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Interfacial and Monolayer Properties of Poly(vinylcaprolactam)

Anjing Lou, Brian A. Pethica,* and P. Somasundaran

Langmuir Center for Colloids and Interfaces, 500 West, 120th Street, Room 911, Mudd Building, Columbia University, New York, New York 10027

The surface properties of a polydisperse poly(vinycaprolactam) (48 kDa) have been studied at the air/water and hexane/water interfaces. Adsorption of the polymer at both interfaces shows substantial time-dependent surface tension lowering at remarkably low concentrations in the aqueous phase. This adsorption is increased by addition of electrolyte, which also lowers the lower consolute temperature (LCT) of the polymer in solution. Adsorption is endothermic, corresponding with the approach to the LCT as the temperature is raised. Spreading of the polymer at the air/water interface from aqueous solutions is near quantitative. The surface pressure−area isotherms indicate extensive coiling in the monolayer at low pressures and looping of the polymer monolayer into the aqueous phase in the higher pressure range.

Poly(vinyllactams), including poly(vinyl-2-pyrrolidone), poly(vinyl-2-piperidone), and poly(vinylcaprolactam) (PVCAP) form a class of nonionic water-soluble polymeric cyclic amides. The advantageous properties of these polymers, such as good resistance to hydrolysis[1] and the formation of complexes with dyes and proteins[2] have become of increasing industrial interest. The polymer nitrogen atoms are p-electron donors capable of strong hydrogen bonding with water molecules, so that the compounds are soluble in water.[3] PVCAP is distinguished by its complete miscibility with water at low temperatures and phase separation at higher temperatures with a lower consolute temperature (LCT) at 32 °C.[4] Like other polymeric lactams, PVCAP is characterized by a high density of amide groups near the aliphatic chain and can therefore serve in some respects as a model for the hydration of amide groups and hydrophobic interactions in the solvation of proteins.[5] Studies on those polymers to date have emphasized their solution and phase separation properties, with most publications focused on poly-(vinyl-2-pyrrolidone).[1]

In this work, we investigated the interfacial properties of PVCAP at the air/water and paraffin/water interfaces by measuring interfacial tensions, using Wilhemy plate and drop volume methods, and observing the effects of electrolytes and temperature. The spread monolayer behavior of PVCAP at the air/water interface was also studied by measuring the surface pressure−area isotherm at 23 °C using a Langmuir balance.

Experimental Section

Materials. The poly(vinylcaprolactam) was provided by International Specialty Products, Inc. The polymer as supplied was precipitated twice by addition of acetone to concentrated aqueous solutions of the polymer at room temperature and drying the precipitate under vacuum. The number average molecular mass of the purified polymer, determined by gel permeation chromatography (GPC) using a multiangle light scattering detector, was 48 kDa with a polydispersion ratio of 2.68. The polymer is denoted as PVCAP48. The water was triple distilled, the second distillation from alkaline permanganate. The hexane was a spectroscopic grade and used as supplied.

Methods. The surface tension was measured using both the Wilhelmy method with a platinum plate coupled to a Cahn microbalance and the drop volume method with the Harkins and Brown corrections.[6] The drop volume method was used to confirm that contact angle effects on the surface tension as measured by the plate did not occur in the high concentration range of the polymer. The surface pressure (Π) and the corresponding surface area (*A*) of spread monolayers of PVCAP were measured with a Teflon Langmuir surface balance. The monolayer was spread from an aqueous solution of the polymer by expressing aliquots from a microsyringe down a glass rod dipping into the water, a technique found useful for spreading monolayers of water-soluble polymers such as proteins. The surface pressure was measured with a platinum Wilhelmy plate to a sensitivity of 0.01 mN m^{-1} with the Cahn balance. At the larger areas the reproducibility was ± 0.02 mN m^{-1}. After spreading to a chosen density, the area was reduced stepwise and the pressures were read after stabilizing, requiring a few minutes at low pressures and up to 10 min at the higher pressures before definite monolayer dissolution. After first being compressed to 15−16 mN m^{-1}, the monolayer was expanded stepwise, recording the steady pressures observed in times similar to those in the compression. The diffusion coefficient of PVCAP48 in aqueous solution was measured by inhomogeneous field NMR over a range of concentrations.

