Determination of the Critical Concentration of Partially Hydrolyzed Polyacrylamide by Potentiometry in an Acidic Medium

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ABSTRACT: The literature presents different methods for quantifying and characterizing partially hydrolyzed polyacrylamide (HPAM) in solution. However, only a few of these are suitable for determining the critical overlap concentration (C^*). The evaluation of C^* is important for describing the transition from the dilute to the semidilute regime, that is, when the solution depicts a characteristic viscosity at concentrations above C^*. This article describes the determination of C^* for HPAM in solution by potentiometry. The molecular weight, degree of hydrolysis, and polymerization degree are determined by mathematical manipulation of the constant of formation of aggregates, which is based on the law of mass action. The potentiometric curves were initially linear; asymptotic behavior followed. The inflection point was determined by the intersection, and the resulting equation of mathematical development statistically satisfied the experimental data and described the number of moles of monomers, the equilibrium constant for the formation of the aggregate, C^*, and the acidity constant of the polymer. The results for C^*, the degree of copolymerization, and the molecular weight proved that this method is a good alternative for the characterization of polymers with ionizable monomers and that are soluble in water. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Partially hydrolyzed polyacrylamide (HPAM) is a copolymer composed of acrylamide and sodium acrylate. In neutral water, it behaves as an anionic polyelectrolyte, with a high ionic strength.[1,2] Because of its physical and chemical characteristics, HPAM is widely used in food products,[3] paper manufacturing, mining,[1,4] wastewater treatment,[5] and biochemistry in the isolation of enzymes.[6] In the petroleum industry, it is employed in the modification of profile pits[7] and the viscosity of drilling fluids.[8] Because of its wide range of applications, it is crucial to develop methodologies that are able to characterize and determine HPAM's properties and physicochemical parameters.[9]

The literature reports several techniques for quantifying and characterizing polyacrylamide in solution; among these are the total organic carbon method,[10,11] titration complexation,[12,13] fluorescence spectrometry,[14,15] hydrolysis of amide groups with the detection of ammonia,[16,17] colloidal titration,[18,19] turbidimetry;[20,21] viscometric method,[22,23] polarography,[24,25] the method of flocculation in alkaline solution,[26] radioactive labeling,[27,28] size exclusion chromatography,[29] and light scattering.[30] However, only some of these methods are suitable for determining the critical overlap concentration (C^*).

At low concentrations (dilute regime), aqueous solutions of HPAM have low viscosities. However, the viscosity of the solution increases almost linearly with the concentration of HPAM. At high concentrations (concentrated regime), the viscosity of the polymer jumps to very high values.[31] C^*, or the semidilute regime, is the point at which the solution changes from the dilute to the concentrated regime. At this point, the balls isolated in solution begin to overlap and interpenetrate, starting intermolecular interactions and increasing the viscosity of the solution. This parameter (C^*) is very sensitive to the properties of the polymer and to polymer–solvent interactions.[32]

The determination of C^* for any polymer–solvent system is of fundamental importance because any polymer solution viscosity characteristic has only a single concentration above the semidilute regime. In this context, we propose in this article the use of the potentiometric titration of HPAM in solution to evaluate C^* by the protonation of its monomers, that is, acrylamide and sodium acrylate, with hydrochloric acid (HCl). Other parameters, such as the molecular weight, degree of hydrolysis (DH), and polymerization, were also determined in this study by the proper handling of mathematical equations based on the law of mass action.
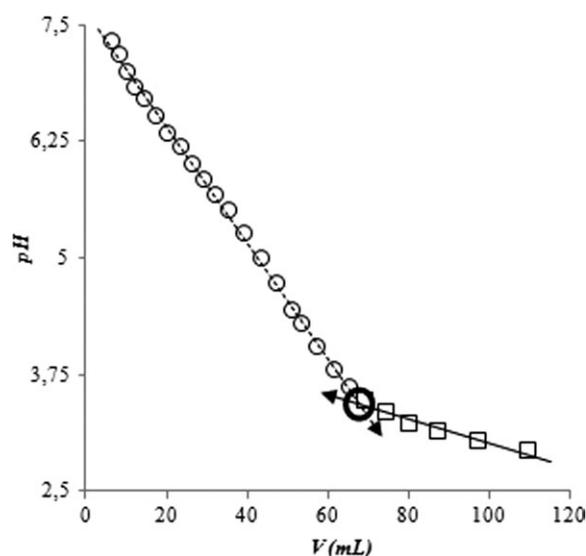
Figure 1. Regression and intersection of two functions in an experimental potentiometric curve. V represents the volume in milliliters of the solution.

