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Interactions of Aqueous Poly(*N*-vinylpyrrolidone) with Sodium Dodecyl Sulfate. I. Equilibrium Dialysis Measurements[1a,b]

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The interactions of sodium dodecyl sulfate (SDS) and aqueous poly(*N*-vinylpyrrolidone) (PVP) were studied by means of equilibrium dialysis at 25 and 30° and at several polymer concentrations. The analytic concentrations of SDS were measured by conductivity. In order to interpret the dialysis data, it was necessary to consider the Donnan equation for the distribution of unbound SDS across the semipermeable membrane in concentrations above its cmc. The data indicate that the addition of PVP to aqueous SDS solution produces an association polyelectrolyte. At constant polymer concentration and varying SDS concentration, three regions of behavior can be distinguished. At very low ratios of detergent to polymer (*S*/*P*) minimal interaction occurs. At intermediate (*S*/*P*) ratios, clusters, or submicelles, are formed. At high (*S*/*P*) ratios, these submicelles are converted to mixed regular micelles at a cmc lower than that of pure SDS, which have a constant surface charge density and are in equilibrium with a fixed concentration of detergent ions. In region three, the fixed detergent ion concentration decreases with increasing polymer concentration while the fraction of bound sodium counterions decreases. Thus, PVP acts as a nucleating agent for detergent micelles and stabilizes detergent clusters larger than dimers but smaller than observable in the absence of polymer.

It has been shown that water soluble polymers become "association polyelectrolytes" in the presence of large, ionizable molecules such as ionic detergents, many dyes, etc.[2-11] Below, we present an investigation of the state of aggregation of a detergent ion, dodecyl sulfate, and its counterion, Na, in the presence of the macromolecule in pure or complexed form. The results, we believe, are of importance for the understanding of the effects of cosolutes on the state of solution of polymers, for the formation of coacervates, mixed precipitates, and of protein–lipid complexes.

In pure aqueous detergent solution, emf measurements have been used by Botre, Mele, and Crescenzi[12] to measure counterion binding to detergent micelles. Botre, *et al.*,[10] have extended this method to polymer–detergent solutions, but in doing so had to make an assumption concerning the value of the detergent cmc[13] in the presence of the polymer–detergent complex. In our studies, the approach of Botre, Mele, and Crescenzi has been changed by employing conductimetry and by introducing the equilibrium dialysis technique.

The chief advantage of our method is that it permits one to eliminate *a priori* assumptions of the value at which the cmc occurs in the presence of the macromolecule. Previous investigators[9-11] have assumed that the monomeric detergent concentration in equilibrium with micelles and polymer–detergent complex is the same as obtained in the absence of polymer. The data to be presented in these studies show that this assumption is not correct. Further, our data show that while this assumption may be acceptable at low polymer concentration, it becomes increasingly poorer with increasing polymer concentration.

Experimental Materials. Poly(*N*-vinylpyrrolidone) (PVP) was synthesized from 1-vinyl-2-pyrrolidone obtained from General Aniline and Film Corp. The monomer was freed of stabilizer (0.1% NaOH), by vacuum distillation immediately prior to the bulk poly-

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(6) S. Saito, *ibid.*, **158**, 120 (1958).

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(9) M. N. Jones, *J. Colloid Sci.*, **23**, 36 (1967).

(10) C. Botre, F. De Martiis, and M. Solinas, *J. Phys. Chem.*, **68**, 3624 (1964).

(11) S. Gravsholt, L.T.D. Thesis, Fysisk-Kemisk Institut, Technical University of Denmark, Feb 1969.

(12) C. Botre, V. L. Crescenzi, and A. Mele, *J. Phys. Chem.*, **63**, 650 (1959).

(13) In our context we define the cmc as the fixed concentration of monomeric detergent ion in equilibrium with micellized detergent.

merization which was carried out in sealed tubes containing the azobisisobutyronitrile initiator. The PVP thus obtained was freed of monomer and low molecular weight polymers by twice dissolving it in $CHCl_3$ and precipitated into anhydrous ether, drying the polymer, dialyzing it against deionized water, and freeze drying it. By utilizing viscometry constants determined by Frank and Levy,[14] the molecular weight measured in water was found to be 420,000 and 400,000 in methanol.

