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Effect of poly(vinyl alcohol-co-vinyl acetate) copolymer blockiness on the

dynamic interfacial tension and dilational viscoelasticity of polymer/anionic

surfactant complex at the water/1-chlorobutane interface

Leonard Ionut ATANASE[a*], Sophie BISTAC[a], Gérard RIESS[a]

[a] University of Haute Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse,

Laboratoire de Photochimie et d'Ingénierie Macromoléculaires, 3 rue Alfred Werner, 68093

Mulhouse Cedex, France

Correspondence to: Leonard Ionut Atanase (E-mail: leonard.atanase@yahoo.com)

Contact details of corresponding author:

*E-mail: leonard.atanase@yahoo.com

Telephone: +33 3 89 33 68 47

Contact details of contributing authors:

E-mail: sophie.bistac-brogly@uha.fr ; gerard.riess@uha.fr

Abstract

Poly(vinyl alcohol-co-vinyl acetate) (PVA) copolymers obtained by partial hydrolysis of

poly(vinyl acetate) (PVAc) are of practical importance for many applications, including

emulsion and suspension polymerization processes. Their molecular characteristics have a

major influence on the colloidal and interfacial properties. The most significant characteristics

are represented by the average degree of hydrolysis $\overline{DH}$, average degree of polymerization

$\overline{DPw}$ but also by the average acetate sequence length n_0^{VAc} which designates the so-called

blockiness. Colloidal aggregates were observed in the aqueous PVA solutions having a $\overline{DH}$

value of 73 mol%. The volume fraction of these aggregates at a given $\overline{DH}$ value is directly

correlated to the blockiness. Three PVA samples with identical $\overline{DH}$ and $\overline{DPw}$ but different

blockiness were examined. By pendant drop and oscillating pendant drop techniques it was

shown that the PVA sample having the lowest blockiness and thus the lowest volume fraction of colloidal aggregates has lower interfacial tension and elastic modulus E' values. On the contrary, the corresponding values are highest for PVA sample of higher blockiness. In the presence of sodium dodecyl sulfate (SDS), the colloidal aggregates are disaggregated by complex formation due to the hydrophobic-hydrophobic interactions. The PVA/SDS complex acts as a partial polyelectrolyte that induces the stretching of the chains and thus a reduction of the interface thickness. In this case, the interfacial tension and the elastic modulus both increase with increasing SDS concentration for all three PVA samples and the most significant effect was noticed for the most "blocky" copolymer sample.

Keywords: PVA; blockiness; colloidal aggregates; PVA/SDS complex; dynamic interfacial tension; dilational viscoelasticity; 1-chlorobutane/water emulsions.

Highlights:

➢ The blockiness of PVAs determines the volume fraction of colloidal aggregates

➢ A low proportion of aggregates leads to low interfacial tension γ_i and elastic modulus E' values

➢ Colloidal aggregates are disaggregated by complexation with sodium dodecyl sulfate (SDS)

➢ PVA/SDS complexes lead to a increase of the γ_i and E' values with increasing SDS concentrations

➢ The partial polyelectrolyte complex induces the stretching of the chains at the 1-chlorobutane/water interface

1. Introduction

Poly (vinyl alcohol-co-vinyl acetate) copolymers, obtained by partial hydrolysis of poly (vinyl acetate) (PVAc) and usually designated as PVAs, are of particular interest as they combine in their molecular structure the hydrophobic characteristics of PVAc with the water-solubility of poly (vinyl alcohol) (PVOH). The molecular composition and the architecture of PVAs (i.e. average degree of hydrolysis $\overline{DH}$, average acetate and alcohol sequence lengths, tacticity, structural irregularities, degree of polymerization $\overline{DPw}$ and the polydispersity index), have an important influence on the behaviour of these polymers in aqueous solutions as well as on the adsorption at the liquid-liquid interface.[1-3]

PVAs, with a $\overline{DH}$ in the range of 70-90 mol%, have been the most extensively studied in the literature due to their surfactive properties and have found important application possibilities as sizing agents and adhesives, as emulsifiers, dispersing agents in various industrial areas such as in emulsion and suspension polymerization processes where PVAs in the $\overline{DH}$ of 70 to 75 mol% are of major interest due to their pronounced amphiphilic characteristics. [4-6] A particular feature of these polymers is their strong tendency to form colloidal aggregates in water by inter- and intramolecular hydrophobic interactions of the vinyl acetate sequences.[7-10]

The proportion of these colloidal aggregates is influenced not only by the $\overline{DH}$ but also by the average acetate sequence length n_0^{VAc}, which is representative for the blockiness, and they may have an incidence on the PVAs emulsifying efficiency.[9,10]

It was demonstrated by different authors that the adsorption of these polymeric surfactants at the interface between two immiscible liquids reduces the interfacial tension and thus enhances the emulsion stability.[11-13] In the emulsion technology, it is further well established that the optimum conditions for the preparation of stable emulsion involves a conciliation of: (1) a strong anchoring of the polymeric surfactant at the oil/water interface, (2) optimized elastic properties of the interfacial surfactant film and (3) sufficient steric- or electrosteric repulsion

between the droplets in order to avoid their coalescence. Moreover, He et al.[11,12] as well as

Boscher et al.[13] have demonstrated that the $\overline{DH}$ has a more pronounced effect than the

molecular weight on the interfacial tension of the 1-chlorobutane (ClBu)/water system, which

is a classical model for vinyl chloride monomer (VCM)/water emulsions used for poly(vinyl

chloride) (PVC) synthesis. From these studies it turns out that PVAs, which are characterized

by a higher content of acetate groups and thus by a lower $\overline{DH}$, are more efficient in reducing

the interfacial tension. At this point it is worth noting the lack of literature data concerning the

influence of the PVAs' blockiness on the interfacial characteristics of oil/water systems.

