On the Kinetics of Polyacrylamide Alkaline Hydrolysis

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Received January 6, 1998
Revised Manuscript Received March 3, 1998

Introduction

Alkaline hydrolysis of polyacrylamide (PAM) proceeds with a pronounced retardation and, under mild conditions, almost ceases near 40−50% conversion. The retardation is usually interpreted in terms of the nearest neighbor effect due to the electrostatic repulsion between $-COO^-$ groups formed and hydroxyl ions catalyzing the reaction[1−4] (also a certain change of OH^- ion activity has been considered[5]). Various approximate equations[4−6] were used to describe the kinetics.[3,4]

Sawant and Morawetz[2] were the first who employed correct Keller's equations[7] to describe the reaction kinetics in the framework of neighbor effect model. The equations contain three individual rate constants k_0, k_1, and k_2 characterizing the reactivity of amide groups with 0, 1, and 2 neighboring carboxylate groups, respectively. Using polymer models (statistical copolymers acrylamide−acrylic acid of various composition), the authors[2] estimated the rate constant values (k_0:k_1:k_2 = 1:0.11:0.013) and found that the calculated kinetic curve did not fit the experiment. Moreover, they showed that even for the maximum retarding effect k_0:k_1:k_2 = 1:0:0 calculations predicted a greater reaction rate than observed in their experiments.

Then Sawant and Morawetz[2] tried another approach. They supposed that more remote units, not only the nearest ones, also affect the reactivity of any amide group. Only one rate constant dependent on the total charge of a macromolecular coil was introduced. Following the ideas of Katchalsky et al.,[8,9] they assumed that (a) the concentration of OH^- ions near the charged coil is exponentially small in comparison with their bulk concentration and (b) the electrostatic work W_{el} required to bring a hydroxyl ion to any amide group of a charged reacting PAM coil (in alkaline medium) against the polyion repulsion is the same as that to remove a hydrogen ion from poly(acrylic acid) (PAA) with the same charge density. Using Mandel data on the PAA titration,[10] they obtained the equation $k/k^0 = \exp[-2.3(0.9\alpha + 0.6\alpha^2)]$ describing the rate constant dependency on a conversion degree α, where k^0 is the initial rate constant of hydrolysis of uncharged PAM. The equation described well a dependency of the initial rate constants of hydrolysis of random copolymers acrylamide−acrylic acid on copolymer composition; however, "it completely failed to predict the rapid decrease of the rate of polyacrylamide hydrolysis".[2]

It should be mentioned that the authors of ref 2 were aware of the fact that neither of the two alternative approaches would work. In their concluding remarks they wrote: "it is reasonable to assume that the three parameters k_0, k_1, k_2 are also functions of the overall polymer charge". Putting it in other words, they pointed out that the *separate* treatment of retarding action of the nearest and more remote units on the reaction rate could not fit experimental data.

Our idea is to propose a model *combining* the nearest neighbor effect with the effect of a charged coil. This model demonstrates its efficiency to describe quantitatively the kinetics of PAM hydrolysis. According to ref 11 the data concerning both the reaction kinetics and units distribution in the chain formed are necessary to elucidate peculiarities of a macromolecular reaction. The only publication containing the proper information is the paper of Truong et al.[3] So we used their results to test both the model of the pure neighbor effect and our model.

Results

Pure Neighbor Effect. Truong et al.[3] studied hydrolysis of PAM ($M_w = 6 \times 10^6$) at 50 °C for the following reagents concentrations: [PAM] = 0.1 M, [NaOH] = 0.25 M, [NaCl] = 0.1 M. Using ^{13}C NMR spectroscopy, they estimated the fractions of various triads in the hydrolyzed polymer and described their dependency on conversion in terms of the neighbor effect. Also, the initial rate constant has been estimated; however the reaction kinetics was not calculated. In this section we use Keller's equations for neighbor effect corrected for experimental conditions[3] to describe Truong's data concerning the reaction kinetics.

Let ψ_0, ψ_1, and ψ_2 be the fractions of amide groups (A) with 0, 1, and 2 neighboring carboxylate groups (B), respectively. As the initial concentrations of polymer and alkali were of the same order of magnitude in ref 3, the well-known Keller's equations[7] are to be modified to account for the decay of alkali

$$\dot{\psi}_0/[OH^-] = -(k_0 + 2\bar{k})\psi_0$$

$$\dot{\psi}_1/[OH^-] = -(k_1 + \bar{k})\psi_1 + 2\bar{k}\psi_0$$

$$\dot{\psi}_2/[OH^-] = -k_2\psi_2 + \bar{k}\psi_1 \qquad (1)$$

where $\bar{k} \equiv (2k_0\psi_0 + k_1\psi_1)/(2\psi_0 + \psi_1)$ and $[OH^-] = [OH^-](t)$ is a current concentration of hydroxyl ions.