Sodium dodecyl sulfate (SDS) was synthesized from lauryl alcohol (>99% pure as determined by vapor phase chromatography) obtained from the Givaudan Chemical Co. The SDS, after recrystallization from ethanol, isopropyl alcohol, and a 50:50 mixture, was extracted with hexane for several days. The cmc, taken as the value of the intersection of two straight lines in a plot of specific conductivity against concentration, was found to be 8.24 mM.

Deionized, singly distilled (Corning Model Ag-2 still) water was used in all experiments. The average conductivity measured 1.5 μmhos per centimeter.

Equilibrium Dialysis Apparatus. Figure 1 shows a schematic diagram of the Plexiglas equilibrium dialysis cell. The basic design was suggested by Molyneux.[15] Circular cellulose acetate membranes (80 μ thick) purchased from Carl Schleicher and Schuell Co. were used in all dialysis experiments. Each chamber of the dialysis cell contained a small Teflon ball to aid mixing. In addition, during a dialysis run, the entire cell was contained in a thermostated (±0.2°) shaker bath.

Procedure. In a typical dialysis experiment the cells were thoroughly rinsed with a soap solution and distilled water before assembling and installing the membrane. The cells were then filled with distilled water which was changed daily until the conductivity remained constant. Immediately prior to use they were drained and filled with the solutions to be equilibrated.

After seven or more days on the shaker, the solutions were withdrawn by syringe from each chamber, the liquid volume in each chamber measured, and the SDS concentration found by conductivity.

Seven days was chosen as the minimum time of a dialysis experiment as a result of a series of experiments which were run in the absence of polymer. Initially, 10 mM SDS was placed in one chamber of the dialysis cell and an equal volume of 26 mM solution in the other. Both of these concentrations were chosen to exceed the cmc of SDS because of earlier literature reports[15b-f] that equilibrium was slow, or could not be reached, when both sides of a dialysis cell contained initially unequal concentrations of detergent which both exceeded the cmc.[15g] At regular intervals, the solutions were removed from each chamber and the concentrations analyzed. Corrections were made for slight volume losses which occurred in transferring the solutions from the dialysis cell to the conductivity cell. At the end of 176 hr, the solutions were found to be 98% equilibrated, as shown by concentrations on each side which differed by only 4%. Continuing these experiments for 62 hr beyond 7 days, there was only a very slight further change in concentration (0.1%). Even so, in many of the experiments with PVP the SDS concentrations were set initially equal in both chambers to accelerate the approach to equilibrium.

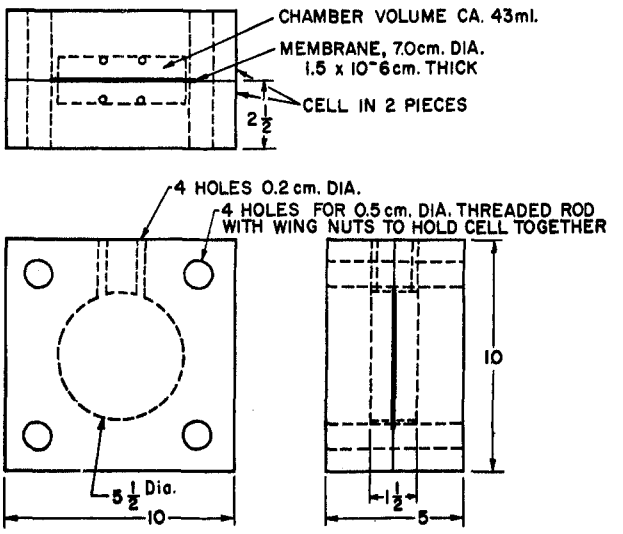

Figure 1. Dialysis cell. (All dimensions are given in centimeters.)

