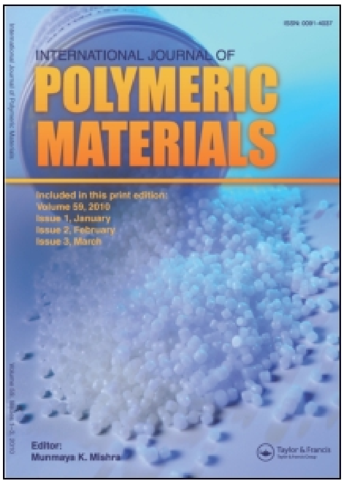

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Calculation of the Molecular Parameters of Poly(Acrylic Acid) Using Intrinsic Viscosity Data

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A detailed review of the available methods for calculating molecular parameters from viscosimetry measurements, is presented. A comparative study utilizing those theories for the case of Poly(Acrylic Acid) was carried out, revealing that only one of the approaches yields predictions agreeable to the experimental results.

Keywords: Poly(Acrylic Acid) intrinsic viscosity; Solution properties; Molecular size

INTRODUCTION

Nowadays we are familiarized with a great variety of ceramic, metallic and polymeric materials. In the particular case of polymers, these materials are so important, technologically speaking, that their annual production has increased enormously because of their applications are so varied to the extent that, in some cases, they have substituted metals. The polymers, as molecular materials, are constituted by molecules bonded by either van der Waals or hydrogen bonds, which provide them with unique properties which, however, are extremely

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*Corresponding author. e-mail: meneses@servidor.unam.mx difficult to explain and understand theoreticaly. Indeed, experimental methods have been developed to determine some values to be used in theories to calculate the molecular dimensions which could explain the observed behavior of the polymeric systems.

In fact, there is a tremendous lack in the available literature of reliable experimental data which can be conveniently used to compare the predictions of various theoretical models, and the actual measurements.

Among the most widely-employed polymeric materials, the so-called polyelectrolytes are of particular interest, both technological and scientifically speaking, due to their use in a wide variety of applications, ranging from rheological modifiers to the production of biocompatible compounds. Nevertheless, only scarce data is available adequate for back-feeding the theoretical models for polyelectrolites. Accordingly, this article is aimed to demonstrate how viscosity data can be conveniently employed to deduce the fundamental molecular parameters of Poly(Acrylic Acid), one of the most conspicuous members of the polyelectrolites family.

THEORETICAL BACK GROUND

Yamakawa [1] has demonstrated that the correct theoretical description of the equilibrium properties of diluted solutions of flexible-chain polymers, requires (except in theta conditions) two molecular parameters: the effective bond length and the binary cluster integral. These parameters describe the properties well enough, provided we do not inquire into the detailed chemical structure of the polymer and solvent molecules. The molecular dimensions, second virial coefficients and intrinsic viscosities of linear flexible chains may be expressed only in terms of these two parameters. Almost all the theoretical models available of polyelectrolytes, are based on the concept of semirigid chains that show discrepancies from the models of high flexible-chains. Flexible polymers in solution have many various configurations, their form and size could only be explained in a statistical fashion. Many of the macromolecular properties, particularly those where the polymer is in solution, are intimately related to the molecular structure, that is, to the geometric arrangement of the atoms that form the chains. Due to the existence of internal rotations of the bonds between different atoms which form part of the chains, which are of sigma class, they generate a great number of different conformations. This is why the problem of the geometry of the macromolecular chains acquires a statistical character and the geometrical magnitudes will be then statistical mean values with a probability associated.

A polymer in solution can not be considered a stationary string, for it coils and uncoils frequently and thus its conformation changes constantly. In a very diluted solution, we could consider that individual molecules act in independent fashion. The manipulation of viscosity data of diluted solutions provides an important parameter of a polymer dissolved in particular solvent: this is the so-called intrinsic viscosity, $[\eta]$. This could be defined as the relationship between specific viscosity and the concentration at infinite dilution:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{\mathrm{sp}}}{c} \tag{1}$$

Experimental viscosity data and solution concentration of diluted polymers are necessary to obtain values of intrinsic viscosity. Intrinsic viscosity and constants K and ν of the Mark-Houwink-Sakurada equation (Eq. (2)) allow to determine viscosimetric molecular weight for a polymer/solvent system:

$$[\eta] = KM^{\nu} \tag{2}$$

Yamakawa gave the methodology of calculus by using intrinsic viscosity and molecular weight data, to obtain the molecular parameters. He assumed that the intrinsic viscosity could be expressed as:

$$[\eta] = [\eta]_{\theta}\alpha_{\eta}^{3} \tag{3}$$

where α_{η} is the expansion factor as a function of viscosity and $[\eta]_{\theta}$ is the intrinsic viscosity in theta conditions (ideal condition).