EXPERIMENTAL

Materials

The materials used included a 50-mL 1/10 burette and a 50-mL 1/10 beaker (Vidrolabor), an IKA-WERKE RT-KT/C (Staufen, Germany) magnetic stirrer, a Fisatom 712 shaker, an OAKTON (Vernon Hills, USA) pH meter (pH 510 series), a Mettler-Toledo (São Paulo, Brazil) Inlab Expert Pro PH electrode, an HCl PA synth (Diadema, Brazil), polyacrylamide/sodium polyacrylate system mud (Carvalho, Brazil) (Supervis), and distilled water.

Potentiometric Titrations

The solution of polyacrylamide (1% w/v) was prepared under constant stirring for 24 h to ensure complete homogenization of the polymer. The volume was controlled by water evaporation under stirring. The solution (1% w/v) was titrated with HCl solutions with the following pH values: 1.64, 1.91, 2.09, 2.29, 2.50, 2.70, 2.99, 3.20, 3.45, and 3.60. The volumes of acid were added to vary the pH in the range from 0.1 to 0.25; this resulted in titration curves with the highest score possible. All titrations were done in triplicate to obtain the average value and standard deviation of C^*.

Data Analysis

The titration curves were separated into two functions, before and after the inflection point. The linear regression used was similar to that applied in the work of Molyneux.[33] We determined the intersection point [critical volume (V^*); Figure 1, marked in red in the online figure] mathematically by equating the functions of the type $pH(V) = aV + pH$ in a manner similar to that used by Uslu et al.[34] $pH(V)$ is the hydrogen potential on the volume, a is the function coefficient of inclination of $pH(V)$, V is the volume in milliliters of solution, pH is the hydrogen potential of the initial pH of the solution.
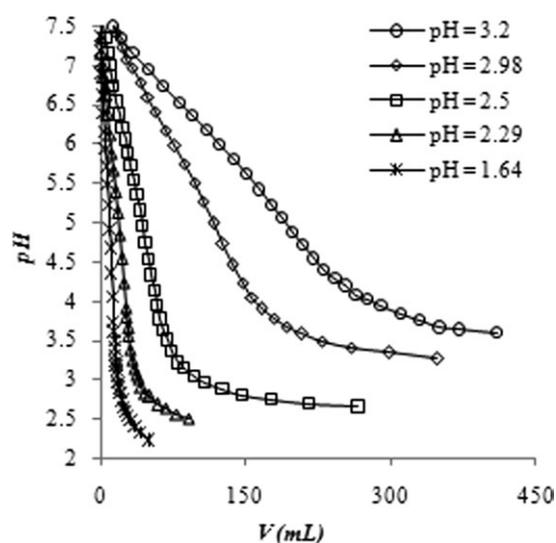
Figure 2. Behavior of HPAM 1% titration with HCl at pH values of 1.64, 2.29, 2.5, 2.98, and 3.2.

RESULTS AND DISCUSSION

Determination of C^* by Potentiometry

The results were shown in a potentiometric pH versus V plot, where pH varied linearly with volume. After a certain point, the curve followed a asymptotic behavior, which tended toward the pH of the titrant. Figure 2 illustrates some of the potentiometric curves obtained experimentally.

Throughout the titration procedure, the viscosity of HPAM gradually decreased, and when the pH changed to the asymptotic behavior, the system completely lost its characteristic viscosity. The protonation of carboxylate groups caused a decrease in the ionic strength of the polymer,[35] with the consequent loss of hydrogen bonds and intramolecular interactions reported by Kulicke.[36] This group was responsible for the strong interaction between the polymer and water, the high hydrodynamic volume, and the high viscosity.[37]

The inflection of the curve (Figure 2) was related to the saturation point, where the polymer–polymer intermolecular interactions were closed and intramolecular interactions prevailed; this was characterized as C^*.[32] This could also be determined by the first derivative curve. Additionally, in both cases, V^* and the critical hydrogen potential (pH*) could be measured.