Under these circumstances, only small concentration changes in the two compartments were observed (<10%) and in general SDS transport occurred from outside to the inside of the cell. In several instances, the initial concentrations were set so that material had to flow from the polymer to the outside chamber. In a few other cases, initial concentrations were set much further from equilibrium, so that larger changes (5–10 mM) occurred. The cells were also left in the shaker bath for various lengths of time in excess of 7 days. None of these variations caused more scatter in the data of Figure 2 than in experiments where SDS transport was minimal and no more than 7 days passed between filling and measuring the contents of the dialysis cells. The raw dialysis data, from which Figure 2

(14) H. P. Frank and G. B. Levy, *J. Polym. Sci.*, **10**, 371 (1953).

(15) (a) P. Molyneux, School of Pharmacy, Chelsea College of Science and Technology, London, S. W. 3, private communication; (b) J. T. Yang and J. F. Foster, *J. Phys. Chem.*, **57**, 628 (1953); (c) B. S. Harrop and I. J. O'Donnell, *ibid.*, **58**, 1097 (1954); (d) H. B. Klevens and C. W. Carr, *ibid.*, **60**, 1245 (1956); (e) K. J. Mysels, P. Mukerjee, and M. Abu-Hamdiyyah, *ibid.*, **67**, 1943 (1963); (f) M. Abu-Hamdiyyah and K. J. Mysels, *ibid.*, **71**, 418 (1967); (g) Suggested by referee. Upon suggestion of referee, references 15b–f were included in addition to pH measurements in the Appendix. The authors were aware of the problem of slow equilibration as indicated by ref 15f which was referred to in M. L. Fishman, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1969. A copy of this is obtainable from University Microfilms, 313 First Street, Ann Arbor, Mich., Order No. 69-17,790; (h) J. Wadman, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1966.

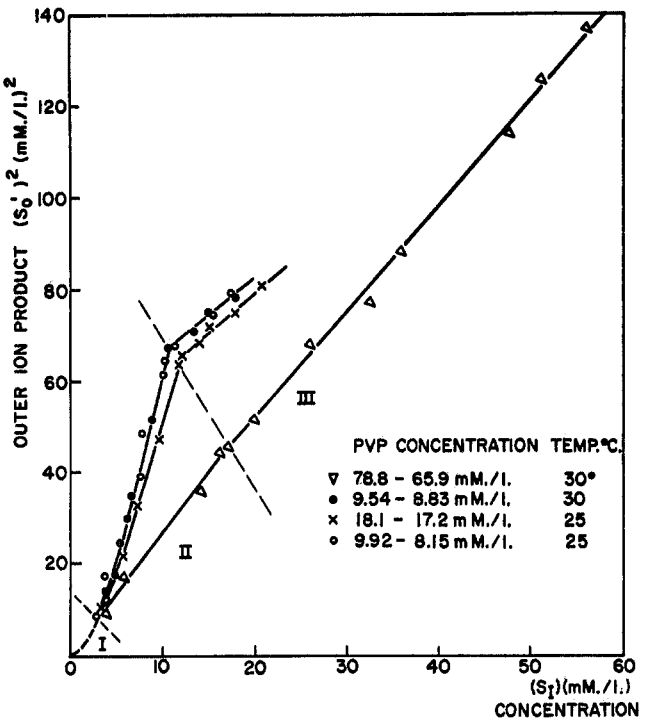

Figure 2. Dependence of outer ion product on total inside detergent concentration.

was obtained, as well as the standard errors for the slopes and intercepts of those figures, can be found elsewhere.[15g]

In addition to the precaution of predialyzing all PVP, an experiment was conducted to verify the impermeability of the dialysis membrane to PVP. Two identical blank experiments were run with a base monomer concentration in polymer of 90 mM on one side of the membrane, and pure water on the other. After 26 days, both sides were analyzed for PVP. In both experiments no PVP could be measured in the aqueous chamber, while the PVP concentration on the other side was found to be unchanged. The analysis of PVP was based on the formation of the PVP–I_3 complex which exhibits an absorption peak at 420 nm (15h). This experiment also provided evidence that PVP was not adsorbed by the container or the membrane. Analysis of the SDS gave material balances to within 5% of the original amounts present, in better than 95% of all dialysis experiments conducted.