Interfacial rheology is an important parameter in many industrial processes like spraying and

emulsification. Indeed, in such applications, the liquid droplets are not static but submitted to

a mechanical stress induced by mixing and stirring. Interfacial dilational viscoelasticity

experiments could therefore be more representative of the real application. This technique is

an interesting method to study the phenomena at the interface when a liquid drop is submitted

to a dynamic solicitation. However, the correlation between the interfacial viscoelastic

properties and the emulsion stability is complex and frequently differ from one system to

another.[14] In some cases, a high elastic modulus will correspond to a better stability of foams

or emulsions but in other cases the link between viscoelastic interfacial properties and

emulsion stability is more complex and strongly dependant on the nature of the surfactants

and of the solicitation time.[15] Despite its industrial interest and with the exception of the

pioneering work of Babak and Desbrieres[16], the interfacial rheology is still largely

unexplored, especially for polymers/surfactants solutions.

At present, it is furthermore well established that the solution and interfacial properties of

polymers can be modified by complex formation with anionic or cationic surfactants.[17,18] It

was shown that PVAs, with a $\overline{DH}$ in the range of 70-90 mol%, form a complex with anionic

surfactants, such as sodium dodecyl sulfate (SDS), by hydrophobic interactions.[10,19] Such a

complex leads not only to the disaggregation of aggregates present in the aqueous solutions, but also to a shift of cloud point to higher temperatures by increasing the hydrophilic characteristic of the polymers.[10] Moreover, this complex also enhances synergistically the ferrofluid oil/water emulsion stability as confirmed by Philips and coworkers[20,21] for a PVA with a $\overline{DH}$ of 88 mol%. These authors stated that the PVA/SDS complex acts as a partial polyelectrolyte and that the electrostatic repulsion leads to the chain stretching at the interface. Mention has also to be made for the studies of Ramirez et al.[22] concerning the minisuspension polymerization of styrene in the presence of PVA/SDS combinations as stabilizers. According to these authors, the colloidal stability is enhanced in the presence of the complex which induces electroesteric stabilization. From these facts, it appears that there is definite interplay between the PVA blockiness, the colloidal aggregates and the complex formation with SDS. However, to the best of our knowledge, no studies have been performed for oil/water emulsions stabilized by PVAs, of fixed DH and DP but different blockiness, concerning their interfacial tension and their dilatational viscoelasticity behavior in the presence of SDS.

In addition to static and dynamic interfacial tension determinations, dilational viscoelasticity would therefore be a very suitable technique to investigate the characteristics of the polymer layer at the oil/water interface.[14,23,24] According to Seta et al.[23] this feature is very sensitive to the interfacial structure, the competitive adsorption and the magnitude of interactions between different emulsifiers at the interface. The dilational viscoelasticity can be determined by different experimental techniques, but nowadays the oscillating drop technique seems to be especially effective.[24]

In this paper, our main objective was to elucidate how the interfacial tension and the dilational viscoelasticity of ClBu/water emulsions are affected by the blockiness of the PVA stabilizers. Within this context, a series of three PVAs, having identical molecular weights and $\overline{DH}$

values of 73 mol% but different blockiness, were investigated in the absence and in the presence of SDS, in order to have an insight n the structural organization of the adsorbed polymer layer at the oil/water interface.

2. Experimental

Materials

The PVAs examined in this study were supplied by Nippon Gohsei and Synthomer. Hereafter, these samples, used without further purification, are designated in the following by their average polymerization degree ($\overline{DPw}$) and the average sequence lengths of vinyl acetate n_0^{VAc}; as for instance, PVA-700-4.3. Their main characteristics, determined by ^{1}H NMR, ^{13}C NMR and SEC, are summarized in **Table 1**.

Table 1: Molecular characteristics of the PVA samples

PVAs	PVA-700-4.3	PVA-705-3.8	PVA-650-3.6
Commercial name	KP08	Alcotex 72.5	Alcotex B72
$\overline{DH}$ (mol%) *	72.5	73.0	73.2
$\overline{DPw}$	700	705	650
Đ (Mw/Mn)	2.1	2.5	2.4
n_0^{VAc} *	**4.3**	**3.8**	**3.6**
n_0^{VOH} *	10.2	9.5	9.4
[η] (cm³/g)**	29.3	31.9	32.1

* average values obtained from ^{1}H NMR and ^{13}C NMR

**intrinsic viscosity in H_2O at 25°C

The average hydrolysis degree, $\overline{DH}$ with a precision of ± 1 mole%, was determined using ^{1}H NMR (Bruker AC-400F operating at 400 MHz) in dimethylsulfoxide (DMSO)-d_6 at 70°C according to Van der Velden and Beulen.[25] These characteristics were confirmed by ^{13}C NMR spectra of polymer solubilized in a 50/50 (v/v) D_2O and deuterated acetone mixture. This technique gives in addition access to the average sequence lengths of vinyl acetate n_0^{VAc} and vinyl alcohol respectively n_0^{VOH} defined by Moritani and Fujiwara.[26]

The SEC measurements were carried out with a Shimadzu LC-20AD liquid chromatograph equipped with two Varian PL gel 5 µm MIXED-C columns (column, injection and refractometer temperature: 30°C; injection volume: 100µL; solvent: tetrahydrofuran at 1 mL min^{-1}) and a refractive index detector (Shimadzu RID-10A). PVA samples were previously reacetylated as recommended by Bugada and Rudin[27] and the "universal calibration technique" with polystyrene standards was applied for the calculation of $\overline{DPw}$ as well as for the molar mass dispersity Đ.

