Skerjanc, *Acta Chim. Slov.* **46 (2),** 269 (1999)
41. K. Yoshida, P. Dubin, *Colloids Surfaces,* **147**, 161 (1999)
42. K. Hayakawa, J.C.T. Kwak, *J. Phys. Chem.*, **86,** 3866 (1982)
43. K. Kogej, J. Skerjanc, J. Cerar, *Langmuir*, **15,** 5023 (1999)
44. A. Malovikova, K. Hayakawa, J.C.T. Kwak, *J. Phys. Chem.,* **88,** 1930 (1984)
45. A. Malovikova, K. Hayakawa, J.C. T. Kwak, *ACS Symp. Ser.*, **253**, 225 (1984)
46. K.Ohbu, O. Hiraishi, I. Kashiva, *J. Am. Oil. Chem. Soc.* **54,** 108 (1982)
47. K. Shirahama, M. Tashiro, *Bull. Chem. Soc. Japan,* **57,** 377 (1984)
48. J.P. Gong, Y. Osada, *J. Phys.Chem.*, **99,** 10971 (1995)
49. H.Okuzaki, Y. Osada, *Macromolecules,* **28,** 4554 (1995)
50. N. Isogai, T. Narita, L.Chen, M. Hirata, J.P. Gong, Y. Osada, *Colloids Surfaces,* **147,** 189 (1999)