Analysis of SDS by Conductivity. An Industrial Instruments conductivity bridge, Model RC-18, and a Klett bridge modified for use with an oscilloscope, gave the same results within 0.1% precision, for the solution conductivities. Even more important, it was found that the total specific conductance of the solutions was the linear sum of the contributions due to water (1.52) μmhos/cm polymer ($0.0268PVP$) μmhos/cm, and SDS ($65.86C + 5.26$) μmhos/cm. This was true to within an error of 1% SDS concentration, in the sub 3.5 mM range of SDS solution, as well as for the polymer concentrations employed. In the above, PVP stands for the millimolar concentrations of polymer (monomeric residues) and C for that of SDS.

At the end of a dialysis run, both chambers of the dialysis cell were diluted separately to 2–3.5 mM range in SDS concentration, and C was determined quantitatively by conductivity. This procedure enabled material balances to be determined at the end of each dialysis experiment.

Results and Discussion

The reaction model used for calculating the binding rests upon the assumption that the amount of total univalent ions present in a solution containing a polyelectrolyte, can be approximated as arising from two states only, *i.e.*, the presence of bound and free ions. The ions which are bound to the polyelectrolyte are assumed to make no contribution to the ionic activities.

The mean activity (A_i) of the free SDS on the inside, or polymer containing, chamber is given as

$$A_i^2 = \gamma_i^2[(DS_f) + \alpha[(S_I) - (DS_f)]]_{(DS_f)} \quad (1)$$

where γ_i = mean activity coefficient of free ions, (DS_f) = concentration of free or unbound detergent ions, (S_I) = total detergent concentration inside the cell, and α = degree of dissociation of sodium ions, acting as counterions to the complex. On the outside, *i.e.*, in the polymer free chamber, two cases may be distinguished. Below the cmc of SDS, the outside mean activity (A_0) is given by

$$A_0^2 = \gamma_0^2(S_0)^2 \quad (2)$$

where (S_0) = total analytic detergent concentration outside. Above the cmc, A_0 is given by

$$A_0^2 = \gamma_0^2(\text{cmc})[(\text{cmc}) + \alpha_m[(S_0) - (\text{cmc})]] \quad (3)$$

where α_m = degree of dissociation of micellar (sodium) counterions. Following Botre,[12] eq 3 assumes that in pure micellar solutions addition of detergent above the cmc merely increases the number, but not the nature, of the micelles. In other words, the concentration of monomeric detergent and the number of detergent ions per micelle are assumed to remain constant.

In eq 2 and 3, the right side, excluding γ_0^2, represents the outside ion product. If one denotes this product by (S_0'), then (4) will suffice to describe the equilibrium concentration of detergent ion on the inside, regardless of whether or not the outside detergent concentration exceeds the cmc. Of course $(S_0')^2$ must be calculated in accordance with (2) below the cmc, and in accordance with (3) above

$$(S_0')^2\gamma_0^2 = \gamma_i^2(DS_f)[(DS_f) + \alpha[(S_I) - (DS_f)]] \quad (4)$$

If one assumes that

$$\gamma_0 \cong \gamma_i \quad (5)$$

(4) can be rearranged to

$$(S_0')^2 = (DS_f)^2(1 - \alpha) + \alpha(DS_f)(S_I) \quad (6)$$

Before proceeding one should note that, when the outside detergent is below the cmc and α is unity, eq 6 becomes

$$(S_0)^2 = (DS_f)(S_I) \quad (7)$$

which is merely a form of Donnan's equation[16] for the distribution of a uni-univalent salt across a semipermeable membrane with a polyelectrolyte on one side.

