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Poly(vinyl alcohol) Polymers with a Low Degree of Hydrolysis. II.* Complex Formation with Ammonium Laurate and Sodium Lauryl Sulfate

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The binding of tensides (sodium laurate, SL, ammonium laurate, AL, and sodium layryl sulfate, SLS) to a number of commercial PVAL polymers of different degrees of hydrolysis have been studied at tenside concentrations below the critical micelle concentration using membrane and gel filtration techniques. The results showed that SLS binds much more readily to the polymer than SL or AL. The tendency to bind tensides increased rapidly as the degree of hydrolysis of the polymer became lower. Binding of laurate seems to require the presence of acetate groups on the polymer, whereas SLS was found to bind also to a fully hydrolyzed polymer. In all cases studied, binding became more favourable at higher tenside concentrations. Attempts to study the enthalpy of binding using flow micro calorimetry indicated that complex formation with the polymer was energetically slightly more favourable than micellization.

As discussed in the previous paper in this series, poly(vinyl alcohol) polymers with a rather low degree of hydrolysis are of interest as suspension stabilizers in the manufacture of suspension PVC.[1] In aqueous solution and at room temperature, polymers of this type were found to associate. The relative amount of associated molecules increased rapidly with a decrease in the degree of hydrolysis. The results indicated that the phenomenon was caused by interactions between hydrophobic poly(vinyl acetate) blocks remaining in the polymers. It was also found that the associated molecules dissociated on addition of ammonium laurate. It was suggested that this was due to binding of laurate to the hydrophobic parts of the polymer molecules. These observations and the fact that in suspension polymerization of vinyl chloride the polymeric stabilizer often is used in combination with tensides, initiated the present study on complex formation between tensides and a set of commercial poly(vinyl alcohol) polymers. The study refers to concentrations of tensides below their critical micelle concentration, c.m.c. A lot of work has been done on complex formation between tensides and poly(vinyl alcohol)[2] but no previous studies have been made involving the composition of complexes between tensides and the type of polymers used here.

EXPERIMENTAL

Poly(vinyl alcohol) polymers, PVAL. The commercial PVAL polymers used in this study are presented in Table 1. The values given for the degree of hydrolysis [the relative number of the acetate groups in the parent poly(vinyl acetate) converted to hydroxyl groups] were determined by a method described by Finch.[3] The polymers were used as received except for in the experiments with Rhodoviol. In this case the polymer was purified either by reprecipitation from acetone–water or by ultrafiltration in a stirred membrane filter cell fitted with an Amicon PM 10 membrane, in order to eliminate the small error caused by the presence of low molecular weight impurities (see below).

Tensides. Ammonium laurate, AL, and sodium laurate, SL, were prepared by dissolution of lauric acid, LA (BDH, specially pure) in dilute ammonia or

*Part I, see Ref. 1.

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Table 1. Commercial PVAL polymers used in the present study.

Trade name	Degree of hydrolysis %	Producer
Rhodoviol 5/270	71.5	Rhone-Poulenc
Mowiol LP 5.72	70.5	Hoechst AG
Polyviol M 05/290	74.7	Wacker Chemie
Alcotex 72.5 L	71.7	Revertex Ltd.
Alcotex 75 L	72.2	Revertex Ltd.
Elvanol 51-05	87.5	Du Pont
Elvanol 70-05	98.9	Du Pont

sodium hydroxide. The pH of the AL solutions used was between 9.6 and 9.8 and that of SL between 9.2 and 9.3. Sodium lauryl sulfate, SLS (BDH, specially pure) was used as received. Deionized and then distilled water was used for preparing all aqueous solutions.

Binding studies. Two techniques, one based on membrane filtration and the other on gel filtration, were used, With the membrane filtration technique, the sample (300 ml) containing known total amounts of polymer and tenside was placed in a membrane filter cell fitted with stirrer and Amicon PM 10 or PM 30 membranes. The first 10 ml of the filtrate was discarded and the next 5 – 10 ml was analyzed for tenside. The concentration found was assumed to represent that of the free tenside. Laurate was determined by potentiometric titration with 0.1 M HCl after adding a small amount of SLS to the solution to ensure that a sharp end point was obtained in the titration of the excess amount of base.[4] SLS in the filtrates was determined colorimetrically as its methylene blue complex.[5]

The gel filtration method used for determination of bound tensides has been described by Hummel and Dreyer[6] and is outlined in Fig. 1. The column is saturated with a tenside solution of concentration

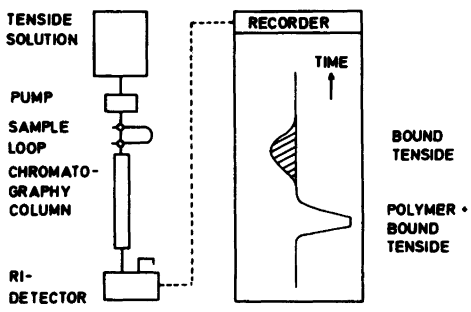

Fig. 1. Determination of the binding of tensides to polymers by gel chromatography.

