

## COLLOIDAL CHARACTERISTICS OF VINYL ALCOHOL-VINYL ACETATE COPOLYMERS BY COMPLEX FORMATION WITH SODIUM DODECYL SULPHATE

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The colloidal aggregates, the so-called “pseudo-micelles” formed in aqueous solution by vinyl alcohol-vinylacetate copolymers (PVA) were examined by dynamic light scattering (DLS). Different samples of similar molecular mass and an average hydrolysis degree, (DH) of 72 mole% were studied.

These colloidal particles, in the size range of 20-30 nm, could be disaggregated by complex formation with sodium dodecyl sulphate (SDS). The reduction in particle size was determined as a function of temperature and SDS concentration. By complex formation, the cloud point of PVA is shifted from 27-28°C to higher temperatures, which are adjustable by the SDS concentration and that can reach values above 70°C. It could be demonstrated that a “blocky” structure of the PVA enhances the hydrophobic interaction between SDS and PVA and as a consequence the efficiency of the complex formation.

### INTRODUCTION

The formation of complexes between non-ionic water-soluble polymers, like poly(ethylene oxide) (PEO),<sup>1,2</sup> poly(vinylpyrrolidone) (PVP),<sup>3,4</sup> as well as poly(vinyl alcohol) (PVOH),<sup>5-10</sup> and anionic surfactants, such as sodium dodecyl sulphate (SDS), is a well established fact. It has been shown that the hydrophobic interaction of the surfactant alkyl chains with the polymer is the main driving force for this complex formation.<sup>5,8</sup>

Quite a number of techniques, such as viscometry, conductimetry, fluorescence spectroscopy, surface tension measurements, etc, were used over the last decades to determine the characteristics of these complexes.<sup>1,3,7,8,11</sup>

If the complex formation between anionic surfactants and PEO or PVP was quite extensively studied, there are only fewer reports on PVOH and especially on partially hydrolysed poly(vinyl acetate) (PVAc), with an average degree of hydrolysis DH in the range of 70-75 mole%. These copolymers are of particular interest as stabilizers, so-called protective colloids, in emulsion and

dispersion polymerization of vinylic and acrylic monomers, such as styrene or vinylchloride.<sup>12-15</sup>

In connection to this problem, mention was made by Lewis and al,<sup>16</sup> and later on by Aladjoff *et al*,<sup>17</sup> as well as by Meehan *et al*,<sup>18</sup> that SDS not only forms complexes with partially hydrolyzed PVAc but also that SDS disrupts the polymer aggregates which are known to be formed by P(VOH-co-VAc) copolymers in aqueous solution. These copolymers will be designated by PVA in the following of this article. Lewis and al<sup>16</sup> came to this conclusion by viscosity measurements, whereas Aladjoff *et al*<sup>17</sup> and Meehan *et al*<sup>18</sup> confirmed this effect by SEC techniques.

The objective of this present study was to investigate into more details and directly by dynamic light scattering (DLS), the desaggregation phenomena, by complex formation with SDS, of a series of PVA's, having similar molecular weights and DH of 72 mole%.

Although these samples might have quite similar characteristics, it turns out in the industrial practice of VCM suspension polymerization, that their performances could be very different.

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Table 1  
Characteristics of the PVA samples

	KP08	KP08R	Al 72.5	B 72
$\overline{DH}$ (mole %)	72±1	72±1	72±1	72±1
$\overline{M}_w$ (g mol <sup>-1</sup> )	39 200	40 900	39 500	36 400
$\overline{M}_w/\overline{M}_n$	2.00±0.03	1.96±0.02	2.52±0.10	2.41±0.19
$\overline{DP}_w$	700±35	730±15	705±15	650±20
$\overline{n}_{(VAc)}$	3.9±0.1	3.6±0.1	3.6±0.1	3.4±0.1
$\overline{n}_{(VOH)}$	7.7±0.2	6.2±0.2	6.9±0.2	5.8±0.2

The complex formation with SDS might therefore be of interest as a practical tool to complete the usual characterisation techniques of PVA's, such as spectroscopic techniques, SEC, cloud point determination, etc...

## RESULTS

The characteristics of the PVA samples are summarized in **Table 1**.