Sodium dodecyl sulfate (SDS) with a purity of 99% was purchased from Acros and it was used without any further purification at concentrations below its critical micellar concentration which is equal to 0.24 wt% or 8 mmol.[28]

1-Chlorobutane (>99%), supplied by Acros, was selected as organic phase model for vinyl chloride monomer (VCM). This model has been used quite extensively by different authors as its characteristics such as density, refractive index and solubility are close to those of VCM, with the advantages of easier handling and of lesser toxicity.[13]

Sample preparation

The PVA solutions were prepared by dissolving under agitation the required amounts of copolymer in triple distilled and filtered (0.22 µm Millipore filter) water at room temperature for 24h.

For the preparation of PVA/SDS solutions, the copolymer was added at a concentration of 1 wt% into aqueous surfactant solutions at the required SDS concentrations, agitated over night at room temperature and used immediately afterwards in order to avoid the hydrolysis of SDS. Before use, all solutions have been filtrated with 0.45 µm Chromafil Xtra MV-45/25 filter.

Dynamic light scattering (DLS)

DLS measurements, carried out with a Malvern Nano-ZS Zetasizer equipped with a 4mW He–Ne laser operating at a wavelength of 532 nm, were made at a scattering angle θ = 173°

and at a fixed temperature of 20 °C. Using the Stokes–Einstein equation, with the viscosity of the continuous phase, the software package of the instrument calculates the hydrodynamic diameter (volume average) D_V, the Z-average diameter, which is an intensity weighted average size, the volume fraction of different populations and the polydispersity index PDI of the sample. The "data quality report" incorporated in the software indicated "good quality" for all the obtained data. For each experiment, the average of 5 consecutive measurements is indicated in tables and figures.

Cloud point determination

The starting PVAs and their complexes with SDS were characterized by their cloud point determined from the DLS experiments. The onset of precipitation as a function of temperature was determined by monitoring the Z-average values of PVAs, at a concentration of 1 wt%, as the temperature was increased stepwise at a rate of 0.5°C min $^{-1}$. The cloud point is given by the temperature corresponding to the onset of the precipitation curve.

Interfacial tension

The dynamic interfacial tension between ClBu and aqueous PVA solutions was measured at 20°C using a pendent drop tensiometer (Krüss DSA 100) with constant drop volume of 10 mm^3. The evolution of the interfacial tension as a function of time was determined by analyzing the axial symmetric shape (Laplace profile) of a pendent aqueous drop containing the desired PVA or PVA/SDS concentration. This drop was formed at the tip of a needle inside a ClBu-filled glass cuvette by the computer-driven dosing system. All the measurements were made during 400 s, which represents a quasi equilibrium state, and the average accuracy was typically of ± 0.1 mN/m.

Interfacial dilational viscoelasticity

Interfacial dilational viscoelasticity of aqueous PVA or SDS solutions in ClBu was determined with a Krüss DSA100 (Germany) tensiometer equipped with an Oscillating Drop

Module (ODM). The measurement is based on monitoring the oscillating pendent drop shape with a CCD camera. The volume and thus the area of the droplet were varied by applying a voltage to the piezo-driven membrane after 400 s, a sufficiently long time to achieve a quasi equilibrium conditions at the interface. After this time, several experiments were carried out during 100 s by keeping a constant frequency of 0.1 Hz and by varying the concentration of PVA or SDS in the aqueous solution. According to the recommendations of Santini et al.[29], this frequency has been chosen in order to have an oscillation period much shorter than the time of the re-equilibration of the adsorbed layer. For all experiments, the period of sinusoidal variations of the drop area was 10 s. A video of the oscillating droplet was recorded and was analyzed with the software package supplied by the manufacturer allowing the calculation, from the relaxation measurements via Fourier analysis, of the elastic modulus (E') and viscous modulus (E"), with an accuracy of ±0.02 mN/m. The inverse process consisting in the formation of a ClBu droplet in a PVA or SDS aqueous solution was not possible due to the swelling of the piezo-driven polymer membrane in the presence of ClBu.

3. Results

3.1 Colloidal characteristics obtained by DLS for the PVA aqueous solutions

The PVA samples investigated in this study are characterized by identical $\overline{DH}$ and $\overline{DPw}$ but different average acetate sequence lengths, as shown in **Table 1**. It was therefore of interest to examine the influence of blockiness not only on the ClBu/water interfacial characteristics but also on the colloidal properties, in the absence and in the presence of SDS.

3.1.1 In the absence of SDS

At the present, the formation of aggregates in the aqueous solutions of PVA, with a $\overline{DH}$ in the range of 70 to 90 mol%, was well demonstrated by different authors.[7-10] These studies have reported that these species are colloidal aggregates formed by hydrophobic-hydrophobic interactions between the acetate sequences and that this aggregation is strongly influenced

mainly by the $\overline{DH}$. Aladjoff et al.[9] have estimated the proportion of aggregates by SEC as a function of the $\overline{DH}$ whereas the influence of the blockiness on the volume fraction of colloidal aggregates has not been previously investigated. **Table 2** summarizes the volume fractions and the hydrodynamic volume diameter (Dv) for all the PVA samples at a concentration of 1 wt% in water. **Figure S1** (**Supporting Information**) shows the bimodal size distribution of sample PVA-700-4.3.