Taking into account the decay of hydroxyl ions in the neutralization of carboxylic groups formed, we may write

$$[OH^-] = [OH^-]_{t=0} - (\alpha(t) - \alpha(0))[A]_{t=0} \qquad (2)$$

where $\alpha(t) \equiv 1 - \psi_0 - \psi_1 - \psi_2$ is a conversion of amide groups and $[A]_{t=0}$ is the initial concentration of these groups.

Truong et al.[3] described the changes of A(amide)-centered triads [AAA], [AAB*] = [AAB] + [BAA], and [BAB] fractions with conversion. They found that the ratios of the rate constants k_0:k_1:k_2 = 1:0.2:0.01 satisfactorily fit NMR data.

To evaluate the reaction kinetics, we solved eqs 1 and 2 numerically with the initial conditions $\psi_0(0) = 1$ and $\psi_1(0) = \psi_2(0) = 0$ using the relation k_0:k_1:k_2 = 1:0.2:0.01 and the value $k_0 = 5.8 \times 10^{-4}$ L·mol^{-1}·s^{-1} found in ref 3.

S0024-9297(98)00016-3 CCC: $15.00
Published on Web 06/20/1998

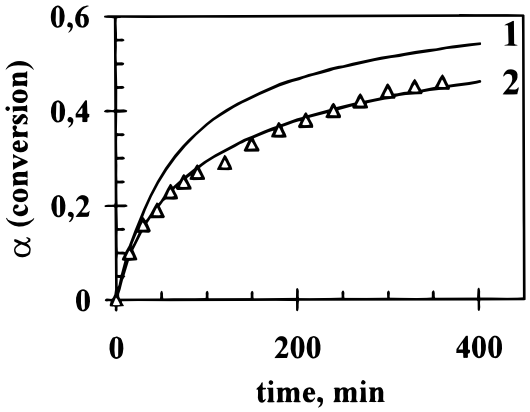

Figure 1. Kinetics of polyacrylamide alkaline hydrolysis: (△) - experimental data of Truong et al;[3] (curves) predictions of the pure neighbor effect model (1) and of the model combining the neighbor effect with the effect of a charged coil (2). See text for explanations.

The kinetic curve $\alpha(t) = 1 - \psi_0 - \psi_1 - \psi_2$ is plotted in Figure 1 (curve 1). It is seen that the model of the nearest neighbor effect does not describe the kinetics of PAM alkaline hydrolysis quantitatively, calculated conversions being greater than experimental values.[3]

Neighbor Effect Combined with the Effect of a Charged Coil. Now let us consider a contribution of a charged coil in the reaction kinetics. It follows from the results of Truong et al.[3] that the same relations between rate constants k_0:k_1:k_2 describe the triad distribution for all conversion degrees studied. So we may conclude that these relations remain unchanged in the course of hydrolysis and the total charge of the coil affects identically each individual rate constant. In such a case, according to refs 2, 8, and 9, the rate constants k_i should depend on the chain composition as follows:

$$k_i = k_i^{(0)} \exp(-W(\{\psi_i\})/kT) \qquad i = 0, 1, 2 \qquad (3)$$

where constants $k_i^{(0)}$ characterize the electrostatic repulsion of the nearest neighbor while the exponential term describes the repulsion of more remote groups. The electrostatic work W may be calculated as

$$W(\{\psi_i\}) = W_c(\alpha) - W_n(\{\psi_i\}) \qquad (4)$$

where the first term in the right side is the work against the repulsion of a whole polyion and the second term is the work against the electrostatic field of the nearest neighbors. To estimate $W_c(\alpha)$, we use the parabolic approximation found by Mandel[10] for poly(acrylic acid)

$$W_c(\alpha)/kT = 2.3(\phi_1\alpha^2 + \phi_2\alpha) \qquad (5)$$

where ϕ_1 and ϕ_2 are the adjustable parameters dependent on the polymer molecular mass and ionic strength of a solution.

