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Surface activity of water soluble amphiphilic chitin derivatives

J. Desbrières[1], **M. Rinaudo**[1], **V. Babak**[2], **G. Vikhoreva**[2]

[1] Centre de Recherches sur les Macromolécules Végétales, affiliated with the
Joseph Fourier University, CNRS-CERMAV, BP53, F-38041 Grenoble, Cedex, France
[2] INEOS RAS, 28 Vavilova Str., Moscow 117813, Russia

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Summary

Chitin was derivatized to extend its applications in the field of water soluble systems. It was first carboxymethylated and then alkylated. Two technics were used for that purpose : ionic surfactants playing the role of counterions form an electrostatic complex, and covalent derivatization. The difference between covalent alkylation and dynamic association (SPEC) is discussed in relation with the length of the alkyl chain and the density of alkylation.

Introduction

Chitin is a natural polysaccharide extracted from crustaceous shells. It can be considered as a poly(N-acetyl-glucosamine) partially deacetylated. The free -NH_2 can be chemically substituted to extend the applications of this natural polymer. The -OH groups can also be modified by carboxymethylation to produce a water soluble derivative in neutral and alkaline conditions (1).

Carboxymethylchitin (CMCh) was modified to obtain amphiphilic system in which the hydrophobic moiety counterbalances the electrostatic repulsions but also leads to tensioactive properties. In that respect, these derivatives will be available to stabilize emulsion or foam. Our objective is to compare the covalent alkylcarboxymethylchitin with the dynamic association of carboxymethylchitin with alkyl quaternary ammonium as counterions (usually called SPEC).

Experimental

Materials

CMCh-sodium salt was synthetised using the improved method (2) consisting in the treatment of crab chitin with NaOH followed by the reaction with monochloracetic acid in water-isopropanol media. The purification and fractionation of CMCh water solution were carried out by ultrafiltration through a selective membrane followed by the freeze-drying of CMCh solution.

The substitution degrees (DS) on carboxyl and N-acetyl groups were estimated by IR-spectrometry of acidic (pH ~ 0.7) CMCh solution in D_2O (3). Contents in carboxyl and N-acetyl groups were calculated from the integral intensity of the absorption bands ν (C = O) and ν (amide I) at 1728 cm^{-1} and 1640 cm^{-1}, respectively, assuming molar coefficients of integral intensity as being equal to 50000 l. mol^{-1} cm^{-2}

and 43000 l. mol^{-1} cm^{-2} respectively. DS of CMCh in -COOH and -$NHCOCH_3$ groups were 1.1 and 0.85 respectively. Identical results were received by using ^{13}C n.m.r. method (4). By this method it has been shown that 90% of carboxymethyl substituents are located at C-6 atoms of monomeric units. Molecular weight of the investigated fraction of CMCh has been determined by the diffusion-sedimentation method : M_w = 140 000 g mol^{-1}.

The carboxymethylated polymer was then N-alkylated with C_{12} or C_{14} aldehyde through a reductive amination (5). The degree of akylation was $\tau = 0.01$ with C_{12} chain and $\tau = 0.03$ with C_{14} chain. It was determined by ^1H n.m.r. as previously discussed (5).

The anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant tetradecyltrimethylammonium bromide (TDAB) were from Fluka, and were used without further purification.

Method

Surface tension σ was measured using the Wilhelmy plate method with K-10 tensiometer (from Krüss, Germany) with the accuracy of $\pm$ 0.3 mJ . m^{-2}. The solutions were prepared using bidistilled water followed by exposure for one day. The surface tension measurements were carried out at 25°C.

The surfactants are progressively added to stoechiometric ratio based on carboxylic groups and expressed as Z. It must be pointed out that all the isotherms of surface tension $\sigma(C_p)$ or $\sigma(C_s)$ (where C_p and C_s are concentrations of polymer and surfactant expressed in monomol/l and mol/l, respectively) were measured at constant value of Z. For this purpose, the mixed solutions with decreasing concentration C_p (or C_s) were obtained from the stock solution by the progressive dilution with water.

The pH was around 6 and the glucosamine units are admitted not to be protonated; then the carboxymethylchitin is a purely anionic polymer.

Results and discussion

The surface tension of aqueous solution of carboxymethylchitin in presence or absence of ionic surfactants was determined.

Carboxymethylchitin has no tensioactive properties but the alkyl carboxymethyl chitin presents some activity when the polymer concentration C_p is larger than 10^{-4} monomol/l. The larger effect is observed when the alkyl chain is longer (Figure 1).