Modeling of C^*

The law of mass action[38] was used to evaluate the behavior at equilibrium between the dissociated monomers in the formation of bulbs around C^*. Considering that the copolymer had all its monomers in acid–base equilibrium, we assumed that n
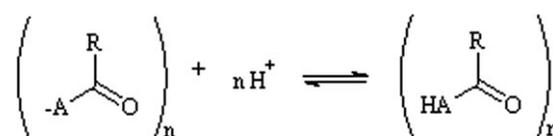
Figure 3. Acid–base equilibrium in the monomers of the HPAM solution.
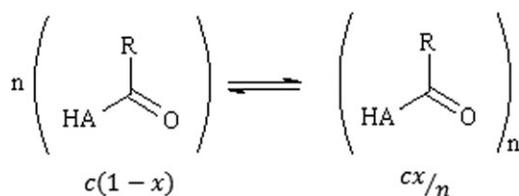
Figure 4. Balance of monomers in the solution and the bulb. HA represents the generic atom "A" protonated.

monomers of type $R(COA)^-$ belonging to a chain of any HPAM were in equilibrium with the free protons in solution (Figure 3).

The acidity constant (K_a) for the equilibrium (Figure 3) can be expressed by equation (1):

$$K_a = \frac{[H^+][RCOA^-]}{[RCOAH]} = \frac{[H^+][Ac^-]}{[Ac]} \qquad (1)$$

The protonated monomer concentration ([RCOAH]) was represented by the acid concentration ([Ac]), whereas the unprotonated monomer ([RCOA$^-$]) was represented by [Ac$^-$].[39]

In the aggregate, n protonated monomers no longer interacted with other polymer chains. On the other hand, the interaction with water prevented unfavorable interactions of the solvent with the carbon chain of HPAM,[40] which formed a bulb (Figure 4) with n monomers.

c is the concentration of monomers in equilibrium, x is the conversion factor of monomers into the bulb, and n is the number of moles involved in the equilibrium. The equilibrium constant (K) is expressed by eq. (2), that is, by the ratio between the concentration of reactants and products and their respective high stoichiometric coefficients:[38]

$$K = \frac{cx/n}{[c(1-x)]^n} = \frac{cx}{n[c-cx]^n} = \frac{C^*}{n([Ac]-C^*)^n} = K^* \qquad (2)$$

Near C^*, c is the concentration of free protonated monomers ([Ac]), and cx is the critical overlap concentration (C^*), where x tends toward 1 as the equilibrium free monomers are added

to form the bulb. Therefore, eq. (2) can be rewritten, where K^* is the critical aggregation constant of the bulb polymer.

Isolating the term [Ac] [eq. (1)] and substituting [eq. (2)], we obtained eq. (3):

$$K* = \frac{C^*}{n\left(\frac{[H^+][Ac^-]}{K_a} - C^*\right)^n} = \frac{C^*}{n\left(\frac{[H^+]^2 - K_a C^*}{K_a}\right)^n} = \frac{C^*}{n\left(\frac{[H^+]^2}{K_a}\right)^n} \qquad (3)$$

This equation relates the formation of the bulb (K^*, C^*) in solution with its constant acidity. Because the polymer was a weak acid and had a very low value of C^*, the following approximation $[H^+]^2 - K_a C^* \approx [H^+]^2$ could be made.[39]

Isolating $[H^+]$ as a function of C^* [eq. (3)] and applying a logarithm to base 10, we obtained eq. (4), which represents the dependence of C^* with respect to pH*. In the case of polymer-present copolymerization or hydrolysis, the curve has a linear function (or equation) for each type of ionizable monomer that is added, with different values of n and K^*. Therefore, the equation takes on the following form:

$$pH* = \frac{1}{2n_i}\log\left(\frac{1}{C^*}\right) + \frac{1}{2n_i}\log(K_i^* n_i) - 2pK_a \qquad (4)$$

where K_i^* is the bulb critical aggregation constant and refers to the type of monomer present in the polymer chain, n_i is the number of moles of the corresponding monomer in the formation of the bulb, and pK_a is the potential acidity constant of the polymer obtained experimentally.