Table 2: Colloidal characteristics obtained by DLS of the PVA samples at a concentration of 1 wt% and at 20°C

PVAs	Colloidal aggregates		« Free-chains »	
	Volume fraction (%)	Dv (nm)	Volume fraction (%)	Dv (nm)
PVA-700-4.3	22.9 ± 0.5	39.8 ± 0.5	77.1 ± 0.6	14.2 ± 0.4
PVA-705-3.8	20.7 ± 0.7	41.5 ± 0.5	79.3 ± 0.6	11.9 ± 0.6
PVA-650-3.6	18.0 ± 0.8	38.0 ± 0.9	82.0 ± 1.2	11.4 ± 0.5

From this table it appears that the volume fraction of colloidal aggregates is directly correlated to the blockiness of PVAs. The PVA-700-4.3, which is the most "blocky" copolymer, is characterized by the highest proportion of aggregates whereas for the PVA-650-3.6, having the lowest average acetate sequence length n_0^{VAc}, the proportion of these species is much smaller. This difference may be explained by the fact that these aggregates are formed by hydrophobic-hydrophobic interactions between the VAc rich sequences and an increase in the average acetate sequence length or blockiness induces stronger interactions. Concerning the size of these aggregates, it can be noticed that their Dv is not influenced by the n_0^{VAc} values but a correlation could be established between this size and the $\overline{DPw}$ values, as previously demonstrated by Atanase and Riess.[10]

3.1.2 In the presence of SDS

Different authors have already demonstrated that PVAs form a complex in the presence of anionic surfactants such as SDS.[10,19] In correlation with the results of Aladjoff et al.[19], obtained by SEC, it could be demonstrated for the first time by DLS that this complexation leads to the disaggregation of the colloidal aggregates formed in aqueous medium. In addition of low SDS concentration, such as 0.01 wt%, the peak attributed to aggregates has partially disappeared and a monomodal distribution was observed. Therefore, at this point it is impossible to determine precisely the proportion of remaining colloidal aggregates and only a mean size value is accessible. For such multicomponent systems, it is recommended to use the Z-average particle size which is more representative than Dv to characterize the larger size particles such as the colloidal aggregates.[30] **Table 3** shows the variation of the Z-average values for all the PVA samples, at a concentration of 1 wt%, as a function of the SDS concentrations.

Table 3: Variation of the Z-average values for a PVA concentration of 1 wt% as a function of the SDS concentrations at 20°C

PVAs	Z-average (nm)			
	0 wt% SDS	0.01 wt% SDS	0.05 wt%SDS	0.1 wt% SDS
PVA-700-4.3	37.5 ± 0.2	22.5 ± 0.3	12.3 ± 0.2	10.7 ± 0.3
PVA-705-3.8	41.8 ± 0.4	34.3 ± 0.2	24.1 ± 0.3	22.8 ± 0.2
PVA-650-3.6	39.6 ± 0.4	32.3 ± 0.4	23.3 ± 0.4	22.0 ± 0.3

From this table it turns out that the Z-average value decreases with increasing SDS concentrations for all the PVA samples. At a given SDS concentration, it can further be noticed that the size reduction is more important for PVA-700-4.3, which is characterized by the highest blockiness. This difference might be attributed to higher volume fraction of colloidal aggregates, initially present in the system and it seems that the complex is

preferentially formed between these species and SDS. At a SDS concentration of 0.1 wt% (e.g. 10 wt% with respect to the PVA), these aggregates have almost been disaggregated.

PVA/SDS complexes are known to be formed by hydrophobic-hydrophobic interactions, inducing an increase in their hydrophilicity.[10,19] As a consequence, it was of interest to examine the cloud point of these systems as a function of the SDS concentration. A cloud point of around 28°C, which represents the onset of precipitation as a function of temperature, was already observed for these PVAs in aqueous medium, in the absence of SDS, due to the disruption of the hydrogen bonds between the OH groups and water.[19] In the presence of SDS, the cloud point values are shifted to higher temperatures, as illustrated in **Table S1** (**Supporting Information**). It is worth noting that at a SDS concentration of 0.05 wt% in the aqueous phase, a very important difference exists between these PVA samples. The cloud point for the PVA-700-4.3, which is the most "blocky", is around 68°C whereas for the other two copolymers this value is equal to 48°C. This is another direct evidence of the influence of the acetate sequence distribution on the colloidal characteristics of PVAs in water.

3.2 Dynamic interfacial tension for ClBu/water

One of the most important parameters influencing the emulsions properties, such as the droplets size and the stability, is the interfacial tension γ_i, as already shown by different authors for ClBu/water system stabilized by PVAs.[11-13] As the interfacial characteristics of a system are directly correlated to the conformation of the adsorbed emulsifier at the interface, in the following, the interfacial tension was determined for all samples in the absence and in the presence of SDS.