In the presence of SDS, an anionic surfactant, this effect disappears as evidence of hydrophobic interaction between SDS and the alkyl chain of chitin derivative. No effect is observed with the carboxymethylchitin. The interacting SDS-chitin derivative gets a larger charge density and an increased solubility (Figure 1).

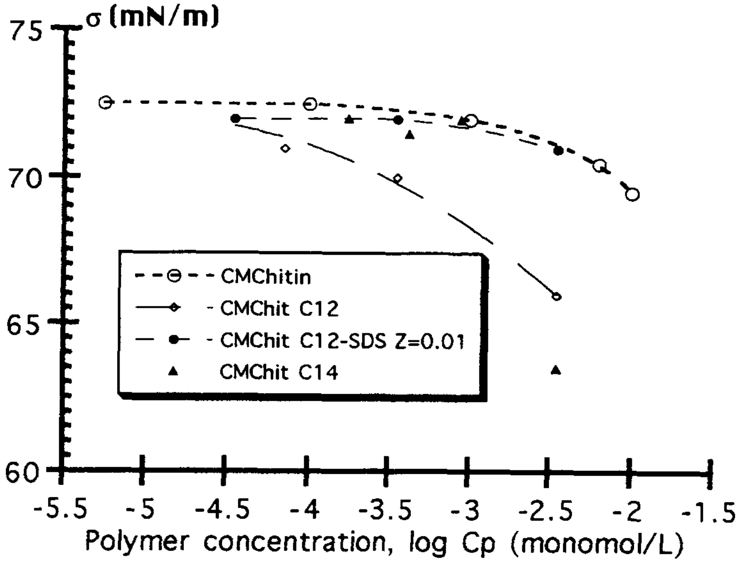


Figure 1 : Role of the hydrophobicity on tensioactive properties of chitin derivatives

The addition of a cationic surfactant (TDAB) able to interact with the highly charged anionic polymer (charge parameter λ ≃ 1.5), causes a significant effect. With carboxymethylchitin ion pairs are formed in presence of TDAB and tensioactive properties occurs as previously discussed (6,7) (Figure 2).

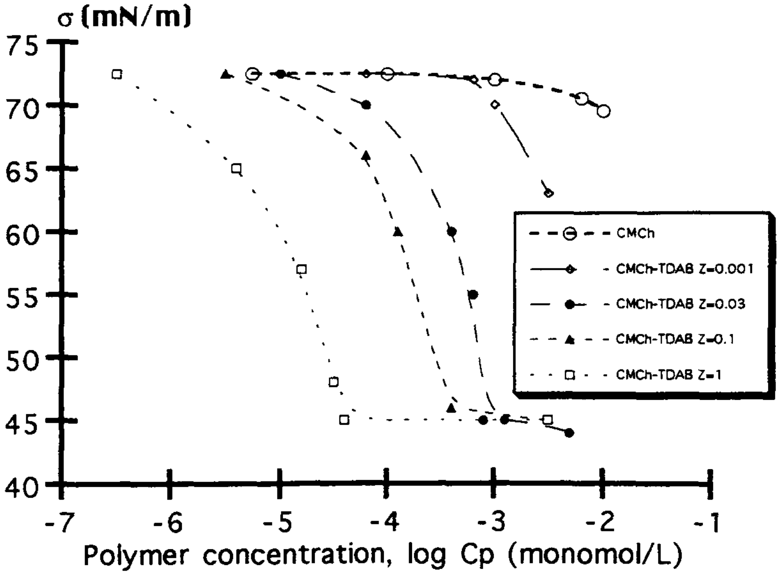


Figure 2 : Role of the cationic surfactant content (represented by Z) on the tensioactive properties of carboxymethylchitin

The effect is directly related to the stoechiometric ratio Z : the higher Z gives the lower surface tension at a given monomole concentration; in addition, it goes to a characteristic limit over a critical monomole concentration (Cp*) depending directly on Z ; one demonstrates that Cp*Z $\simeq$ const = 4 x 10^{-5} (mol/l). This quantity corresponds to a critical aggregation concentration (CAC) much lower than the CMC of TDAB (CMC ~ 8 x 10^{-3} mol/l) determined from figure 4. Rheological experiments were performed with cationic hydroxyethylcellulose (cat-HEC) and ionic surfactants (SDS) by H. Hoffmann and al. (8). It was concluded that strong interactions were due to a mixed micelle formation including polyelectrolyte and surfactant molecules.