Potentiometry

The results of potentiometric titration (Table I) show that the higher the acidity of the titrant was, the higher the value of C^* was with the protonation of carboxylate groups to a greater extent. This facilitated interactions with water and, consequently, the formation of tangles in concentrations higher than that of HPAM.

The values of pH* and C^* were modeled according to eq. (4) and resulted in a plot with two straight regions (Figure 5), whose equations are given in Table II. The system was homogeneous when there was aggregation of the polymers. n_i represents the

Table I. Values of C^* and pH* Obtained Experimentally and Log(1/C^*)

pH of the titrant	C^* (g/cm^3)	Log(1/C^*)	pH*
1.64	0.0008925	0.0494 ± 0.0007	3.1924 ± 0.0061
1.91	0.0007726	0.1120 ± 0.0006	3.2302 ± 0.0313
2.09	0.0006767	0.1697 ± 0.0089	3.2649 ± 0.0265
2.29	0.0005750	0.2403 ± 0.0021	3.3226 ± 0.0258
2.50	0.0003760	0.4248 ± 0.0030	3.4565 ± 0.0248
2.70	0.0002908	0.5364 ± 0.0054	3.5798 ± 0.0405
2.99	0.0001989	0.7015 ± 0.0147	3.8507 ± 0.0102
3.20	0.0001358	0.8672 ± 0.0048	4.0985 ± 0.0501
3.45	0.0000932	1.0306 ± 0.0102	4.3403 ± 0.0050
3.60	0.0000626	1.2040 ± 0.0203	4.5689 ± 0.0161
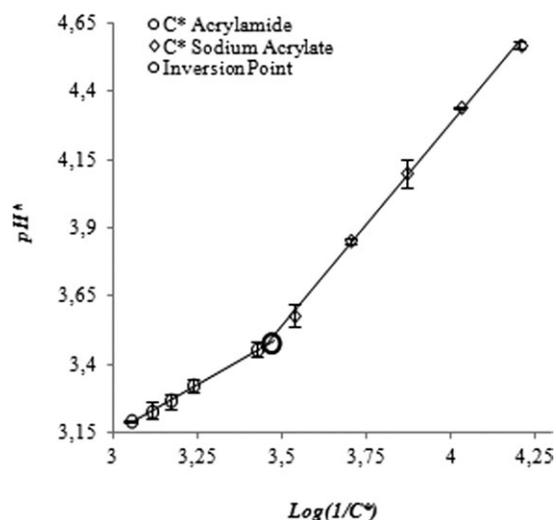
Figure 5. Intersection (IP) of two curves of Log(1/C^*) versus pH*.

number of moles of monomers in the formation of bulbs, and N is the total number of moles per polymer chain [eq. (5)]:

$$N = \sum_{i=1}^{i} n_i \qquad (5)$$

where MM is the polymer molecular weight.

From the value of N (Table II), it was possible to calculate DH of HPAM.[2] Comparing the results of DH (%) and the value specified by the manufacturer, we found n_2 to correspond to the molar fraction of acrylate copolymer because its DH (%) was equal to 32.45%. It corresponded to a specified amount ($\cong$30–35%). Therefore, HPAM had an average composition of 32.4% sodium acrylate and 67.55% acrylamide. Because there were two different equations, the equation constants of acrylamide are identified by subscript 1, and those of sodium acrylate are identified by subscript 2.

Under acidic conditions, the monomers were in equilibrium according to the following equations:

$$-[CH(CONH_2)CH_2]n^- + nH^+ \equiv -\left[CH(CONH_3)^+CH_2\right]_{n-}$$

Table II. Regression Results of Eq. (4) Obtained from the Experimental Data of C^* and pH*