Results and Discussion

Interfacial Tension. Measurements of the surface tension of water over the temperature range reported here agreed well with the values in the tabulation of Vargaftik et al.[7,8] Figure 1 shows the surface tension of aqueous PVCAP48 solutions as a function of concentration and

* Corresponding author.

(1) Eisele, M.; Burchard, W. *Makromol. Chem.* **1990**, *191*, 169.
(2) Kirsh, Y. E. *Prog. Polym. Sci.* **1993**, *18*, 519.
(3) Tager, A. A.; Safronov, A. P.; Sharina, S. V.; Galaev, I. Y. *Colloid Polym. Sci.* **1993**, *271*, 868.
(4) Kirsh, Y. E.; Krylov, A. V.; Belova, T. A.; Abdel'sadek, G. C.; Pashkin, I. I. *Russ. J. Phys. Chem.* **1996**, *70*, 1302.
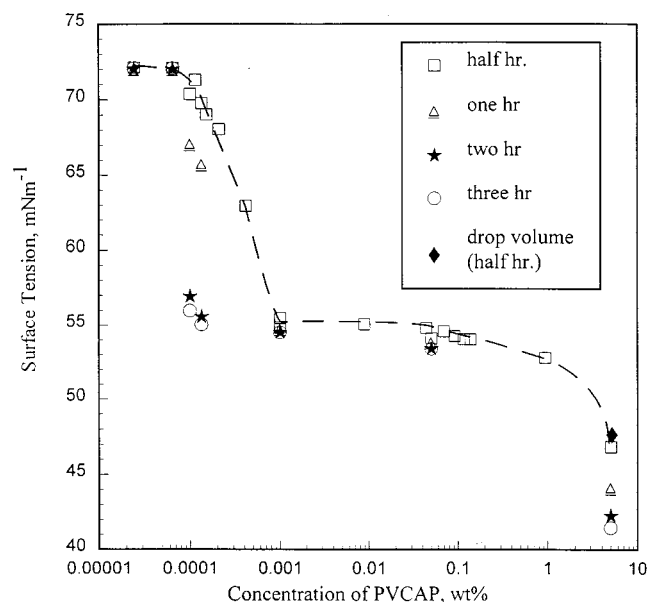(5) Brandts, J. F. In *Structure and Stability of Biological Macromolecules*; Stewart, J., Young, J., Eds.; Marcel Dekker: New York, 1969.

(6) Harkins, W. D. In *The Physical Chemistry of Surface Films*; Reinhold: New York, 1954; p 71.
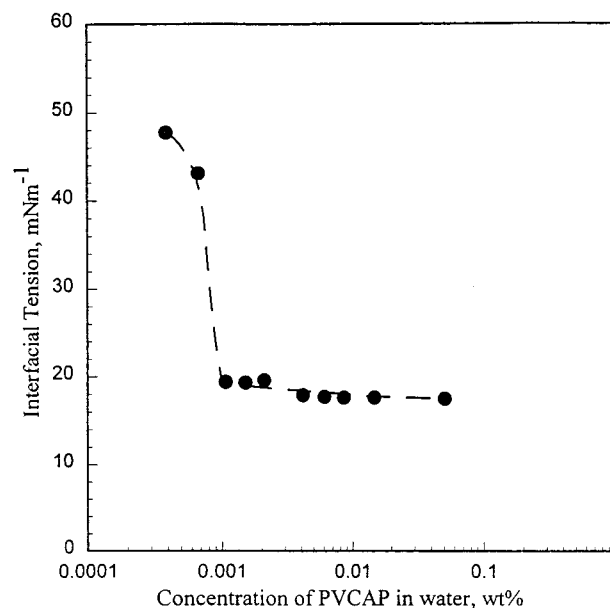(7) Pallas, N. R.; Pethica, B. A. *Colloids Surf.* **1983**, *6*, 221.
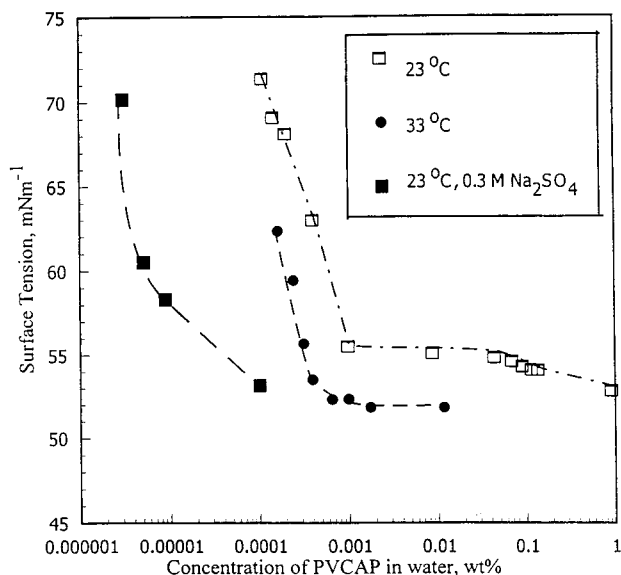
Figure 1. Surface tension of PVCAP at the air/water interface. All tensions at 30 min.

