Colloid Polym Sci 280:203–205 (2002)

SHORT COMMUNICATION

**J. Hong**
**R. Pelton**

# The surface tension of aqueous polyvinylamine and copolymers with *N*-vinylformamide

Received: 20 August 2001
Accepted: 26 September 2001

J. Hong · R. Pelton (✉)
McMaster Centre for Pulp and Paper Research, Department of Chemical Engineering, McMaster University
1280 Main Street West, Hamilton
Ontario Canada
e-mail: peltonrh@mcmaster.ca

**Abstract** The surface tensions of aqueous poly(*N*-vinylformamide) (PNVF), polyvinylamine (PVAM), and PNVF–PVAM copolymers were measured as functions of pH. The nonionic PNVF gave a pH-independent surface tension of 68 mN/m. The surface tension of PVAM was pH dependent; at pH 10 it was 56 mN/m, whereas it was 71.5 mN/m at pH 3.5. The transition from higher to lower surface tension values occurred most dramatically between pH 8 and 9, reflecting the dissociation behavior of the amine groups. The copolymers showed intermediate behavior.

**Keywords** Polyvinylamine surface tension · Polyamine · Poly(*N*-vinylformamide) hydrolysis · Aqueous polymer surface tension · pH-dependent surface tension

## Introduction

Primary amine functional groups in water-borne polymers are important reactive basic centers in both biopolymers and synthetic industrial polymers. Although linear polyvinylamine (PVAM) is one of the simplest synthetic amine-containing polymers [1], it received little attention before the 1990s because it was relatively difficult to make. In the last few years the preparation of PVAM from the polymerization and subsequent hydrolysis of poly(*N*-vinylformamide) (PNVF) has been described in the patent literature [2, 3] and commercial sources of the polymer are coming on stream this year. Increased availability means that PVAM will be evaluated in many potential applications in the next few years. In new applications where wetting or foaming issues are important, the surface tension behavior of aqueous PVAM may be a significant property. Maggio et al. [4], as part of a surfactant binding study, reported that the surface tension of PVAM solutions at pH 5 was essentially that of water over a wide range of polymer concentrations. We have found no other published information about the surface tension of PVAM.

Here we report the surface tension of PVAM and its copolymers with vinyl amide as a function of pH. The surface activity increased with pH and the number of amide groups.

## Experimental

Analytical grade solvents were used as received. Millipore-Q water was used for all the experiments. *N*-Vinylformamide (NVF, 98%) from Aldrich was purified by distillation under vacuum at 70 °C to give clear colorless liquid. Sorbitan monostearate (Span 60) also from Aldrich was used as received. 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized in ethanol before use.

Water-soluble PNVF was prepared by the precipitation polymerization of NVF using a free-radical polymerization initiator, AIBN [5]. The polymerization was carried out in a three-necked 500-ml glass reactor, equipped with an impeller stirrer (750 rpm) and continuously purged with nitrogen. The reactor was immersed in a NESLAB water bath at 62 °C. Following the work of Gu et al.

[3], 30.8 g NVF, 3.00 g Span 60 and 190 g toluene were added in sequence. After reaching a steady-state temperature, 0.031 g AIBN dissolved in 10 g toluene was injected into the reactor. The ratio of NVF to Span 60to AIBN was 1000:100:1. The mixture was stirred under nitrogen for 8 h, yielding a white precipitate. The product was washed in methanol six times by filtration to remove the solvent, toluene, and unreacted monomer. The resulting polymer, PNVF, was vacuum dried at 20 °C for 48 h.

Three samples of PNVF, 10 wt%, were hydrolyzed in a 1.30 molar excess of 36.5% aqueous hydrochloric acid (BDH) at 75 °C with vigorous stirring. The hydrolysis times were 0.5, 1 or 70 h giving 56, 82 and 100% conversion of formamide to amino groups. The polymers were precipitated with methanol and vacuum dried.

The molecular-weight distribution of PNVF was obtained by gel permeation chromatography using a Waters 2410 differential refractive index detector and a Waters 2690 separations module with three Waters ultrahydrogel TM linear columns. The system was calibrated with polyacrylamide (PAM), using 0.05 N $NaNO_3$ as a solvent with a flow rate of 0.8 $cm^3$/min at 30 °C. The calibration curves were determined from PAM (Polyscience) at various standard molar masses of 12,000, 22,000, 65,000, $4 \times 10^5$, $6 \times 10^5$ and $10^6$ Da.

The degree of hydrolysis of PNVF was determined by $^1H$ NMR and by polyelectrolyte titration with potassium poly(vinyl sulfate), Details of the methods have been reported elsewhere [6].

The surface tensions were determined by the pendant drop method using a Kruss v1.50 drop shape analyzer, equipped with an environmental chamber. The relative humidity and temperature in the chamber were maintained at 100% and 25 °C. The drop volumes were 20 ± 0.5 $\mu$l. The polymer solution concentrations were 7 g/l, which gave steady-state surface tension values within 10 min of drop formation.

