

Effect of the carboxylate group distribution on potentiometric titration of acrylamide-acrylic acid copolymers

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SUMMARY

The potentiometric behavior of acrylamide-acrylic acid copolymers is discussed as a function of their method of preparation: base hydrolysis of polyacrylamide or radical copolymerization. The values of pK_0 (the intrinsic pK at zero degree of ionization) and the variations of pK_a versus the ionization degree are found to depend on the origin of the polymers and such differences are qualitatively attributed to significant discrepancies in the carboxylate group distribution.

INTRODUCTION

In previous papers, we have compared, using ^{13}C n.m.r. spectroscopy, the microstructure of acrylamide-acrylic acid copolymers obtained either by base hydrolysis of polyacrylamide or by copolymerization of the two corresponding monomers^(1,2). The number average lengths of acrylamide and acrylate sequences are always higher for copolymerization products (whatever the pH of the reaction may be) than that found in samples obtained by base hydrolysis (see fig.1). It is well known that the polyacrylamide base hydrolysis obeys auto-retarded kinetics and sodium acrylates tend to be incorporated along the chain as isolated groups. One could expect from such differences some discrepancies in the behavior of these copolymers in aqueous solution.

For instance, we have already shown that their stability in aqueous solution in presence of Ca^{++} cations must be correlated with their microstructure⁽³⁾. In the case of radical copolymers, the binding of Ca^{++} on two adjacent carboxylate sites is favoured by the presence along the chain of short blocks of acrylate. Their stability is then much poorer than that of hydrolysis products.

The purpose of the present paper is to show that the microstructure of the copolymers also plays an important role on their potentiometric behavior.

EXPERIMENTAL

Three series of copolymers were used:

-commercial series "AD" (from Rhone-Poulenc) of polymers obtained by radical photopolymerization at high pH, of high molecular weight ($M_w = 5 \cdot 10^6$)

- series of copolymers "H" obtained by base hydrolysis of a polyacrylamide of $M_w = 5 \cdot 10^6$

- series of low molecular weight copolymers "CP" ($M_w = 2 \cdot 10^4$ to $5 \cdot 10^4$) prepared by radical copolymerization at low pH.

The fraction r of acrylate of the copolymers is given in table 1.

These samples have been studied by ^{13}C n.m.r. spectroscopy under conditions already described^(1,2).

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Potentiometric titration: The sodium acrylate-acrylamide copolymers were acidified in solution on excess cationic resin exchangers (Class I, Merck). The acidified samples were precipitated in methanol-ethanol mixture and dried during 24 hours at 40°C under vacuum. All the titrations by 0.01 M NaOH solutions, were performed in pure water at a same carboxylic acid concentration (7 to 8 10^{-4} M/L) without adjusting the ionic strength of the solution, in 2 cm³ cells thermostated at 25 ± 0.1 °C, under argon atmosphere. We used a Metrohm pH meter, model 605 fitted with a microglass combined electrode (Metrohm EA125) and an automatic microburette (multidosimat 645). Data treatment was carried out according to the Wolf-Fortuin method⁽⁴⁾.

RESULTS AND DISCUSSION

In fig.1, the microstructure of polymers obtained by copolymerization is compared with that of hydrolysis products, in terms of fractions of acrylamide (MMM) and acrylate (AAA) triads. It is obvious that copolymerization favours a sequential distribution. There is no acrylate triads in the hydrolyzed samples, when τ is lower than 35%.

The apparent ionization constant K_a of a polymeric weak acid changes with the degree of ionization α because the ionization of an acid group must be accompanied by electrostatic work done against the charges already present on the molecule. In general, the pK_a of such an acid is given in terms of the changes of electrostatic free energy G_{e1} accompanying the ionization process by the expression.:

$$pK_a = pK_0 + \frac{0.434}{RT} \left(\frac{\partial G_{e1}}{\partial z} \right) = pK_0 + \Delta pK_a \quad (1)$$

K_0 is the intrinsic dissociation constant of a carboxylic acid group and z is the charge number on the polyion.