The free energy of adsorption $\Delta_{ad}G^{o}{}_{298}$ of electrostatically stabilized dynamic complexes between surfactants and polyelectrolytes (surfactant-polyelectrolyte complexes , SPEC) may be formally evaluated according to the relationship

$$\Delta_{ad}G^{o}{}_{298} \cong RT.\ln(C_p/\Delta\sigma) \qquad (1)$$

where $\Delta\sigma$ is the difference between the surface tension of pure water σ_0 and that of the solution σ taken in the decreasing region of the $\sigma(C_p)$-curve where the differential dσ / dlg Cp is approximately constant (6). It may be shown that the following relationship between the standard adsorption free energy $\Delta_{ad}G^{o}{}_{298}$ and Z is satisfied

$$\Delta_{ad}G^{o}{}_{298} \cong -34.0 - \mathrm{RT.ln\,Z} \qquad (2)$$

where $\Delta_{ad}G^{o}{}_{298}$ is related to one monomole of polymer and expressed in kJ/monomol and Z is varied in the range of 0.001 - 1.

The value of $\Delta_{ad}G^{o}{}_{298}$ characterizing the ability of the SPEC to adsorb at the air-water interface and consequently to decrease the surface tension, the possibility appears of engineering "new" macromolecules with finely controlled adsorption activity via formation of SPEC between oppositely charged surfactants and polyelectrolytes. In our case the very low adsorption ability of CMCh in aqueous solution may be highly improved and finely "corrected" by binding this macromolecule with the exact number of TDAB molecules calculated according to Eqn.(2).

In the presence of alkylated carboxymethylchitin, no synergistic effect is observed in the low range of surfactant concentration (Z = 10^{-3}). When Z = 0.03, the surface tension decreases over a polymer concentration in the range of 10^{-4} monomol/l. Then, it goes to a limit. The limit of the surface tension is imposed by the polymer structure whose hydrophobicity increases from CMCh to CMCh12 and CMCh14 (Figure 3).

In figure 4, the role of the nature of the carboxymethylchitin derivatives and concentration of the surfactant TDAB is shown. On this figure the surface tension is plotted as a function of the surfactant concentration (Cs = Cp x Z). The behaviour of the surfactant is given as reference. The limits of surface tension are imposed by the polymer and characterized by a critical aggregation concentration (CAC). At the limit, the surface tension decreases when the length of the alkyl chain increases ; the CAC increases in the same way due to hydrophobic interactions between the alkylated polymers and the surfactant.

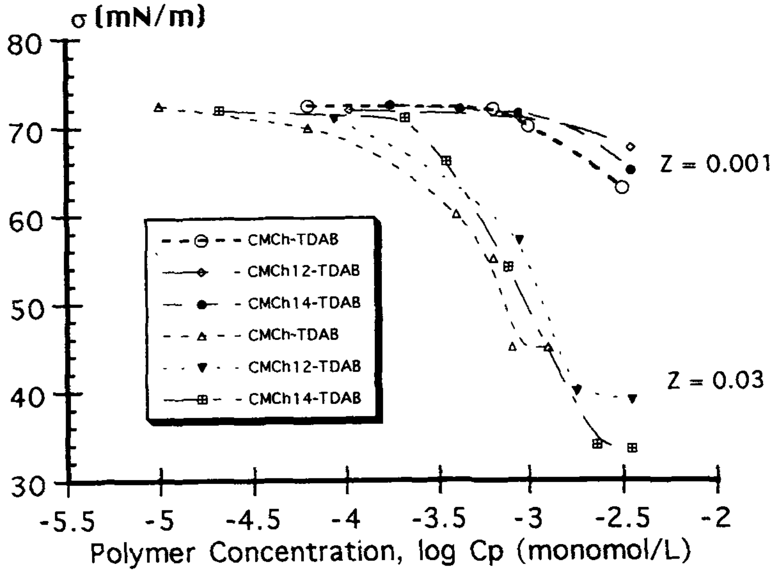


Figure 3 : Tensioactive properties of Surfactant Polyelectrolyte Complexes (SPEC) in presence of TDAB

