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The surface tension of poly(acrylic acid) in aqueous solution

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With 5 figures

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Introduction

Inspite of many investigations of molecular properties of poly(acrylic acid) (PAA) in solution, informations of the surface state of PAA solutions are not obtainable so far.

In our investigation the surface tension σ of PAA in dilute NaCl solution was measured at various pH, pH and time dependence of σ is analysed.

Experiments

PAA had a molecular weight of $2,5 \times 10^5$ prepared by Ega-Chemie. Stock solutions of polymer, sodium chloride and sodium hydride were prepared using boiled distilled water. The desired solutions were made by mixing these solutions with boiled distilled water.

The surface tension of polymer solution was measured at 30 °C by the ring method. Each measurement was continued for 42 hours. The experimental zero of time was taken 10 minutes after a sample was injected into the constant-temperature cell.

pH measurements were made with a Knick-Precision-pH-Meter.

Results

Figure 1 shows the time dependence of surface tension of PAA at various pH in 0,01 M NaCl solution. The polymer concentration was 0,72 mg/l, that is, 0,01 M. The pH values of solutions approximately correspond to the following values of neutralization i: $i=0{,}0$ for pH 3,35 (curve a, fig. 1), $i=0{,}025$ for pH 3,70 (b), $i=0{,}05$ for pH 4,08 (c), $i=0{,}075$ for pH 4,30 (d), $i=0{,}1$ for pH 4,61 (e), $i=0{,}3$ for pH 6,34 (f), $i=0{,}5$ for 7,82 (g), $i=0{,}7$ for pH 10,55 (h), $i=0{,}9$ for pH 11,0 (i) and $i=1{,}0$ for pH 11,19 (j). This investigation therefore was made between $i=0{,}0$ and $i=1{,}0$. The starred curves of σ at pH 6,70 (curve k, fig. 1) and pH 11,62 (l) denote values σ^s of 0,01 M NaCl solution (k) and 0,01 M NaOH plus 0,01 M NaCl solution (l) without polymer. The former increases while the latter slightly decreases with time. The value of σ^s of pure water remained constant. It is not shown in figure 1. As is obvious from figure 1, the surface tension of PAA increases as the pH value increases. In the low pH region (pH 3–4), the time dependence of σ is large. At 4<pH<6 σ values increase again after a minimum value. In

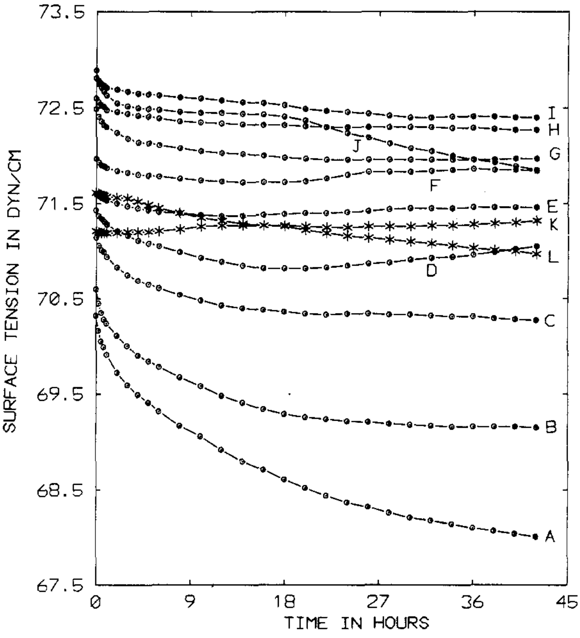

Fig. 1. time dependence of surface tension σ of PAA in 0,01 M NaCl solution at various pH at 30 °C. a: pH 3,35, b: pH 3,70, c: pH 4,08, d: pH 4,30, e: pH 4,61, f: pH 6,34, g: pH 7,82, h: pH 10,55, i: pH 11,00, j: pH 11,19, k: pH 6,70 (without polymer), and l: pH 11,62 (without polymer).

the high pH region (pH 6–11) σ remains constant after a small decrease. The shape of the curve at pH 11,19 is quite different from that of the others. This indicates a peculiar behaviour of PAA molecules at this pH, which remains unexplained.

Katchalsky and *Miller* (1) measured the surface tension of polymethacrylic acid (PMA) in aqueous solution, and evaluated the dependence of surface activity on the molecular weight of the polymer, pH and the ionic strength. They found that time dependence is not very marked i.e. after 5 minutes no measurable changes in the surface tension could be detected. This differs from our results.

For mathematical description of the time dependence of σ we have used (2–5) an Avrami equation

$$(\sigma-\sigma_\infty)/(\sigma_0-\sigma_\infty) = \exp(-Kt^n) \qquad [1]$$

where σ_0 ist the dynamic surface tension at time zero and σ_∞ is the static equilibrium value at infinite time. The two constants K and n are determined so as to fit best the experimental values. Avrami developped this equation for a description of rain drops falling on a water surface causing ring waves covering it as a function of time t.