3.2.1 In the absence of SDS

He et al.[11,12] as well as Boscher et al.[13] have determined the interfacial tension (IFT) and the adsorption of a series of PVA, characterized by different $\overline{DH}$ and $\overline{DPw}$, at the ClBu/water interface as a function of the copolymer concentrations. These authors have shown that the

interfacial tension is mainly influenced by $\overline{DH}$ and to a lesser extent by the $\overline{DPw}$ but the influence of the blockiness at a constant $\overline{DH}$ and $\overline{DPw}$ was not yet taken into account. As a typical example, the variation of the interfacial tension as a function of the copolymer concentration is given in a semi-logarithmic scale in **Figure S2** (**Supporting Information**) for PVA-700-4.3. From this figure it appears that this sample, as well as for the others two, the interfacial tension decrease sharply until a copolymer concentration of 0.1 wt% which corresponds to the onset of aggregates formation in the aqueous medium. For higher concentrations, γ_i is less sensitive to the copolymer concentration.

In order to analyse the influence of the colloidal aggregates on the interfacial tension, **Figure 1** illustrates the evolution of the γ_i as a function of time for all the PVA samples, at a concentration of 1 wt%. The evolution of the γ_i as a function of time and copolymer concentration for PVA-700-4.3 is given in **Figure S3** (**Supporting Information**).
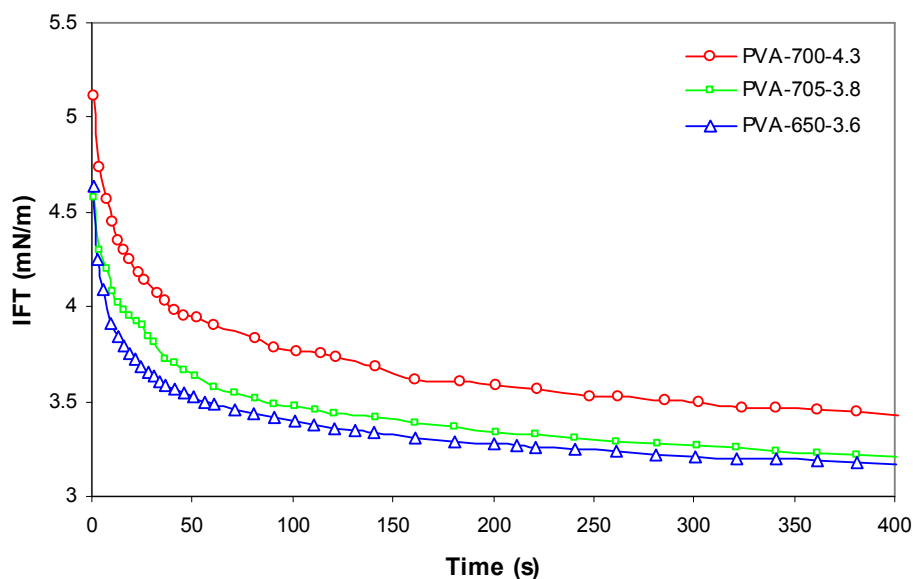

Figure 1: ClBu/water interfacial tension γ_i as a function of time for all the PVA samples at a concentration of 1 wt%

From this figure it can be observed that the interfacial tension decreases rapidly in the first 50 s, for all de copolymer samples, which corresponds to a diffusion-controlled adsorption of the macromolecules at the ClBu/water interface. This phenomenon is followed by conformation changes of the copolymer at the interface which is characterized by a slower decrease of the interfacial tension until a pseudo-equilibrium is reached in the time interval of 300 to 400 s. This behaviour, which is characteristic for amphiphilic polymers, was also observed by different authors for PVA solutions as a function of $\overline{DH}$ and $\overline{DPw}$ [11-13].

Figure 1 illustrates clearly the influence of blockiness and thus of the aggregates content from the PVA aqueous solutions on the variation of the interfacial tension. In fact, PVA-650-3.6, with the lowest aggregates volume fraction of 18%, is systematically more efficient to reduce the γ_i values in comparison to PVA-700-4.3 which has the highest aggregates content of 23%. This difference of behaviour might be attributed most probably to conformation and concentration differences of the PVA chains at the interface. Indeed, a part of acetate rich chains are forming the colloidal aggregates and, therefore, they are no longer available to cover the interface, as it is the case for PVA-700-4.3. Moreover, it might be admitted that these species, due to their micellar type structure, are less surface active than the corresponding free chains.

3.2.2 In the presence of SDS

An original aspect of this study was to examine the evolution of the interfacial tension γ_i versus time for PVA/SDS complexes as a function of the SDS concentration. A typical example is provided in **Figure 2** for PVA-700-4.3.
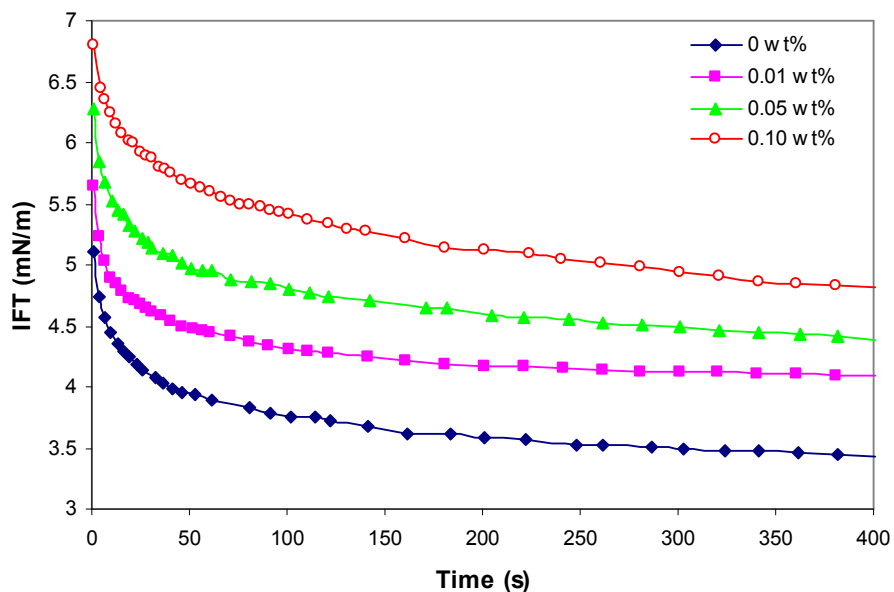
Figure 2: ClBu/water interfacial tension γ_i as a function of time and SDS concentration for PVA-700-4.3 at a concentration of 1 wt%