Determination of the Cmc, and of Counterion Binding above the Cmc. Figure 2 shows the relationship of $(S_0')^2$ with (S_I) at three different polymer concentrations and two temperatures. Among other things, it shows that a 5-degree shift of temperature at the lowest polymer concentration does not produce a noticeable change in the data.

According to the simplified model of micelle formation assumed above, if micelles were to form in the polymer–detergent solution, α and (DS_f) would be invariant with (S_I) and $(S_0')^2$. Consequently, the data plotted in Figure 2 should be linear over the concentration range of micelle formation. Moreover, the intercept and slope of these lines would permit a calculation of α and (DS_f) by the simultaneous solution of eq 8 and 9.

$$\text{intercept} = (DS_f)^2(1 - \alpha) \quad (8)$$

$$\text{slope} = \alpha(DS_f) \quad (9)$$

The linear portion of Figure 2 (*i.e.*, for the polymer concentrations at the higher detergent concentrations) yielded the values of α and (DS_f) which appear in Table I. Also included in Table I for comparison are the values of the cmc and of α[17] for pure aqueous, SDS.

Table I shows an orderly decrease in the value of the cmc together with an increase of α as the polymer concentration increases.

Table I

PVP concn, m*M*/l.[a]	*T*, °C	Cmc	α
0	25	8.24[b]	0.18
9.92–8.65	25	7.88	0.208
9.54–8.83	30	7.89	0.209
18.1–17.2	25	7.47	0.248
78.8–65.9	30	4.06	0.556

[a] The ranges of polymer concentrations of this table and in Figure 2 were caused by water transport in the dialysis cells. [b] By conductivity measurement in this study.

Figure 2 shows that at constant polymer concentration, the linear portion of the (S_0') *vs.* (S_I) plot extends over a large range of polymer detergent ratios. This suggests a polymer participation in the micelle formation, *e.g.*, the formation of a mixed polymer–detergent micelle.

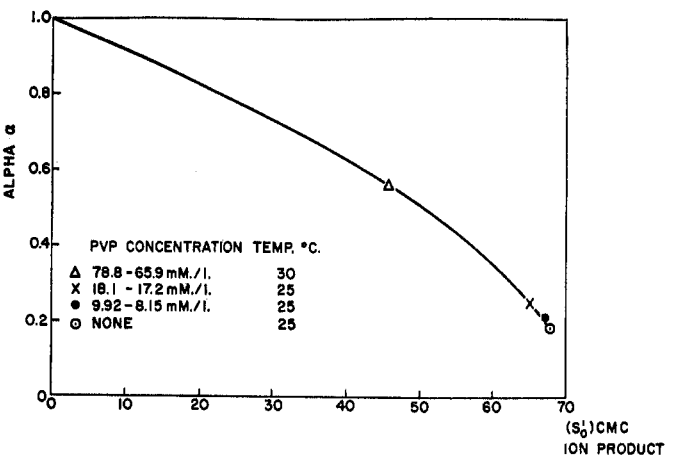

Figure 3. Dependence of α on outside ion product at the cmc.

Determination of the Unbound Detergent Ion Concentration and of Counterion Binding, below the Cmc. In view of the curvature of the lines in Figure 2 at lower polymer and detergent concentrations, the assumption of a constant (DS_f), or α, is not warranted. The line for the highest polymer concentration at the low detergent concentrations appears linear, but calculations of (DS_f) and α according to eq 7 and 8 yield a value of α which is greater than unity. Therefore, α and (DS_f) cannot be assumed to be constant either.

Nevertheless, it is possible to estimate reasonable values of α by the following empirical method based on general considerations of ion binding to polyelectrolytes. At constant polymer concentration, α, must be a decreasing function of (S_I) and, in the same way, of the outside ion product, $(S_0')^2$. Moreover, α should approach unity as $(S_0')^2$ approaches zero. Figure 3 shows α at the cmc plotted against $(S_0')^2$ at the cmc for the various polymer concentrations under the assumption that α is 1 when $(S_0')^2$ equals zero. The concentration of the pure solution at cmc is shown as a point. Since the trend of α with $(S_0')^2$ is similar to that expected at constant polymer concentration we are led to make a further assumption of correspondency, namely that solutions of the same $(S_0')^2$ have identical values of α, regardless of polymer concentration. Utilizing this assumption, eq 6 can be solved with the aid of Figure 3, by the quadratic formula for (DS_f) at all the values of (S_I) below the cmc. The difference between (S_I) and (DS_f) represents the bound sulfate. In other words, we have replaced the inadequate assumption of a constant α for bound SDS below the cmc by an estimate of α which is in accord with known similar behavior of polyelectrolytes.