Monomer	Acrylamide	Sodium acrylate
Equation	$y = 0.7123x +$ 1.0120	$y = 1.4825x -$ 1.6605
n_i	n_1	n_2
	0.7019	0.3372
N	1.0392	
K_i^*	K_1	K_2
	6.6×10^{11}	3.05×10^{20}
K^*	2.01×10^{32}	
pK_a	7.89	
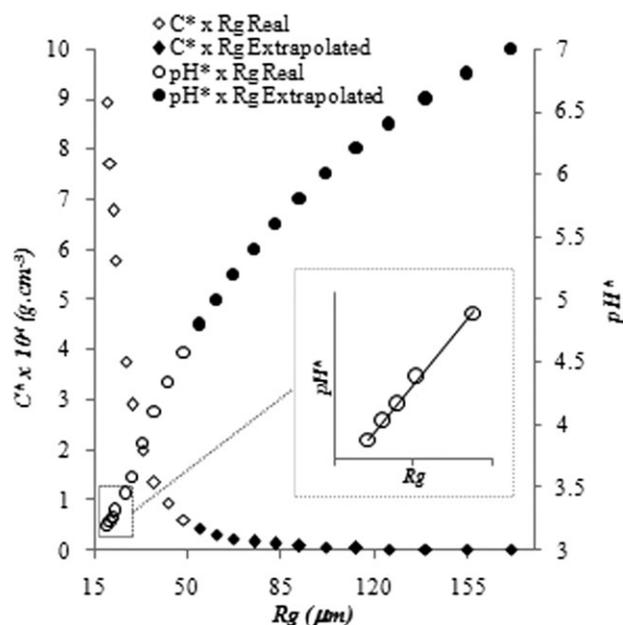
Figure 6. Variation of R_g as a function of pH* and C^*.

$$-[CH(COO)^-CH_2]_{m-}+mH^+ \equiv -[CH(COOH)CH_2]_{m-}$$

As shown in Figure 5, from the inversion point (IP; pH* 3.47, marked in red online), the proton concentration was high enough to convert predominantly acrylamide in —CH [CO(N-H$_3$)$^+$]CH$_2$— and acrylate anions in —CH (COOH)CH$_2$—. These two groups interacted predominantly with water, preventing contact of the hydrophobic chain with the aqueous medium.[40] However, the cation contributed more significantly to aggregation until the pH* was 3.47. The IP was the pH* at which change occurred predominantly in the monomer

Table III. Data from the IP and Results Yielded by Eq. (8)

Equation	$y = 1.0974x - 0.3242$	
A	1.0974	
N	1.0392	
m	0.000338939	
m_s (g)	0.000338939	
MM (g/mol)	20,492,411	
NU	265,473	
Monomer	Acrylamide	Sodium acrylate
%	67.55	32.45
m_{si} (g)	m_{s1}	m_{s2}
	0.0002289	0.0001099
MM_i (g/mol)	MM_1	MM_2
	71.0744	94.0361
MM_{ti} (g/mol)	13,841,807	6,650,603
GP_i	194,750	70,723

'A' is the slope of equation 7 resulting from the sum of the equations (Equation 4 in the general form) of acrylamide and sodium acrylate.

—CH[CO(NH$_3$)$^+$]CH$_2$— for —CH (COOH)CH$_2$— in HPAM bulb formation.

The increase in pH* increased the concentration of the anionic groups, with mainly hydrogen bonds between water and —COO$^-$. However, due to equilibrium, the concentration of cations was reduced, and acrylamide was its molecular form.

Before and after the IP (Figure 5), there was a predominance of the ionic forms in C^*. The aggregate acrylate was more stable (Table II), exhibiting an equilibrium constant (K_2) orders of magnitude higher. This stability was due to the larger electrone-gativity difference in the hydrogen bonds between water and —COO$^-$ than in the hydrogen bonds between water and [—(NH$_3$)$^+$][40] and a lower load distribution in the anion acrylate.[41]

The values of the hydrodynamic radius (R_g) were obtained from eq. (6),[42] where the calculated data (measured and extrapolated) were compared with C^* and pH*:

$$C^* \left(\frac{4\pi}{3} R_g^3 \right) = \frac{MM}{N_a} \quad (6)$$

From Figure 6, R_g increased at higher pH* values. In a more acidic medium, HPAM had protonated acrylate anions; this consequently reduced the number of intramolecular bonds[36] and reduced R_g.[43] The values of R_g of 20–25 μm at pH* 3.0–3.5 and 120–170 μm at pH* 6.5–7.0 (Figure 6) suggested that there was a high agglomeration of polymer molecules; this was con-sistent with those reported by Hecker et al.,[43] who evaluated, by light scattering, the distribution of the R_g of HPAM in deionized water with the addition of salts and organic cosol-vents with mean values of 0.4 μm to individual polymer molecules.