From this figure it turns out that the γ_i values increase as the SDS concentration increases. Moreover, it can be noticed that the γ_i values are always intermediate between those of pure components. For example, for PVA-700-4.3/SDS complex, at a PVA concentration of 1 wt% and a SDS concentration of 0.10 wt%, the γ_i value at 400 s is around to 5.0 mN/m whereas for 1 wt% PVA solution in absence of SDS this value is equal to 3.5 mN/m. It has further to be noticed that a SDS solution of 0.10 wt% leads to a γ_i value at 400 s of 10 mN/m (**Figure S4** in **Supporting Information**). This indicates that the PVA/SDS complexes are less efficient to reduce the interfacial tension than the PVA itself but more efficient than the corresponding SDS solutions. A comparison of γ_i at 400 s for all three PVA samples as a function of SDS concentration is given in **Figure S5 (Supporting Information)**. As above mentioned for PVA-700-4.3, the γ_i values of PVA/SDS complexes increase with increasing SDS concentration for all the polymer samples and this increase is even more pronounced at low SDS concentration. Moreover, at a given SDS concentration, it turns out that a correlation

exists between the γ_i values of the PVA/SDS complexes and the blockiness of the copolymer samples, which is similar to that observed of pure PVA solutions (see **Figure 1**).

At this point, it appears that the γ_i values observed for PVA/SDS complexes are directly related to the interfacial organization of these systems. The complex acquires a more extended conformation at the interface with a minimum of loops and tails. This chain conformation is a consequence of a partial polyelectrolyte complex formation and of the disaggregation of the colloidal aggregates by increasing SDS concentration as well as of changes in the hydrophobic-hydrophilic balance, as suggested by Philip et al.[20] and by Ramirez et al.[22]

3.3 Interfacial dilational viscoelasticity for ClBu/water

In the case of PVA with a $\overline{DH}$ of 73 mol%, the distribution of the acetate hydrophobic groups within the chain should have significant effects on the interfacial viscoelasticity as it was observed for hydrophobic modified dextran or cellulose derivatives.[31,32] Dilational viscoelasticity, influenced not only by the variation of interfacial coverage, but also by the inter-molecular interactions, provides a deeper insight in the interface association or reorganization. Moreover, additional information can be obtained concerning the PVA/SDS complex formation at the interfaces and therefore the elastic modulus E' and the viscous modulus E" were determined in the absence and in the presence of SDS at a fixed PVA concentration.

3.3.1 In the absence of SDS

The **Figure 3** illustrates the variation of the E' and E" moduli as a function of concentration for PVA-700-4.3.
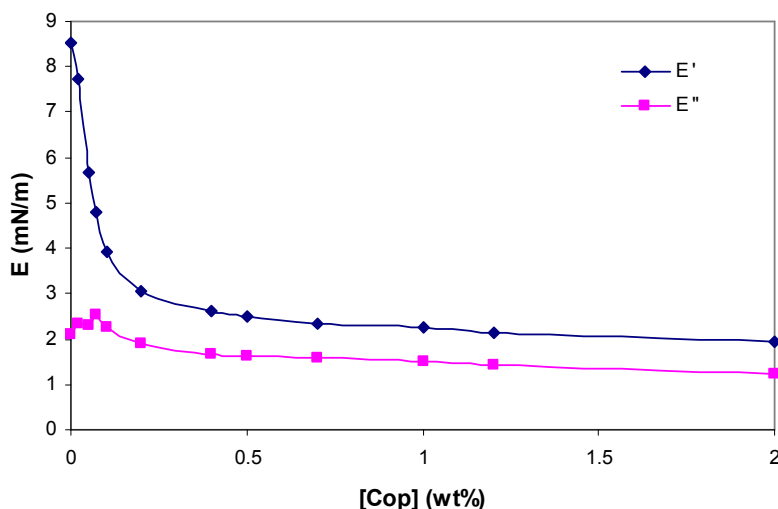
Figure 3: Elastic E' and viscous E" moduli for ClBu/water as a function of the PVA-700-4.3 concentration

E" being almost constant as a function of the copolymer concentration, **Figure S6 (Supporting Information)** shows for all the PVA samples the variation of the elastic modulus E' as a function of concentration. From this figure it can be observed that the elastic modulus E' decreases sharply with increasing the copolymer concentration up to around 0.1 to 0.2 wt%, concentration range which corresponds to the onset of colloidal aggregation. In agreement with different authors, this behaviour may be explained by the fact that a structural reorganization and inter-molecular interactions take place at the interface upon dilation or compression.[32-34] The E' values decrease as a function of the PVA concentration, while the E" values are still constant and lower than E'. The decrease of the ratio E"/E', characteristic of the retardation of the interface reorganization, is a proof of lower mobility in the sense of slower reorganization. Colloidal aggregates, being indeed less mobile compared to free chains, lead then to a lower elastic character of the interface due to their reduced ability to respond instantaneously to a strain or stress application and consequently the E' value decreases in the presence of aggregates.