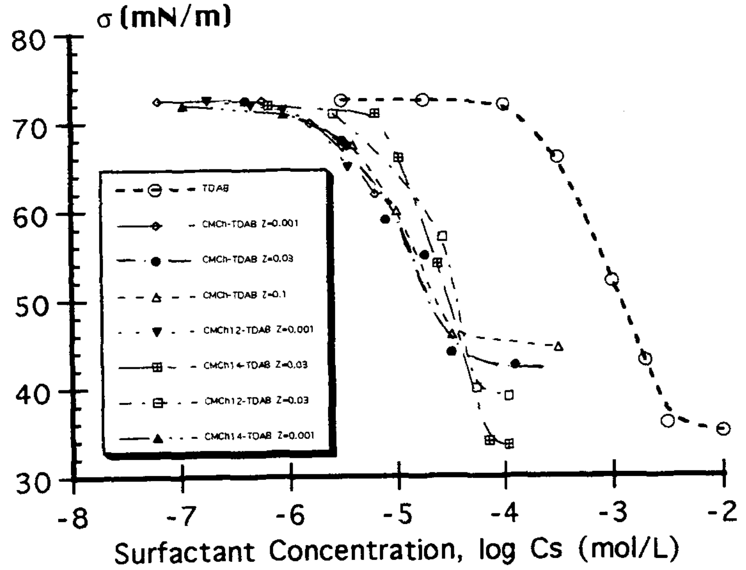


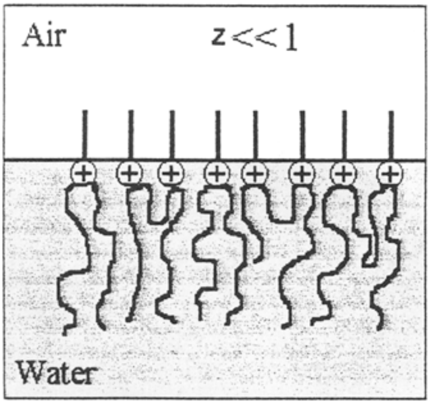
Figure 4 : Role of the nature of CMCh derivatives and TDAB surfactant concentration on tensioactive properties

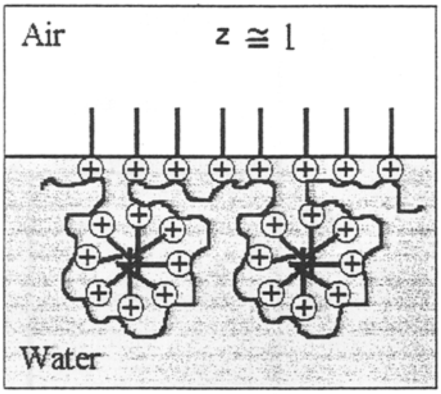
It is interesting to point out that all the isotherms σ(lg Cs) corresponding to the dynamic complexes between CMCh (alkylated and nonalkylated) and TDAB practically coincide and reveal to be displaced to the left over two orders of magnitude with regards to the concentration C_S. The adsorption amount Γ of TDAB in the presence of CMCh can be evaluated according to the Gibbs' adsorption equation {Γ=(1/nRT).(dσ/d ln C)}

$$\Gamma = \frac{1}{nRT}\frac{d\sigma}{d\ln C} \qquad (3)$$

(where n = 2 for ionic surfactants in the solution dissociating as AB → $A^+ + B^-$ and n=1 for SPECs) and is found to increase more than 100 times comparing to that of pure TDAB at the same bulk concentration (2.10^{-4}mol/l). However, Γ for SDS at the same concentration is identical to that of TDAB but, unlike TDAB, it does not depend on the presence of nonalkylated CMCh. Thus, it is obvious that SPECs are formed between CMCh and TDAB in their mixed solutions, and that such complexes do not form between nonalkylated CMCh and SDS.

The fact of the coincidence of the curves σ(lg Cs) whatever the value of Z allows to assume that the area A =1/Γ per one mole of surfactant molecule in the adsorption layer is practically independent on Z. This may be imagined if one assumes that the conformation of macromolecular backbone of SPEC at the interface differs with varying Z : at low Z one has the long « tails » and « loops » of macromolecules, whereas at high Z the macromolecule adopts a « flat » conformation at the interface.





Conclusion

The alkylated carboxymethylchitins present tensioactive properties which may be compared with the complex formed between the anionic polyelectrolyte and a cationic surfactant. Nevertheless,when comparing alkylCMChitin at a given τ (C14 τ=0.03) with a SPEC having the same degree of alkylation due to surfactant association (Z = 0.03), the SPEC looks more efficient in view of its surfactive properties.

The alkylation allows hydrophobic interaction with anionic surfactant decreasing the tensioactive properties.

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