C. A sample of the polymer dissolved in the tenside solution is then applied *via* a sampling valve. If the polymer binds the tenside, two peaks will appear. The first is positive and contains the polymer, the second is negative and corresponds to a deficiency in tenside. The area of the negative peak gives the amount of bound tenside. The column can be calibrated in experiments with water samples of various volumes. The method requires that the positive and negative peaks are separated by a horizontal base line. This is a guarantee that the polymer peak contains free tenside of concentration *C*. The determination of a binding isotherm requires experiments at a set of various concentrations of tenside. Impurities in the polymer with a low molar mass might interfere with the negative peak and give low values for bound tenside.

The binding studies with AL were carried out using Sephadex G10 (35 × 400 mm). With SLS it was necessary to use a more porous gel, Sephadex G25-SF (16 × 600 mm). In this case it was also found necessary to keep the tenside solution reservoir flask at a temperature slightly above room temperature to avoid problems caused by association of the tenside. The columns were jacketed and all experiments carried out at 25 °C. The columns were fed by a peristaltic pump. The flow rate was about 0.8 (Sephadex G10) and 0.5 ml/min (Sephadex G25-SF) and was determined in each of the experiments. The effluent was analyzed by a refractive index (RI) detector (Optilab Multiref 901).

Enthalpy of binding. The enthalpy of binding SLS and AL to Rhodoviol (Table 1) was evaluated from the heat effects observed on mixing solutions of the tenside with solutions of the polymer, or by diluting a polymer – tenside mixture by water. The experiments were carried out in a flow microcalorimeter.[7] Corrections were applied for the heat of dilution of the component solutions. The same technique was used for estimating the enthalpy of micellization of AL and SLS. The extent of reaction was calculated from the binding isotherms and values for the c.m.c. of the tensides, respectively.

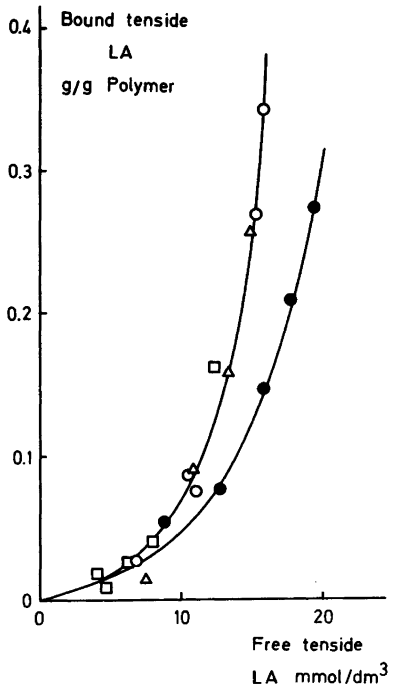

Fig. 2. Binding isotherms for ammonium laurate, AL, and sodium laurate, SL, to Rhodoviol 5/270 as determined by membrane filtration at room temperature. □, AL, PM 10; ○, AL, PM 30, △, AL, – (Data from Table 2); ●, SL, PM 30.

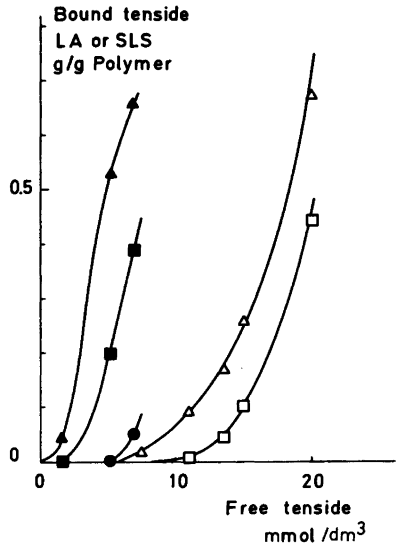

Fig. 3. Binding isotherms for sodium lauryl sulfate, SLS, and ammonium laurate, AL, to some commercial poly(vinyl alcohol) polymers. Open symbols, AL; filled symbols, SLS. △, ▲, Rhodoviol 5/270, 71% hydrolysis; □, ■, Elvanol 51-05, 88% hydrolysis; ●, Elvanol 70-05, 99% hydrolysis.