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In order to determine more specifically the influence of the colloidal aggregates on the viscoelastic interfacial properties, the E' values are given in **Figure 4** for copolymer concentrations between 0.2 and 2 wt%. In this concentration range, the presence of aggregates was confirmed by DLS as well as by interfacial tension (see **Figure S2**).
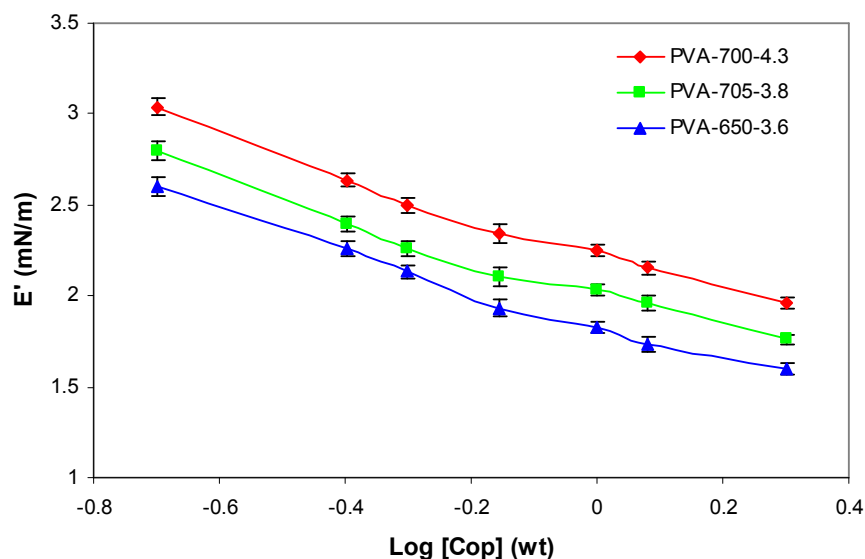

Figure 4: Elastic modulus (E') of the PVA solutions of different n_0^{VAc} values at ClBu/water interface as a function of the copolymer concentrations

From this figure it can be observed that the elastic modulus E' decreases with increasing PVA concentration. This behaviour might be explained by the increase of the PVA chains concentration at interface leading to a less mobile layer (slower reorganization) and less elastic layer, most probably due to the presence of colloidal aggregates at the interface. The evolution of the elastic modulus as a function of the PVA concentration may be correlated with the evolution of the interfacial tension. In fact, at low PVA concentrations, their packing density at the interface is reduced. Moreover, depending on the blockiness, a systematic difference appears between the PVA samples. Lower E' values and thus a lower elasticity of the interfacial layer are obtained for sample PVA-650-3.6 than for PVA-700-4.3 with average

acetate sequence lengths values of 3.6 and 4.3 respectively. An intermediate situation may be noticed for PVA-705-3.8.

3.3.2 In the presence of SDS

The dilational viscoelastic moduli were also determined at a fixed copolymer concentration of 1 wt% as a function of the SDS concentration below its critical micellar concentration (C.M.C) and the obtained values of E' and E'' are given in **Table 4** and **Table S2 (Supporting Information)** respectively.

Table 4: Elastic modulus E' for ClBu/water in the presence of PVA/SDS complexes as a function of the SDS concentration. PVA concentration of 1 wt%

[SDS] (wt%)	E' (mN/m)			
	SDS	**PVA-700-4.3**	**PVA-705-3.8**	**PVA-650-3.6**
0	-	2.25	2.13	2.03
0.01	10.0	2.65	2.41	2.26
0.05	6.5	3.73	3.60	3.12
0.1	5.5	4.17	3.80	3.76

Comparing the values given in **Table 4** with those from **Table S2,** it appears that, for all the samples, E' is systematically superior to E'' in the whole SDS concentration range which is characteristic for the adsorbed polymer layers as suggested by Babak et al. [33]

For pure SDS solutions the E' values decrease with increasing concentration. This behaviour was also observed by Sharipova et al.[35] for SDS solutions at the water/hexane interface as well as by Fainerman et al.[36] at a water/air interface. The decrease of the elastic modulus E' can be explained by the increase of the packing density of the SDS molecules adsorbed at the interface. An increase of SDS concentration being able to decrease the E' value in the case of SDS/water solution, one can indeed expect that the same increase of SDS concentration could also lead to a decrease of E' in the case of PVA/SDS complexes. However, an opposite trend can be noticed in **Table 4**. In fact, at a constant copolymer concentration of 1 wt%, an

interesting effect can be observed which is the systematic increase of E' for all the PVA samples with increasing SDS concentrations.

A quite similar tendency was reported by Babak and Desbrières[16] for the system alkylated chitosan/SDS This characteristic behavior, with an increase of E' as a function of the SDS concentration, was attributed by the authors to the formation of chitosan/SDS complexes by electrostatic interactions.