Mandel⁽⁵⁾ has suggested to adjust the experimental variations of pK_a by a second degree polynomial function

$$pK_a = pK_0 + \Phi_1 \alpha + \Phi_2 \alpha^2 \quad (2)$$

The results of this fit are reported in table 1.

1) Discussion on pK_0

In figure 2, the variations of pK_0 are plotted versus τ . Whatever the origin of the samples may be, pK_0 appears as an increasing function of τ and for a given value of τ , it is higher for samples AD and CP than for samples H. The extrapolation at $\tau = 0$ gives for the three polymer series $4 < pK_{00} < 4.2$ and the pK_0 of polyacrylic acid is much higher: 5.1⁽⁶⁾. These results are in good agreement with those of Lainé et al.⁽⁶⁾ who have investigated the potentiometric behavior of same copolymers obtained by hydrolysis. One could expect a value of pK_{00} very close to that obtained for a low molecular weight acid in absence of electrostatic effect: in fact, it is lower than that of acetic acid ($pK_a = 4.76$) and nearly equal to that of acrylic acid ($pK_a = 4.25$). It is well known that the intrinsic dissociation constant of the carboxylic acid depends on the nature of its chemical neighbourhood and such an effect is probably particularly pronounced when the function is incorporated along a polymeric chain. This result shows that the intrinsic pK_0 of the acid function in these copolymers is approximately 4 when the acrylic unit is surrounded by acrylamide groups and it increases if one or two neighbouring groups are

acrylic units. In copolymers AD and CP, the probability of finding AAA triads is higher than for H samples and this difference induces a higher value of pK_0 .

table 1

sample	pK_0	Φ_1	Φ_2	$\tau(\%)$
AD17	4.82	0.003	0.495	7
AD27	5.04	0.384	0.513	17
AD60	5.48	0.893	0.41	36
H ₁	4.09	0.576	0.611	5
H ₂	4.38	0.691	0.351	9
H ₃	4.41	2.30	- 0.759	19
H ₄	4.80	2.08	- 0.505	36
CP ₁	4.45	0.460	0.650	5
CP ₂	4.59	0.584	0.651	9
CP ₃	4.90	1.143	0.045	17
CP ₄	4.89	1.538	- 0.244	21
CP ₅	5.16	1.713	- 0.395	30

2) discussion on the variation of ΔpK_a with α

In figure 3 we have reported the variations of ΔpK_a as a function of α , for the three series of copolymers and for different given values of τ . The ΔpK_a values have been obtained from results of table 1, by considering, as above discussed, that the changes of pK_0 with the composition and microstructure of the polymer cannot be neglected and constitute a true physical phenomenon. Laine et al.⁽⁶⁾ have considered a constant value of pK_0 , arbitrary taken equal to that of acetic acid (4.76). Our results show that the changes of pK_a with α is also strongly dependent on the origin of the samples: the highest increase of ΔpK_a is obtained with polymers prepared by hydrolysis and the lowest is observed with copolymers of series AD, whatever the value of τ may be. However the biggest discrepancies between the results occur for $\tau = 17\%$.

The literature gives several attempts to determine the variation of the electrostatic free energy with the polyion charge (second term of relation 1). For instance:

a) in the model of expanded coil, the expression proposed by Katchalsky and Lifson⁽⁷⁾ is:

$$\frac{\partial G_{e1}}{\partial z} = \frac{2\alpha r e^2}{D b} \log \left(1 + \frac{6}{\kappa s b} \right) \quad (3)$$

where e is the elementary charge, s the number of monomers per statistical element of the chain, κ^{-1} the screening length of Debye, b the distance between two consecutive charges and D the dielectric constant

b) in a model of rodlike chain^(8,9), the polyion is represented by a long impenetrable rod of radius a with the charges uniformly smeared over its surface. It is assumed that polyions are parallel and equally spaced at a distance $2R$. Lifson et al.⁽⁸⁾ have calculated the electrostatic free energy and an expression of $\partial G_{e1}/\partial z$ versus a charge parameter λ can be obtained:

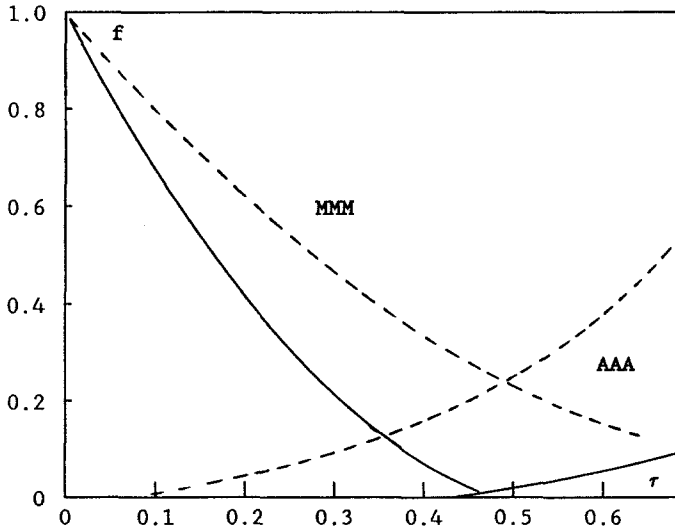


Fig.1: Variation of the acrylamide (MMM) and acrylate triads (AAA) as a function of acrylate content τ , for polymers obtained by copolymerization (- - -) and by base hydrolysis (—). Curves adjusted from ^{13}C n.m.r. results of ref. 1 and 2

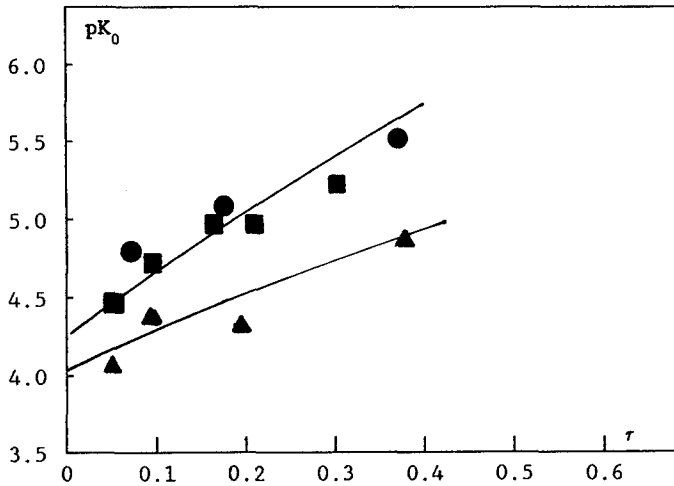


Fig.2: Variation of pK_0 as a function of acrylic content τ copolymers of series AD (●), H (▲) and CP (■)

$$\frac{\partial G_{a1}}{\partial z} = 2\lambda \log \left(\frac{R}{a} \right) + \log (1 - \lambda) - \log \left(\frac{1 - \lambda/2}{1 - \lambda} \right) \quad (4)$$

with
$$\lambda = \frac{\alpha r e^2}{D b k T} \quad (5)$$

The variations of ΔpK_a calculated from relations (1) and (3) or (4) are compared with the experimental results, in figure 3. It turns out:
 i) both models based on uniform charge distribution cannot be able to predict the influence of the origin of the materials on their potentiometric behavior.