When the pH* was analyzed up to the IP (Figure 6), R_g varied linearly. Acrylamide was protonated {—CH[CO(NH$_3$)$^+$]CH$_2$—} and behaved like a linear polymer,[44] and R_g varied at a constant rate. After IP, the acrylate anion {—[CH(COO)$^-$CH$_2$]—} behaved as a branched polymer,[45] and R_g varied nonlinearly as a function of pH*. This behavior suggested that the anion inter-acted with acrylamide and protonated water,[43] as reported for other polymer systems.[46] In this pH* range, cation–anion bonds stabilized the bulb [$K_2 > K_1$ (Table II)]; this reduced the rate of increase of R_g with increasing pH*.

Molecular Weight and Degree of Polymerization
The point of intersection is the meeting of two linear equations (Figure 5); in this intersection, the pH* was the same for both equations [eq. (4)] and allowed the linear combination of equa-tions. The slope $4A$ [eq. (7)], from the resulting equation, was worked mathematically so that eq. (7) became a function of the molar mass of the polymer:

$$4A = \left(\frac{1}{n_1} + \frac{1}{n_2} \right) = \left(\frac{n_1 + n_2}{n_1 n_2} \right)$$
$$= \left(\frac{N}{n_1 n_2} \right) = \left(\frac{\frac{m}{MM}}{\frac{m_1}{MM_1} \frac{m_2}{MM_2}} \right) = \left(\frac{m}{m_1 m_2} \frac{MM_1 MM_2}{MM} \right) \quad (7)$$

When the term in brackets was solved, the sum ($n_1 + n_2$) of the numerator could be replaced by N [eq. (5)]. From the num-ber of moles to the mass ratio and molar mass, the relationships among the molecular weight of the monomers (MM$_1$ and MM$_2$), their masses (m_1 and m_2), MM, and mass (m) present at the IP could be expressed by eq. (7). The rearrangement and isolation of MM yielded eq. (8):

$$MM = \frac{1}{4} \left(\frac{m}{m_1 m_2} \frac{MM_1 MM_2}{A} \right) = \frac{1}{4} \left(\frac{m_s}{m_{s1} m_{s2}} \frac{MM_1 MM_2}{A} \right) \quad (8)$$

In C^*, the polymer solution is a continuous and homogeneous system.[42] Therefore, the masses of monomers present in the polymer chains were proportional to the masses of the mono-mer and polymer in solution (m_{s1}, m_{s2}, and m_s). Thus, the terms could be rewritten according to the following relation-ships: $m_1 \propto m_{s1}$, $m_2 \propto m_{s2}$, and $m \propto m_s$. Because the values of n_i represent the number of moles in a polymer chain and the system is homogeneous and continuous, it can be generally stated that: $m_{si} \approx n_i m/N$ and m_s is sum of m_{si}.

The calculated molar mass MM (Table III) was very close to the molecular weight specified by the manufacturer of HPAM, which was about 20.10^6 g/mol. MM$_{ti}$ was calculated from MM, which corresponded to the molecular weight of the total mono-mers, from the product between MM and the percentage com-position and the degree of polymerization and the number of total units (NU) of the polymer chain (Table III).

CONCLUSIONS

pH*, V^*, and C^* were determined by potentiometry with the intersection method. Under the conditions we used, the law of mass action of Elworthy and Mysels[38] [eq. (4)] was consistent with the profile of the experimental curve and allowed us to determine the equilibrium constant of aggregate formation and its monomers, n, and from these, the calculated molecular mass of HPAM. The results of the molecular weight and degree of polymerization were consistent with those specified by the manufacturer; this showed that the method was reproducible and, within the range of error, accurate. The proposed tech-nique for determining C^*, the degree of polymerization, and the molecular weight by potentiometric titration consisted of a sim-ple alternative for the characterization of polymers with ioniz-able monomers and soluble in water.

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