RESULTS

Most of the binding studies were carried out using the gel chromatography technique. The results obtained are given in Tables 2 and 3. Results obtained with the alternative method, membrane filtration, are presented in Fig. 2. These refer to experiments with laurate and one of the polymers, Rhodoviol, only. Gel chromatography results for this system from Table 2 have been included in Fig. 2 in order to permit a direct comparison between the two methods. A comparison of SLS and AL in terms of binding isotherms with some of the polymers is given in Fig. 3. Fig. 4 shows the effect of SLS and AL on the specific viscosity of Rhodoviol. Values for the apparent enthalpy of binding are given in Table 4.

Table 2. Binding of ammonium laurate, AL, at 25 °C to some commercial poly(vinyl alcohol) polymers expressed as g lauric acid, LA, per g of polymer.

AL[a] % by weight	Rhodoviol	Mowiol	Polyviol	Alcotex 72.5	Alcotex 75	Elvanol 51-05
0.15	0.014	0.016	0.016	0.016	0.016	–
0.22	0.092	0.080	0.076	0.093	0.082	0.009
0.27	0.17	0.16	0.14	0.17	0.16	0.048
0.30	0.26	0.30	0.25	0.27	0.26	0.10
0.40	0.68		0.77			0.45
0.44	1.36					

[a] Conc. of free AL in the solution calculated as LA.

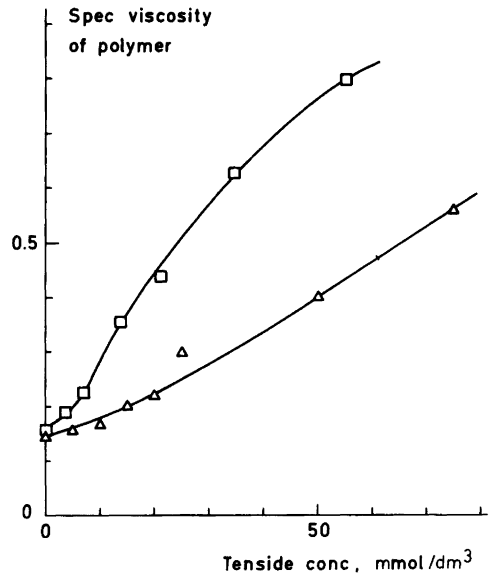

Fig. 4. Specific viscosity at 25 °C for Rhodoviol 5/270 as determined at a polymer concentration of 0.5 % by wt. and in the presence of various amounts of sodium lauryl sulfate (□) or ammonium laurate (△).

DISCUSSION

Methods. As seen from Fig. 2, the agreement between the results obtained with the gel chromatography and the membrane filtration methods was very good. In the gel filtration experiments with Rhodoviol, no systematic differences were observed between polymer samples purified by membrane filtration or by precipitation. The low value obtained with the gel chromatography technique at the lowest concentration can be explained by the difficulty in evaluating the true area under the tails of a low and fairly wide chromatography peak. The difference between SL and AL in Fig. 2 most likely reveals a direct counter-ion effect. The differences in electrolyte concentration between the SL and AL solutions were very small.

Table 4. Apparent enthalpy of binding of sodium lauryl sulfate, SLS, and ammonium laurate, AL, to Rhodoviol 5/270 at 25 °C.

Tenside	Increase in[a] tenside binding g/g polymer	ΔH_b kJ/mol
SLS	0–0.31	−4.8
	0–0.45	−4.8
	0–0.60	−5.0
	0.49–0.72	−3.9
AL	0–0.31	3.3
	0–0.41	3.3
	0–0.64	2.7
	0.27–0.70	5.2

[a] For AL in g lauric acid/g polymer.

Attempts were made to use the membrane filtration method also for the determination of binding isotherms with SLS but were unsuccessful. In experiments with pure SLS solutions the filtrates contained much less SLS than did the parent solutions. The reason for this probably was that the experiments were carried out at room temperature, that is at a temperature slightly lower than 24 °C, which according to recent data seems to be the minimum temperature at which clear solutions of pure SLS can be obtained.[8] This was not understood at the time and experiments with the membrane filtration technique were not carried out at higher temperatures. However, also with the gel chromatography technique difficulties were encountered in experiments with SLS until provisions were made for keeping all parts of the chromatography system at 25 °C.