Figure 2. Surface tension of PVCAP at the air/water interface at 23 °C. The time effect.

temperature and the effect of addition of 0.3 m Na_2SO_4, all taken 30 min after formation of the interface. It can be seen that the (negative) slope of the plot of surface tension against log(concentration) increases with concentration in the very dilute range. Above about 0.001 wt % PVCAP48 in water, this slope decreases sharply, reminiscent of the equilibrium surface tension−concentration profiles seen with typical surfactants at the micelle point. However, the sharp change of slope moves to much lower concentrations when surface tensions at longer times are recorded (Figure 2). Possible aggregation is quite ruled out by the NMR measurements, which gave a constant diffusion coefficient at room temperature corresponding to the known molecular weight over the concentration range up to 0.05 wt %. This result argues

(8) Vargaftik, N. B.; Volkov, B. N.; Voljak, L. D. *J. Phys. Chem. Ref. Data* **1983**, *12*, 817. These data are also given in abbreviated form in: *The Handbook of Physics & Chemistry*, 75th ed.; CRC Press: Boca Raton, FL, 1995.

Figure 3. Interfacial tension of PVCAP at the hexane/aqueous solution interface using the drop volume method at 23 °C. All tensions measured at 30 min.

against any interpretation of the time-dependent surface tensions at long or short times in terms of molecular association of the polymer in solution, at least at 10 °C below the LCT.

The striking feature of the long-term surface tension results is the large reduction over time at very low polymer concentrations. For a given concentration of PVCAP48, the surface pressure of the adsorbed monolayer increases as the temperature is raised or on addition of sodium sulfate to the solution. The temperature effect indicates endothermic adsorption. Since the addition of salt lowers the LCT, the effect either of raising the temperature or of addition of salt correlates with the approach to phase separation as the temperature is raised or Na_2SO_4 is added at constant temperature. At the hexane/aqueous solution interface, the decrease of the interfacial tension with concentration after 30 min follows the same trend as the surface tension at the air/water interface (Figure 3). Interfacial tensions at longer time intervals were not pursued.