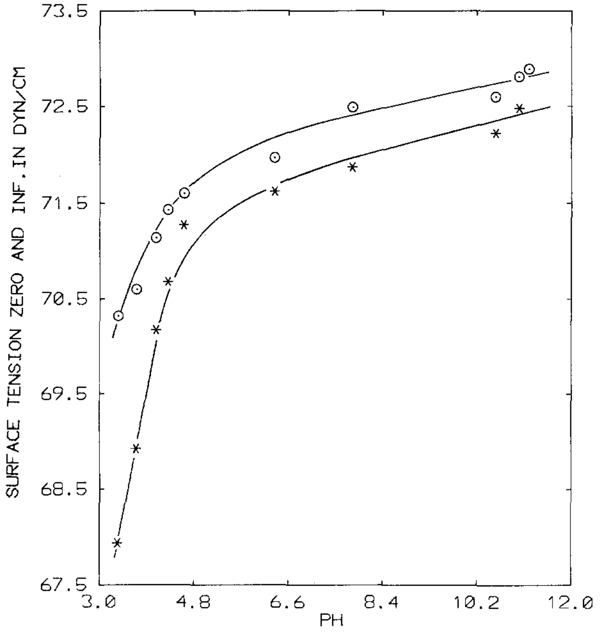

Fig. 2. pH dependence of the dynamic surface tension at time zero, σ_0, and the static equlibrium surface tension at infinite time, σ_∞. σ_0: (⊙), σ_∞: (*).

Figure 2 shows the pH dependence of σ_0 and σ_∞ with values of σ_∞ obtained by equation [1]. The value of σ_∞ at pH 11,19 is not represented in this figure as a reasonable value of σ_∞ could not be obtained owing to the peculiar shape of this curve. As is obvious from figure 2 values of σ_0 and σ_∞ increase with pH, the value of σ_∞ is always smaller than σ_0 independent of pH. The differences of the values σ_0 and σ_∞ at each pH and the pH dependence of σ_0 and σ_∞ are small in the high pH region, but remarkable in the low pH region. Figure 3 shows the pH dependence of the difference of the dynamic and static value of σ, $\Delta\sigma_t = \sigma_0 - \sigma_\infty$. As is obvious from figure 3 $\Delta\sigma_t$ decreases very much in the region below pH 5 and becomes almost constant at higher pH values. The time dependence of σ is remarkable in the low pH region.

Figure 4 shows pH dependence of the difference of the equilibrium values σ_∞ of the solution and σ^s_∞ of the solvent, $\Delta\sigma_s = \sigma^s_\infty - \sigma_\infty$. The σ^s_∞ were calculated from the two values σ^s_∞ at pH 6,70 and pH 11,62 assuming a linear dependence from pH of the others. The $\Delta\sigma_s$ decrease very much in the low pH region and decrease slowly in the high pH region.

The time dependence of the half time τ is plotted against pH in figure 5, it decreases with pH. *Katchalsky* and *Miller* (1) found $\Delta\sigma_s$ of PMA (not PMMA!!) polymer solutions to de-