Figure 4 contains the binding data thus obtained for several polymer concentrations where, r is the molar

(16) C. Tanford, "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1961, p 225.

(17) R. J. Williams, J. N. Phillips, and K. J. Mysels, *Trans. Faraday Soc.*, 51, 728 (1955).

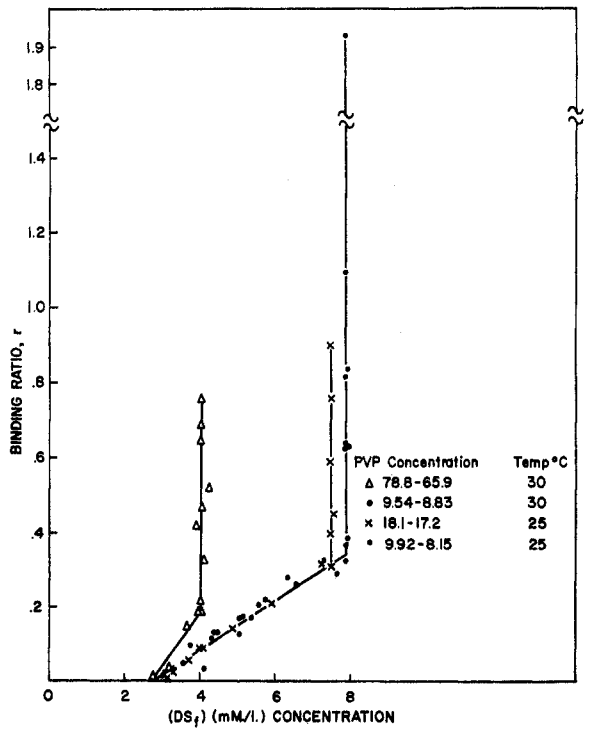

Figure 4. Binding dependence on free detergent ion concentration.

ratio of bound sulfate to total monomer units in the polymer.

The binding isotherms indicate clearly three regions of binding. The first is the low concentration region where little or no binding occurs (no points in Figures 2 and 4). In the second, there is a linear uptake of detergent ion with free SDS concentration, and the third region is marked by a fixed concentration of free DS, a steep increase in binding and/or micelle formation, and therefore by a quantitative deactivation of sulfate. Three regions of behavior have been reported for several polymer–detergent–water systems.[7-9] A mixed micellization was thought to occur in region 2, and a true micellization in region 3. Our Figure 4 indicates a relatively rapid uptake of detergent ion in region 2, particularly at the highest polymer concentration. Nevertheless, cluster or complex formation between PVP and SDS rather than true micellization may be a more accurate description of what occurs in this region, since neither the free detergent ion concentration nor the surface charge density in region 2 appears to remain constant, as should be true for regular micellization.

Binding in region 1, as indicated by Figure 4, is not perceptible under our conditions. Increasing the polymer concentration, however, causes region 2 to begin at lower values of (DS_f). Thus, one might identify region 1 with the binding of single detergent ions to individual sections of polymer, whereas the marked rise in detergent ion deactivation in region 2 should be attributable to a cooperative action of bound detergent ions and polymer chain sections, so as to form nuclei or micelles of low order (clusters or complexes) which eventually turn into true mixed micelles at the start of region 3. Region 2 would appear then to be a transitional region between the binding of isolated detergent ions and region 3 of true micelle formation either on the PVP or independently.