All of them have an average degree of hydrolysis,  $\overline{DH}$ , of 72±1 mole% and a weight average molecular mass,  $\overline{M}_w$ , around 40.000g·mol<sup>-1</sup>. They differ however with respect to the polydispersity index  $\overline{M}_w/\overline{M}_n$ , those of samples Al 72.5 and B72 are around 2.4-2.5, whereas those of KP08 and KP08R are very close to 2.0.

A further difference of the samples, which results mainly from the hydrolysis process of the starting PVAc, is the sequence distribution of the VAc and VOH monomer units in the final product. In fact, as determined by <sup>1</sup>H and <sup>13</sup>C NMR, it appears that all the samples have rather a more or less "blocky" structure, with an average of 3 to 4 and around 6-7 for the VAc and VOH sequences respectively. It is worth noting that sample KP08 has the highest values of  $\overline{n}_{(VAc)}$  and  $\overline{n}_{(VOH)}$ .

Cloud point determination :

The PVA samples in aqueous medium were characterized by their lower critical solution temperature (LCST) that is determined by the onset of precipitation as a function of temperature. A typical example of cloud point determination is given in **Figure 1** for a 1 wt% aqueous solution of sample KP08 and KP08R, in pure water and in the presence of a 0.01 wt% SDS aqueous solution.

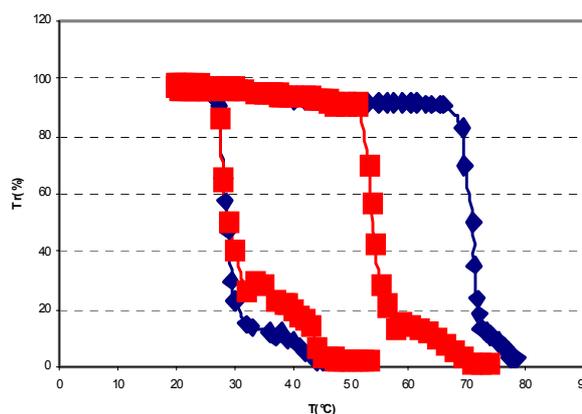


Fig 1 – Cloud point for KP08 and KP08R without and with 0.01 wt% SDS: Optical transmission (%Tr) versus Temperature (°C)

■ - KP08R  
◆ - KP08

The weight ratio SDS/PVA corresponds therefore to 0.01. The SDS concentration with respect to water is under these experimental conditions clearly below the CMC value of SDS, given as 0.23 wt% by Lewis<sup>16</sup>.

It is interesting to observe that in the absence of SDS, the cloud point is between 28 and 29°C for both samples, whereas in the presence of SDS, even in minor amounts of 0.01 wt%, the cloud point is shifted to around 50°C for sample KP08R and even to 70°C for sample KP08. This shift of cloud point is also noticed for sample B 72 and Al 72.5.

As briefly indicated by Aladjoff<sup>17</sup> this is a direct evidence that the solubility of PVA's increases by complex formation with SDS.

Particle size of PVA aggregates:

PVA in aqueous medium is known to form small aggregates, also called "pseudo-micelles", which means that cluster formation by hydrogen bonding could occur even below the cloud point<sup>19</sup>.

The volume average diameters of these colloidal particles, as determined by DLS, are given in **Table 2** for temperatures below the cloud point of the PVA's.

Table 2

The volume average diameters of the PVA's samples in water as a function of temperature (below the cloud point)

T (±0.5°C)	KP08 1% Dv(nm)	B 72 1% Dv(nm)	KP08R 1% Dv(nm)	AL72,5 1% Dv(nm)
20	27.7±0.1	25.4±0.8	30.8±0.4	28.3±0.4
25	32.4±0.2	29.6±1.4	32.5±1.5	33.0±1.5
28	35.2±1.0	35.4±1.5	35.3±1.6	34.4±1.3

At given temperature, slight but significant, differences in size can be observed for the different samples. Furthermore a systematic increase in size with temperature can also be noticed, that seems to be an indication that some agglomeration occurs even before the onset temperature of turbidity.

Particle size of PVA/SDS complexes:

With the cloud point shift to higher temperatures, it became possible to examine the particle size of the PVA/SDS complexes in a temperature range of 20 to 50°C. The particle sizes of the complexes with 0.01% SDS are summarized in **Table 3**.