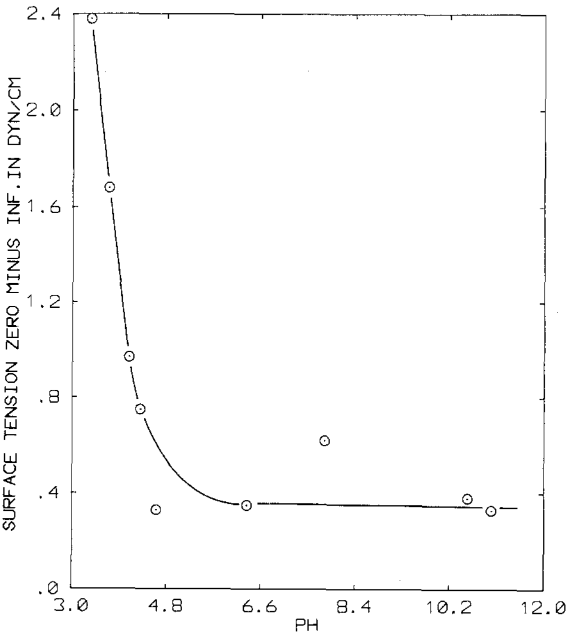

Fig. 3. pH dependence of $\Delta\sigma_t = \sigma_0 - \sigma_\infty$

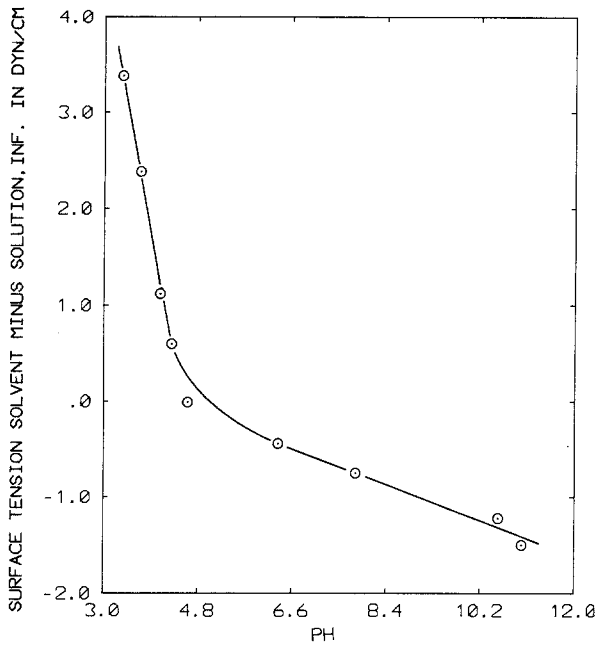

Fig. 4. pH dependence of $\Delta\sigma_s = \sigma^s_\infty - \sigma_\infty$

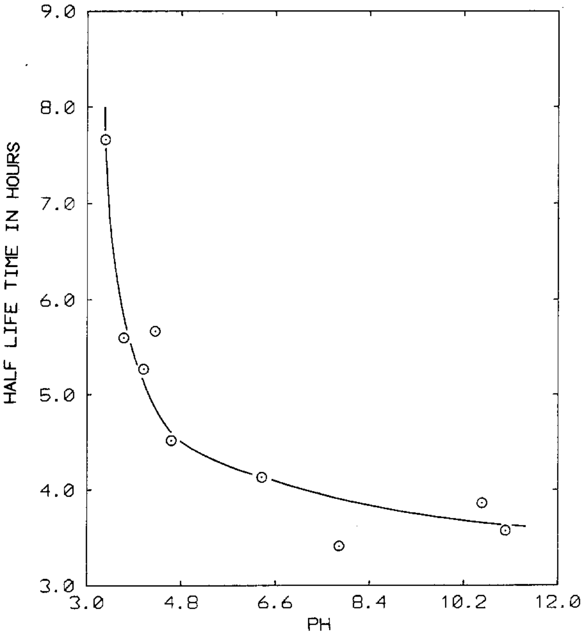

Fig. 5. plot of the half life time, τ, vs. pH

crease with pH, the decrease in activity being very abrupt and surface activity practically vanishing at about 20 percent ionization. These results are in good agreement with ours.

Discussion

A positive $\Delta\sigma_s$ indicates surface activity while a negative value stands for surface inactivity of the solution. This can be explained by ionization of segments of PAA chains. It is wellknown that ionized inorganic salt solutions are in general surface inactive. This fact can be taken for an explanation of the decrease of surface activity (fig. 4) as pH corresponds to the degree of ionization. Increase of numbers of ionized segments within a PAA chain therefore reduces its surface activity indicating that not ionized "neutral" segments only exhibit surface activity.

The explanation of the process of surface equilibrium attainment described by the half time τ has to follow the facts just outlined. τ decreases with ionization (pH) (fig. 5) and the number of neutral segments also (fig. 4). Let us assume the diffusion of neutral segments to the surface to be the time determining step. This can be underlined by the fact that even in surface inactive solutions above pH 4, $\Delta\sigma_t$ the difference between σ_0 and σ_∞, still indicates an increase of surface activity within the frame of inactivity. This means that at time zero the number of neutral segments belonging to an equilibrium distribution of neutral and ionized segments in the surface at this pH is smaller than its equlibrium values. More neutral segments therefore have to migrate to the surface. Their number decreasing rapidly with ionization (pH), this process requires less time for diffusion, τ decreasing with pH.

Summary

Surface tension has been measured of polyacrylic acid-water solutions with pH 3–11. Until approximately pH 4.6 corresponding to 10% neutralization, PAA-solutions are surface active and inactive at higher pH, time dependence of equlibrium surface tension is analysed. Non-ionized "neutral" chain segments are surface active, their diffusion to surface is rate determining.

Zusammenfassung

Es wurde die Oberflächenspannung von wäßrigen Polyacrylsäure-Lösungen der pH-Werte von 3–11 gemessen. Bis zu einem pH-Wert von etwa 4.6, d. h. 10% Neutralisation, sind die Lösungen oberflächenaktiv, bei höheren pH-Werten inaktiv. Es wird die Zeitabhängigkeit der Einstellung der Gleichgewichtsoberflächenspannung analysiert. Nicht ionisierte, „neutrale" Kettensegmente sind oberflächenaktiv. Diffusion zur Oberfläche ist der zeitbestimmende Faktor.

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