## Results and discussion

Three samples of PNVF, $M_w = 5 \times 10^5$ Da, were hydrolyzed to different extents giving PVAM and two intermediate copolymers of vinylamine and vinylformamide. The surface tension as a function of pH for the four polymers is shown in Fig. 1. The nonionic PNVF gave a pH-independent surface tension of 68 mN/m, a value higher than that of poly(ethylene oxide) (58 mN/m [7]) but nearly identical to PAM (69 mN/m [8]). The surface tension of PVAM was pH dependent: at pH 10 it was 56 mN/m, whereas it was 71.5 mN/m at pH 3.5. The transition from higher to lower surface tension values occurred most dramatically between pH 8 and 9, reflecting the dissociation behavior of the amine groups.

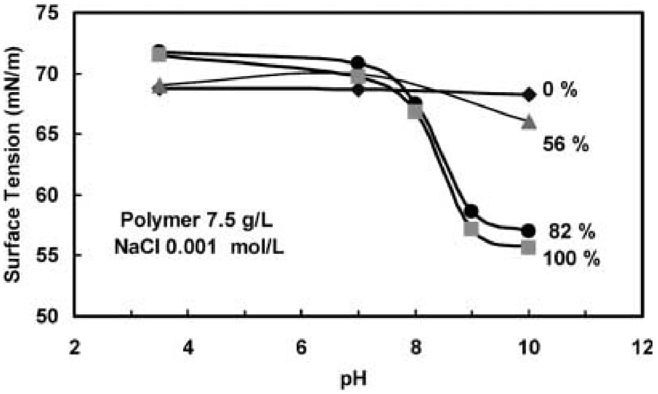

**Fig. 1** Surface tension as a function of pH. The *labels* denote the degree of poly(*N*-vinylformamide) (*PNVF*) hydrolysis; thus, 100% corresponds to pure polyvinylamine

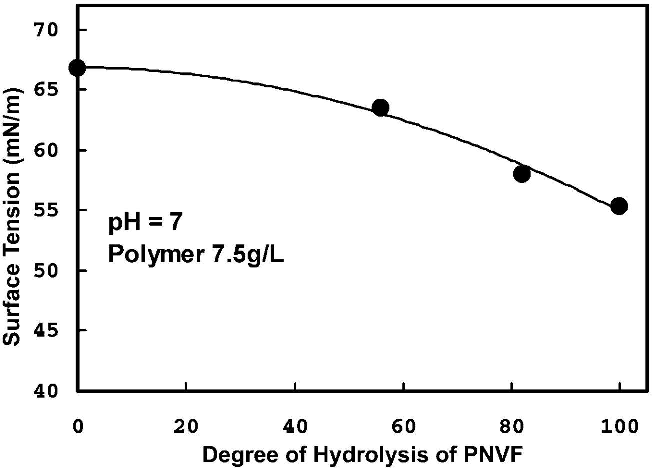

**Fig. 2** The influence of polymer composition on surface tension at pH 7

Many potentiometric titration curves have been reported for PVAM [9]. This interest arises from the very strong polyelectrolyte effect observed. That is, the apparent p$K_a$ is a strong function of the degree of protonation. Kobayashi et al. [10] fitted their titration results in 1 mol/l KCl to Eq. (1), where p$K_a$ = 8.58, $m$ = 5.35 and $\alpha$ is the degree of dissociation. Thus, the apparent p$K_a$ at half neutralization, 8.58, is close to the steepest part of the PVAM titration curve in Fig. 1. On the basis of the results of Kobayashi et al., Eq. (1) predicts that the degree of dissociation at pH 10 will be 0.35; however, the electrolyte concentration was 3 orders of magnitude lower in our experiments ($10^{-3}$ versus 1 mol/l), so probably in our case most of the amine groups at pH 10 were deprotonated.

$$\mathrm{p}K_\mathrm{a} = \mathrm{pH} - m \log\left(\frac{1-\alpha}{\alpha}\right) \qquad (1)$$

The copolymers demonstrated intermediate behavior. The surface tension is shown as a function of the degree of hydrolysis at pH 7 in Fig. 2. The surface tension decreased monotonically with the increasing number of amine groups. Note that there was no added electrolyte, so the effects are greater than for the results shown in Fig. 1.

In summary, in a charged state PVAM is not surface active. Uncharged (unprotonated) PVAM is somewhat more surface active, giving values about the same as poly(ethylene oxide).

**Acknowledgement** The authors acknowledge the Wood Pulps Network in the Canadian National Centres of Excellence Program for financial support.

## References

1. Jones GD, Zomlefker J, Hawkins K (1944) J Org Chem 9:500
2. Yokohama TI, Machida MS, Yokohama SS, Zama KS (Mitsubishi, Japan) (1991) US Patent 5,064,909
3. Gu L, Zhu S, Hrymak AN, Pelton RH (2001) Polymer 42:3077–3086
4. Maggio SV, Presken DV, Lochhead RY (1999) Polym Prepr Am Chem Soc Div Polym Chem 40:242–243
5. Badesso RJ, Lai TW, Pinschmidt RK Jr, Sagl DJ, Vijayendran BR (1991) Polym Prepr Am Chem Soc Div Polym Chem 32:110–111
6. Hong J (2001) MEng thesis. McMaster University
7. Kim MW (1997) Colloids Surf A 128:144–154
8. Hai M, Han B, Yan H, Han Q (1998) J Chem Eng Data 43:1056–1058
9. Katchalsky A, Mazur J, Spitnik P (1957) J Polym Sci 23:513–532
10. Kobayashi S, Suh K, Shirokura Y (1989) Macromolecules 22:2363–2366