The value of $W_n(\{\psi_i\})$ may be evaluated according to Sawant and Morawetz[2] as

$$W_n(\{\psi_i\})/kT = 2\beta(\{\psi_i\})W^*/kT \qquad (6)$$

where $\beta(\{\psi_i(t)\}) = (\psi_1/2 + \psi_2)/(\psi_0 + \psi_1 + \psi_2)$ is the probability that a COO^- group is next to the amide group given and W^* is the work to bring a $[OH^-]$ ion into the vicinity of an amide group if its nearest neighbor definitely bears a COO^- ion. The value of $W^*/kT = 0.92$ has been extracted by Sawant and Morawetz from their results concerning titration of 2,4-dimethylglutaric acid as a low molecular weight analogue of PAA.[2] It is worth noting that eq 6 gives the work W_n averaged over all A-centered triads. It is rather simple to write out this work explicitly for each triad, but in such a case we should do the same for the work W_c. This seems to be a too difficult task. We avoid it by using the average expression (5). Therefore, it is consistent to use the average expression (6) for the work W_n.

So, combining (1) and (2) with (3)−(6), we obtain the closed set of equations. To evaluate the kinetic curve $\alpha(t) = 1 - \psi_0 - \psi_1 - \psi_2$, we solved it numerically with the initial conditions $\psi_0(0) = 1$ and $\psi_1(0) = \psi_2(0) = 0$ using the relation $k_0^{(0)}$:$k_1^{(0)}$:$k_2^{(0)}$ = 1:0.2:0.01 and the value $k = 5.8 \times 10^{-4}$ L·mol^{-1}·s^{-1}. The values of the two adjustable parameters ϕ_1 and ϕ_2 in (5) were chosen by using their dependencies on the polymer molecular weight and NaOH and NaCl concentrations found in ref 10. The best fit to experimental points corresponds to the values $\phi_1 = 2.2$ and $\phi_2 = -0.3$ (see Figure 1, curve 2).

Thus, the model combining both the neighbor effect and the effect of a charged coil describes the kinetics of PAM alkaline hydrolysis fairly well.

Certainly, the model describes also the units distribution because the latter depends on the rate constants' ratios only; meanwhile, the ratios do not change with conversion as in our model in accordance with NMR data.[3]

It should be noted that our model accounts for neither counterion condensation nor the coil expansion.

The former effect was ignored due to the high ionic strength of the solution used by Truong et al.[3] In fact, the Debye radius $R_D = (4\pi Q\rho)^{-1/2}$, where $Q = q^2/4\pi\epsilon\epsilon_0 kT$ is the Bjerrum length and ρ is the total number density of small ions. In the case under consideration, q is an elementary charge, $\epsilon = 81$, $T = 323$ K. For electrolyte concentrations used in ref 3 it yields $R_D < 10$ Å and $a/R_D \cong 1$, where a is the monomer length. Meanwhile, counterion condensation is believed to occur when $a/R_D \ll 1$.[12]

Nevertheless, if necessary, this effect resulting in the screening of a polyion charge can be easily taken into account in our model by fixing the values of rate constants k_i at a corresponding degree of hydrolysis.

The effect of coil expansion might be important for dilute solutions, while simple estimation shows that in the case under consideration (for polymer molecular mass $M_w = 6 \times 10^6$) a crossover regime was realized.[13]

It is worth noting that, according to Sawant and Morawetz[2] data, imidization proceeds in a small extent during hydrolysis due to 3−4% head-to-head structures in the PAM chain. Note also that microtacticity of the polymer chain might affect the reaction kinetics, though up to now nobody established such an influence. Therefore, Sawant and Morawetz,[2] Truong et al.,[3] and we as well used averaged rate constants related to the neighbor effect unavoidably. Let us underline, however, that Truong et al.[3] succeeded in interpreting NMR data on triad distribution in hydrolyzed PAM. Thus, usage of averaged rate constants appears to be admissible now. Certainly, our model (as any other theoretical model) will be improved as the knowledge concerning macromolecular reactions with electrostatic effects will extend.

Conclusions

The model of a polymer analogous reaction is suggested by combining the neighbor effect and the effect of a charged coil. The model permits us to describe fairly well the kinetics of alkaline PAM hydrolysis. It may be concluded that, besides the main contribution of the nearest neighbors, the electrostatic field of remote units also affects significantly the reaction kinetics. This approach might be fruitful in studying other reactions if necessary to account for an interaction between the charged macromolecular coil and small ions.

Acknowledgment. This work was supported by the Bayer AG. Ya.V.K. is also grateful to the Robert Havemann Foundation.

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MA980016Y