Spread Monolayer Behavior. The formation of "insoluble" monolayers of water-soluble proteins by direct spreading of aqueous solutions at the air/water interface is well-known. The films are often practically persistent over a range of surface pressures and densities. The method has been used to estimate molecular weights of proteins.[9,10] If the molecular weight of a soluble polymer is known, the low-pressure region of the isotherm of the spread polymer can be used to estimate the spreading efficiency and hence infer the packing density in the monolayer. Figure 4 shows the surface pressure−area ($\Pi-A$) isotherm of PVCAP48 at the air/water interface at 23 °C. Compression was stopped at about 16 mN m^{-1} where the pressure was observed to decrease indefinitely after compression, indicating loss of polymer from the monolayer to the water phase. The minor hysteresis shown on Figure 4 indicates good retention of the monolayer over the range studied. Analysis of the data in the low-pressure range shows that the spreading method
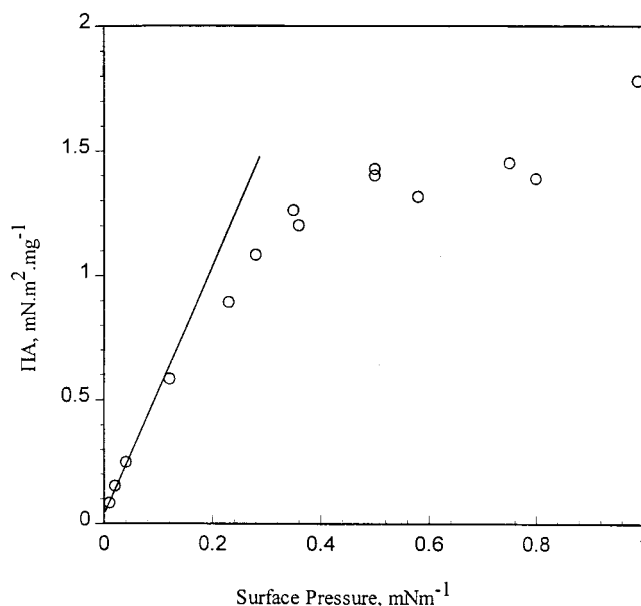
(9) Cheeseman, A. D.; Davies, J. T. *Adv. Protein Chem.* **1954**, *9*, 439.
(10) Zhou, N. F.; Pethica, B. A. *Langmuir* **1986**, *2*, 47.
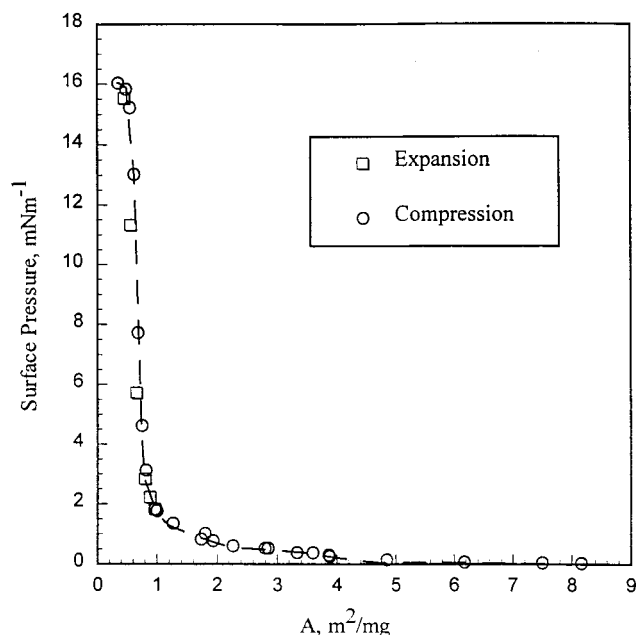
Figure 4. Surface pressure against area isotherm for PVCAP at the air/water interface at 23° C.

Figure 5. Plot of ΠA vs Π for PVCAP monolayer at the air/water interface in the low-pressure range.

gives near-quantitative delivery of the polymer to the surface. The plot of ΠA against Π (Figure 5) is consistent with an initial linear region at low pressures with an intercept corresponding to a number average molecular weight of 50 ± 5 kDa, compared to 48 kDa from GPC. Measurements at a higher pressure sensitivity are required to be more precise. The surface second virial coefficient of the polymer was also estimated from the limiting slope of the plot shown in Figure 5 to give a value of 1.25 nm²/monomer subunit. This large positive value shows that repulsive forces predominate at low pressures, probably due to chain coiling—giving a large excluded volume term and reduced van der Waals interaction between the polymer subunits[11]—and possibly from repulsions between the large amide dipoles aligned in adjacent folded chain segments. As the pressure increases

to about 0.4 mN m⁻¹, the shape of the isotherm suggests a higher order transition to a closer packing. At pressures close to 16 mN m⁻¹ the area corresponds to 0.1 nm²/monomer, indicating substantial looping into the aqueous phase.

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(11) Pethica, B. A.; Glasser, M.L.; Mingins, J. *J. Colloid Interface Sci.* **1981**, *81*, 41.