From this table, it is worth noting that the particle sizes decrease by addition of SDS, which in agreement with Lewis and al<sup>16</sup> is an indication that SDS disrupts, at least partially, the initial PVA aggregates. Also, the particle sizes slightly increase with temperature, the effect being the most pronounced for the PVA samples KP08R, B72 and Al 72.5, approaching their cloud point temperature around 50°C. In contrast, the particle sizes of sample KP08 remains almost constant between 20 and 50°C, due to the fact that its cloud point is near to 70°C.

## DISCUSSION

With DLS it was confirmed that partially hydrolysed PVAc, with an average  $\overline{DH}$  of 72 mole% forms colloidal aggregates in aqueous medium at temperatures below the LCST. Although PVA's with a  $\overline{DH} \geq 65$  mole% are considered as being "water-soluble", the solutions are not directly molecular dispersions, they contain in fact small aggregates, so-called "pseudo-micelles" which are formed by intermolecular hydrogen bonds and/or by hydrophobic interactions between the residual acetate groups. It was shown by NMR that these acetate groups are not randomly but block wise distributed along the polymer chain. Such a "blocky" structure could therefore facilitate the hydrophobic interactions.

The complex formation between SDS and PVA was furthermore demonstrated quite clearly by DLS. In fact, even minor concentrations of SDS with respect to PVA, leads by hydrophobic interaction with acetate blocks, to the disruption of the colloidal aggregates and to an electrostatic stabilization of the system.

As a practical consequence, the cloud point, that is initially around 27-30°C, is shifted to higher temperatures and becomes adjustable with the SDS concentration.

It is worth noting that these effects, obtained with 0.01 wt% SDS with respect to PVA, correspond on a molar base to approximately 1 mole of SDS per 100 moles of residual acetate groups for the samples examined in the present study.

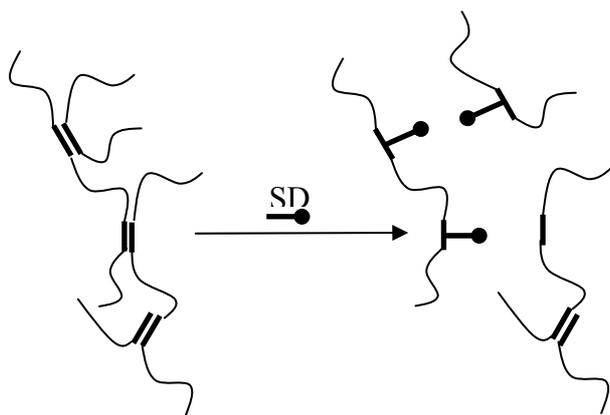
The interaction between SDS and PVA leading to the disruption of the aggregates and the electrostatic stabilization of the resulting species can therefore be schematically indicated as follows:

Table 3

The volume average diameters of the PVA's samples in 0.01 wt% SDS aqueous solution (SDS/PVA ratio is 0.01)

T (±0.5°C)	KP08 1% SDS 0,01% Dv(nm)	B72 1% SDS 0,01% Dv(nm)	KP08R 1% SDS 0,01% Dv(nm)	AL72,5 1% SDS 0,01% Dv(nm)
20	15.0±0.1	19.0±1.0	24.0±0.2	22.1±1.3
30	16.4±0.1	22.6±1.7	25.7±0.7	25.4±1.8
40	17.5±0.2	25.9±0.9	29.6±1.0	28.8±1.4
50	19.1±0.4	32.4±1.3	35.7±1.3	35.6±1.8

### Scheme 1: Interaction between SDS and PVA:



In a semi-quantitative approach, one can consider the efficiency of the complex formation for the different PVA samples, by taking into account, at a given SDS concentration, the size reduction of the aggregates.

These values are listed in **Table 4**.

Table 4

The size reductions of the aggregates:

[SDS](wt%)	KP08	B72	KP08R	Al 72.5
0.01	46%	25%	22%	22%

Even if it might be difficult to draw a straightforward conclusion for samples KP08R, B72 and Al 72.5, it appears that sample KP08 behaves quite differently.

Since KP08 has definitely the blockiest structure as indicated in **Table 1**, it can be assumed that the presence of hydrophobic blocks is in favour of the complex formation by hydrophobic interactions.