In our case, the PVA/SDS complexes may play a major role. As a preliminary remark, it should be kept in mind that, according to our experimental procedure, the aqueous PVA/SDS phase of the droplet was prepared in advance by mixing the aqueous solutions of PVA and SDS, respectively. The disaggregation of the colloidal species and the formation of the SDS/PVA complexes mostly occur in this step. As these unimer-type complexes are becoming more and more hydrophilic, with the SDS increase, their tendency will be less to migrate to the oil/water interface. In this case the interface is predominantly formed by more mobile free chains complexed with SDS that can reorganize themselves rapidly during the drop oscillations. As a consequence, the interfacial tension and E' are increasing with increasing the SDS concentration. Moreover, due to the enhanced water solubility of the colloidal complexes, the packing density at the interface will be reduced. In fact, the PVA/SDS complex is formed by hydrophobic interactions between the acetate groups and the hydrophobic parts of SDS therefore this system may be considered as a partial polyelectrolyte.

Furthermore, it may be pointed out that the highest E' values are obtained for the PVA-700-4.3 sample, having the highest blockiness value and thus the highest volume fraction of aggregates.

A schematic representation of this system at the ClBu/water interface, in the absence and in the presence of SDS, is given in **Scheme 1**:
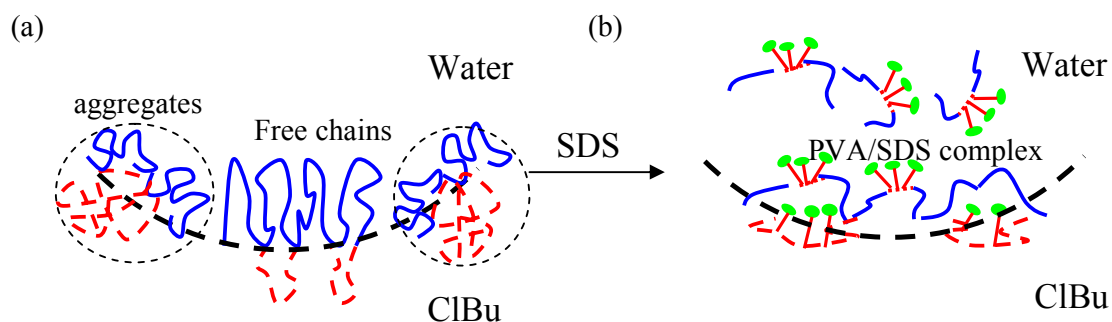
Scheme 1: Schematic representation of the PVA chains in the absence of SDS (a) and PVA/SDS complexes (b) at the ClBu/water interface

In the absence of SDS (a), the interface is covered by colloidal aggregates and by PVA free-chains which are organized in the classical way of tails and loops. Such a conformation gives rise to a relative thick adsorbed layer leading to low E' and E'' moduli values, with E'>E''.

In the presence of SDS (b), the complexation leads to the disaggregation of aggregates and to the formation of PVA free chains complexed with SDS. These polyelectrolyte type species are becoming more hydrophilic which induces a reorganization of the interface. In this case, the increase of the elastic modulus may correspond to a decrease of the adsorption energy of acetate groups at the ClBu phase.

According to Noskov et al.[37], for a polyelectrolyte system such as poly(vinyl pyridinium chloride), the adsorbed macromolecules do not longer form extended loops and tails at the interface. In fact, the repulsion between the neighbouring charged groups of complexed SDS induces the stretching of the chains and thus the reduction of the interface thickness.

From a practical point of view concerning the stabilization of emulsions, it appeared from this approach that the interfacial characteristics of the PVA/SDS system can easily be adjusted in order to optimize their emulsifying efficiency.

Conclusions

The present study was carried out in order to gain an insight into the influence of the molecular characteristics of PVAs on their colloidal and interfacial properties. These properties where determined for a series of three PVA samples having identical DH and DPw but different average acetate sequence lengths n_0^{VAc} which is indicative of the blockiness.

This type of copolymers was investigated due to their practical interest in emulsion and suspension polymerization processes and in particular of vinyl chloride monomer (VCM). 1-Chlorobutane (ClBu) was selected as a model system for VCM as their characteristics are close to those of VCM, with the advantages of easier handling and of lesser toxicity.

For the colloidal aggregates present in the aqueous solution, at a concentration of 1 wt%, of these copolymers a direct correlation could be established between their volume fraction and the PVA blockiness. Furthermore, it could be demonstrated that the PVA-650-3.6 leads to lower interfacial tension and elastic modulus E'. On the contrary, the corresponding values are the highest for PVA-700-4.3, which is the most "blocky".

A further original aspect of this study was to examine the interfacial characteristics of PVA/SDS complexes at the water/ClBu interface. These partial polyelectrolyte complexes are generated by the disaggregation of the colloidal aggregates in aqueous solutions. Moreover, the repulsion between the neighbouring charged groups of complexed SDS leads to the stretching of the chains and thus to the reduction of the interface thickness. For these PVA/SDS systems, the interfacial tension and the elastic modulus increase with increasing the SDS concentration for all three PVA samples whereas the viscous modulus is almost constant. The highest E' values of the interfacial layer was obtained for the PVA-700-4.3/SDS complexes.

In addition to the electrosteric stabilization at the water/ClBu interface provided by the PVA/SDS complex, this higher and adjustable interfacial elasticity may be a definite advantage for the emulsions stabilization not only in static but also in dynamic conditions. It

will be of interest to investigate, in a further step, the stability of ClBu/water emulsions in the presence of PVA/SDS complexes in order to establish a correlation with the interfacial viscoelastic characteristics. It would be also interesting, in order to better understand the role of the blockiness, to increase in a controlled manner the length of the acetate sequences by using an original PVAc-PVOH block copolymer.

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(a)

nanogels

Free chains

Water

SDS

ClBu

(b)

Water

PVA/SDS complex

ClBu