Figure 4 shows binding isotherms which are dependent on polymer concentration. Their form precludes the use of Klotz-type isotherms, or modifications thereof, as a representation of the more common types of binding.[18] Tanford[18] attributes the kind of behavior observed here to complexes involving more than one polymer molecule. In this case the molecular weight of the complex should be dependent upon polymer concentration, which our viscosity data (to be published) indicate. Accepting this premise, it would follow also that different sections of the same chain may become bridged by a detergent cluster, or micelle. This would lead to a decrease of η_{red} with increasing S/P ratio, which some viscosity data indicate. A corresponding observation has been found in the case of iodine–iodate binding to PVP.[2]

A second possibility, also likely to cause a polymer concentration dependence, is a molecular weight dependent binding in the presence of broad polymer distributions leading to a kind of fractional binding. This case could be distinguished from the first in that binding studies on narrow molecular weight fractions would fail to show a concentration dependence. Corresponding studies are in progress.

In conclusion, our results permit a quantitative description of surfactant binding to a water soluble polymer and how this affects the cmc. Moreover, the data indicate that polymers can permit the occurrence of otherwise unstable premicellar complexes and that the polymer is involved in the premature micelle formation.

Appendix

It has been suggested[15gf] that even highly purified SDS could undergo appreciable hydrolysis if allowed to stand for 7 days or more in aqueous media and, further, by a reviewer, that an "interaction between a 'basic' polymer and an anionic surfactant doubtless depends strongly on pH," particularly in our binding regions 2 and 3. To check on these possibilities, polymer detergent solutions were made up to include one sample in region 2, and one in region 3, for the three polymer concentrations studied by us. Also, control solutions of pure aqueous polymer and detergent were made up at these concentrations. The pH values of all solutions were measured immediately upon temperature equilibration, and then 8 days later. During the interim, the solutions were kept in tightly stoppered bottles at

(18) See ref 16, p 528.

25°. All pH measurements were taken on a radiometer PHM4C meter fitted with a Thomas No. 4858-Li5 combination electrode.

The results of these measurements are given in Tables II and III and indicate that our samples of PVP were either neutral or slightly acidic and that SDS was also slightly acidic. The acidity of PVP has been observed before[19] and is likely due to a small amount of COOH end groups. The acidity of SDS may be explained either by a slight hydrolysis in the solid state, unlikely in view of the absence of hydrolysis in aqueous solution, or by the presence of traces of unneutralized dodecylsulfuric acid. In any case the SDS contained less than 0.5% acid impurity.

Table II[a]

	Concn of SDS[b]			
PVP	0	9.00	15.00	25.00
0	5.27	4.51	4.24	4.22
9.92	4.93	4.51	4.34	
18.1	5.27	4.60	4.53	
78.8	3.90	4.07		4.17

[a] pH at 25° immediately upon preparation. [b] pH values in the same row have the same concentration of PVP as indicated by the value which is given in the first column of that row. pH values in the same column have the same concentration of SDS as indicated by the value which is given in the first row of that column. All concentrations are millimolar.

Table III[a]

	Concn of SDS[b]			
PVP	0	9.00	15.00	25.00
0	5.29	4.34	4.25	4.24
9.92	5.42	4.62	4.69	
18.1	5.55	4.60	4.65	
78.8	3.96	4.10		4.21

[a] pH at 25° 8 days after preparation. [b] pH values in the same row have the same concentration of PVP as indicated by the value which is given in the first column of that row. pH values in the same column have the same concentration of SDS as indicated by the value which is given in the first row of that column. All concentrations are millimolar.

Since the pH of all polymer–detergent solutions, except one, fell between 4.1 and 5.1, with no apparent trend, it is most unlikely that a change in pH plays a significant role in our PVP–SDS interaction, particularly in view of the quantities of DS^- deactivated which were more than 10 to 100 times as great as the change in pH over these same concentration ranges. Barkin, Frank, and Eirich[4] also found that pH plays no role in the interaction of PVP with the anionic sulfonate dyes Orange II and Benzopurpurine.

(19) P. G. Assarsson, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1966.