## EXPERIMENTAL

### Materials

KP08 and KP08R are commercial PVA samples supplied by Nippon Gohsei under the trade names Gohsenol KP08 and KP08R respectively. KP08 is obtained by a batch hydrolysis process of PVAc, whereas KP08R is prepared in a continuous hydrolysis process. Al 72.5 and B 72 are supplied by Synthomer under the trade names Alcotex 72.5 and Alcotex B 72. These two PVA's are obtained by a batch hydrolysis process of PVAc prepared in a continuous process.

Their characteristics, determined using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and SEC on freeze-dried commercial samples, are summarized in **Table 1**.

$\overline{\text{DH}}$  and the average sequence lengths of vinyl acetate  $\overline{n}_{(\text{VAc})}$  and vinyl alcohol  $\overline{n}_{(\text{VOH})}$  were determined using  $^1\text{H}$  NMR in dimethylsulphoxide (DMSO)- $d_6$  at  $70^\circ\text{C}$  according to Van der Verden and Beulen.<sup>20</sup> The SEC measurements were performed in tetrahydrofuran (THF) at  $30^\circ\text{C}$  using reacylated samples as recommended by Bugada and Rudin.<sup>21</sup>

The "universal calibration technique"<sup>22</sup> with polystyrene standards was applied for the calculation of  $\overline{M}_n$  and  $\overline{M}_w$  from which it was straightforward to obtain the corresponding degree of polymerization of the PVA samples.

Sodium dodecyl sulphate (SDS) with a purity of 99% was purchased from Acros. It was used without any further purification.

Cloud point determination:

The starting PVA's and their complexes with SDS were characterized using the lower critical solution temperature (LCST). The onset of precipitation as a function of temperature was determined by monitoring the turbidity of the solution at a concentration of 1 wt% as the temperature was increased stepwise at a rate of  $1^\circ\text{C min}^{-1}$ . The cloud point is given by the temperature corresponding to the onset of the turbidity curve.<sup>23</sup>

Preparation of the PVA/SDS complexes:

The required amounts of SDS were dissolved in triple distilled and filtered ( $0.22 \mu\text{m}$  Millipore filter) water. The PVA was dissolved in the SDS solutions for 16h under agitation at room temperature.

Particle size determination:

The particle size of the PVA "pseudo-micelles" and of the PVA/SDS complexes was determined by dynamic light scattering (DLS) at different temperatures using a Nanotracc NPA 250 particle size analyzer (Microtrac Inc.). This apparatus, equipped with a laser (wavelength 780 nm), is adapted for particle size determinations in the size range of 0.8 nm to  $6.54 \mu\text{m}$ .

The average of 5 consecutive measurements is indicated in the tables.

## CONCLUSIONS

The present study was carried out in order to characterise the colloidal aggregates, the so-called "pseudo-micelles", formed in aqueous solutions of partially hydrolysed PVAc. Four PVA commercial samples of similar molecular weights and same average degree of hydrolysis ( $\overline{\text{DH}} = 72$  mole %), which are of current use as stabilizers in suspension polymerization of vinylchloride, were examined by dynamic light scattering. With this technique it could be shown that the colloidal particles, formed by hydrophobic interactions between PVAc sequences of the copolymer, are in the size range of 20 to 30 nm. In connection to this study, and knowing that anionic surfactants, such as SDS, form complexes with PVA's, it was of interest to investigate directly by DLS, the disaggregation phenomena of the PVA "pseudo-micelles" in the presence of SDS.

At first, it was shown that the PVA/SDS complex formation leads to the disruption of the colloidal PVA aggregates, to the increase in solubility and therefore to an important shift to

higher temperatures of the cloud point. As a practical consequence, it becomes possible to adjust with minor amounts of SDS the cloud point of PVA and to adapt it to the reaction conditions of an emulsion or suspension polymerization.

In a semi-quantitative approach of the complex formation, it was demonstrated that a "blocky" structure of the PVA, that is to say the presence of long VAc sequences, enhances the hydrophobic interaction between SDS and PVA.

Further work is in progress in order to determine the influence of the PVA polydispersity in molecular weight, composition and sequence distribution on the complex formation with SDS. In this respect, one of the major approaches will be to test the behaviour of well-defined PVOH-PVAc block-copolymers.<sup>24</sup>

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