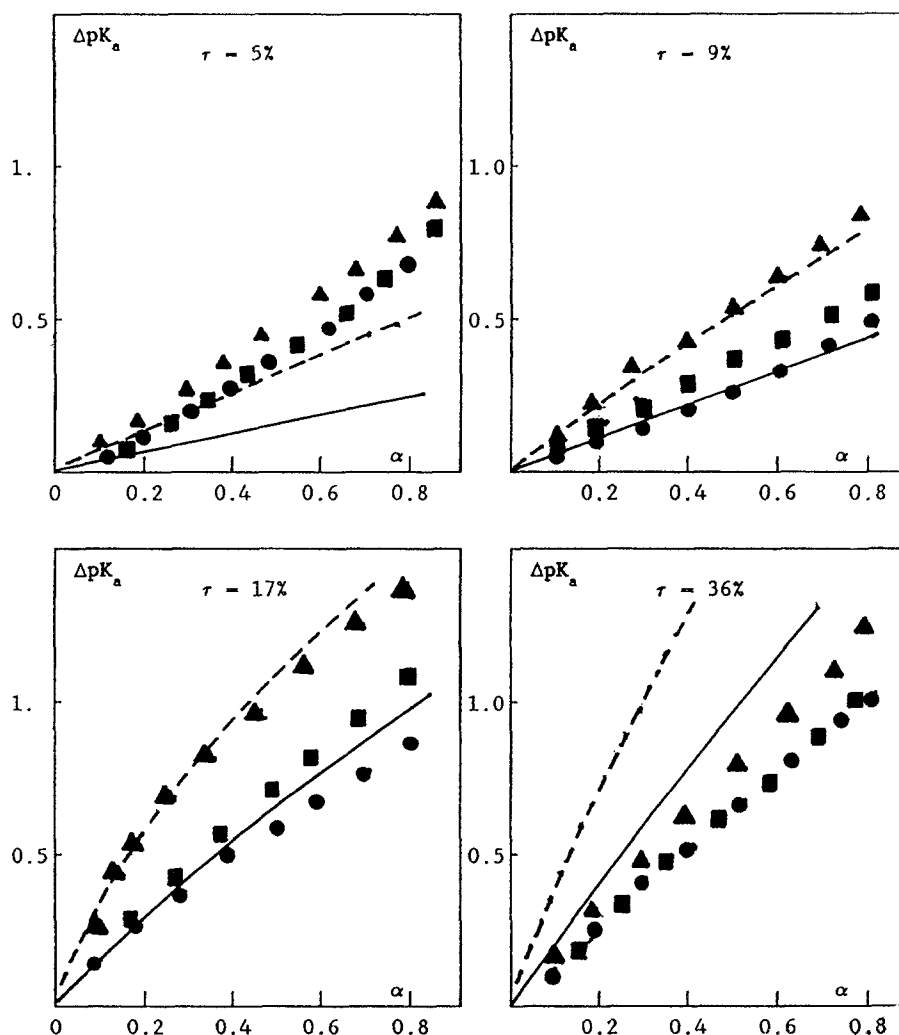


Fig.3: Calculated and experimental variations of ΔpK_a as a function of ionization degree α for different values of the acrylate fraction τ in the copolymers: (- - -) expanded coil model , (———) rodlike model (●) series AD, (▲) series H, (■) series CP

ii) the expanded coil model gives values of ΔpK_a generally higher than the rodlike chain model

iii) both models underestimate ΔpK_a for low values of r , overestimates it for high values of r ($r > 20\%$) and the best agreement is obtained for $r = 17\%$.

We attribute all these observations to the effects of the distribution of the charged groups along the chain. Manning et al.⁽¹⁰⁾ have shown that the ionic condensation phenomenon has a drastic effect on the slope of the curves $\Delta pK_a = f(\alpha)$: this average slope is expected to become approximately 10 times lower for charge parameter λ varying beyond λ^* than for $0 < \lambda < \lambda^*$. (λ^* is the critical value of λ beyond which ionic condensation occurs, $\lambda^* = 1$ for monovalent counterions). In fact a series of experimental results obtained on polyacrylic or polymethacrylic acid^(11,12) do not show this abrupt change in the variations of $\Delta pK_a = f(\alpha)$ for $\lambda = \lambda^*$, and Manning et al.⁽¹⁰⁾ deduce that condensation takes probably place more progressively and is effective even for $\lambda < \lambda^*$. On the other hand, this theory also uses a model of uniform charge density along the polyion. Although the charge parameter of all copolymers studied in this work does never exceed λ^* , it has been shown by Zema et al.⁽¹³⁾ that the ionic condensation cannot be neglected. These authors show that the activity coefficient of Na^+ for a series of hydrolyzed polyacrylamide in the same range of r is always much lower than the value predicted by Manning⁽¹⁴⁾ for $\lambda < \lambda^*$.

Such an excess of condensation may be due to the presence of acrylate sequences more or less pronounced according to the copolymer preparation. It should be useful to develop a theoretical approach taking into account not only the average charge density but also all the details of the microstructure. Such an approach could be based on the previous attempts to calculate the neighbouring effects⁽¹⁴⁻¹⁶⁾.

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