Binding isotherms. As can be seen from Fig. 3 and Tables 2 and 3, SLS and AL gave binding isotherms

Table 3. Binding of sodium lauryl sulfate, SLS, at 25 °C to some commercial poly(vinyl alcohol) polymers in g per g of polymer.

SLS[a] % by weight	Rhodoviol	Mowiol	Polyviol	Elvanol 51-05	Elvanol 70-05
0.05	0.061	0.046	0.033	0	0
0.15	0.48	0.50	0.47	0.23	0
0.20	0.74	0.79	0.68	0.39	0.05

[a] Conc. of free SLS in the solution.

of the same general shape. In all cases studied, binding became more favourable at higher concentrations. This is a behaviour quite different from that observed for the adsorption of tensides of hydrophobic colloids, which normally can be fairly well described by Langmuir isotherms.

It can be seen that the tendency to bind SLS and AL decreases with an increase in the degree of hydrolysis. It is also seen that SLS binds much more readily to the polymer than does AL. Thus, with SLS a significant extent of binding was observed even in the experiments with the fully hydrolyzed polymer, in which case no detectable binding of AL could be observed. The higher complex ability of SLS was reflected also in a much stronger viscosity effect than that produced by AL (Fig. 4). These differences between SLS and AL are in agreement with previous information.[9] An analysis of the data in Fig. 4 using the binding isotherms in Fig. 3 showed that also when compared at the same amount of bound tenside (g/g polymer), the specific viscosity of the SLS polymer complex was higher than that of the AL polymer complex.* Within the concentration range covered by the isotherms, the difference between SLS and AL in its effect on the specific viscosity seemed to increase with an increase in the amount of bound tenside.

In the previous paper, it was shown that the cloud point temperature (which in these systems is reached by heating from room temperature) of a 0.5 % solution of Rhodoviol increased from 35 to 75 °C on addition of 5 mmol/dm^3 of AL.[1] From Fig. 2 it can be calculated that this effect was produced by the binding of 0.015 g lauric acid per g polymer, which would correspond to only about 1 molecule of lauric acid per 240 monomer residues or about 1 molecule of lauric acid per 70 vinyl acetate residues. It is likely that the large effect on the cloud point temperature observed in this case was due to a selective binding of the tenside to polymer molecules with a higher than average content of acetate groups. The acetate groups in partly hydrolyzed poly(vinyl acetate) are unevenly distributed over and along the molecules in a manner which depends on the conditions used during hydrolysis (*cf. e.g.* Refs. 1, 10). This makes a closer discussion of the binding isotherms very complicated.

* The data in Fig. 4 include the viscosity effect of the free tenside. The contribution of this effect to the specific viscosities would be rather small and would not even at the highest tenside concentration exceed 10 %.

The methods used for the binding studies were based on separation of the free tenside from the tenside polymer complex. Because of the size of tenside micelles, studies were not possible at tenside concentrations above the c.m.c. As can be seen from Table 2, AL concentrations approaching the c.m.c value (0.44 % by weight LA as determined by conductometry) the polymer bound more than its own weight of LA. The highest concentration observed corresponded to a binding of about 1.3 molecules of lauric acid per vinyl acetate residue. This result suggests that the polymer acted more or less as a catalyst for the association of the tenside.

Enthalpy of binding. The results in Table 4 suggest that the binding of SLS to Rhodoviol was exothermic and that of AL endothermic. The difference, however, compares rather well with the difference in enthalpy of micellization. The enthalpies of micellization were estimated as 7.3 kJ/mol for AL and about zero for SLS. This means that with both tensides, complex formation with the polymer was energetically slightly more favourable than micellization. The experimental material is not large enough to permit a full discussion of the results. However, the following comments can be made. The values for the apparent enthalpy of binding obtained in the experiments based on mixing polymer and tenside solutions contained a contribution from the enthalpy of dissociation of the associated polymer molecules. Such a contribution would not be present in the values obtained in the dilution experiments in which the polymer-tenside complexes were partly dissociated. A comparison of the results from these different types of experiments indicates that the formation of polymer associates is an endothermic process. This is in agreement with the fact that the aqueous polymer solution turns turbid on heating.

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