In theta state, $[\eta]_{\theta}$ is proportional to the square-root of the molecular weight for flexible chains without hydrodynamic interactions:

$$[\eta]_{\theta} = K_{\theta}M^{0.5} \tag{4}$$

so the expansion factor could be expressed such as:

$$\alpha_\eta^3 = \frac{[\eta]}{K_\theta M^{0.5}} \tag{5}$$

where

$$K_\theta = \Phi_0 A^3 \tag{6}$$

and

$$A^2 = \frac{\langle R_0^2 \rangle}{M} \tag{7}$$

where A is the molecular parameter associated to the steric hindrace, $\langle R^2 \rangle$ represents the mean-square average end-to-end distance and Φ_0 is a constant.

At non-theta state, the expansion factor α_η is an increasing function of the excluded volume parameter, z:

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{BM^{0.5}}{A^3} \tag{8}$$

where

$$B = \frac{\beta}{M_s^2} \tag{9}$$

B is the interaction polymer/solvent parameter, M_s is the molecular weight of a segment of the polymer and β, the binary cluster integral.

Several theories have been proposed for the thermodynamical characterization of polymer diluted solutions. They allow to calculate the coefficient of interaction polymer/solvent, B. For example, Flory, Fox and Schaefgen [2] proposed a thermodynamical model as a function of the intrinsic viscosity, where they supposed that $\alpha_\eta = \alpha_s$. They represented α_s, the expansion factor, as a function of the square average radius of gyration:

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K^{2/3} + 0.858K^{2/3}\Phi_0 B \frac{M}{[\eta]} \tag{10}$$

where B is the interaction polymer/solvent parameter. Thus, the constant K could be estimated from the ordinate to the origin of the plot, whereas the slope of the plot is the parameter B. The remarkable feature of this plot is that, for good solvent systems, linear extrapolation from large values of molecular weight yields a negative intercept. This demonstrates the inadequacy of model for $\alpha_\eta = \alpha_s$. The theory provides, however, good results in the vicinities of the theta temperature.

Stockmayer and Fixman [3] proposed their model for α_R (expansion factor as a function of the mean-square end-to-end distance) to the third power, this means that their equation is:

$$\frac{[\eta]}{M^{1/2}} = K + 0.51\Phi_0 B M^{1/2} \tag{11}$$

The values of K are better than the previous model; however, for high molecular weight, this has not a linear behavior any longer.

Berry [4] proposed a relationship between $[\eta]$ and molecular weight that leads to good results within a wide range of molecular weights, except for very low weights (oligomers):

$$\frac{[\eta]^{1/2}}{M^{1/4}} = K^{1/2} + 0.42K^{1/2}\Phi_0 B \frac{M}{[\eta]} \tag{12}$$

Another magnitude of interest is the conformation factor or polymer chain stiffness parameter, σ [1, 5, 6]. This quantity is independent of the number of bonds and is given by:

$$\sigma^2 = \frac{(\langle S_0^2 \rangle / M)}{(\langle S_{\text{of}}^2 \rangle / M)} = \frac{(\langle R_0^2 \rangle / M)}{(\langle R_{\text{of}}^2 \rangle / M)} \tag{13}$$

In this expression $\langle S_{\text{of}}^2 \rangle$ and $\langle R_{\text{of}}^2 \rangle$ are the square average radius of gyration and the mean-square average end-to-end distance of the freely rotating chain (freely rotating state is a hypothetical state of the chain in which the bond angle restrictions are retained but the steric hindrances to internal rotation are relaxed). For our polymer, Poly(acrylic acid), this value is:

$$\left(\frac{R_{\text{of}}^2}{M}\right)^{1/2} = \frac{0.308}{M_U^{0.5}} \tag{14}$$

M_U is the molecular weight of the repetitive unit.

The square average radius of gyration, $\langle S_0^2 \rangle$, is defined as:

$$\langle S_0^2 \rangle = \frac{\langle R_0^2 \rangle}{6} \tag{15}$$

Any interaction among segments of the chain is considered in the previous models but some restrictions still exist; the steric effect is an example. The segments have finite volume, they are pushed apart from each other and the chain swells; for this reason, the size of the chain curled with that interaction is greater that the size of an ideal chain. This process is called the excluded volume effect, which is a result of the virtual repulsion between polymer molecules arising from their spatial requirements. Each molecule, in a very dilute solution in a good solvent will tend to exclude all others from the volume which it occupies. Since the excluded volume represents the interaction between distant segments along the chain, the interaction is of long range, in contrast to the short range interaction from near segments. Furthermore, the steric hindrances, van der Waals attractions, affect the attractions between segments of the polymer, segments of chain and molecules of the solvent, and the molecules of the solvent.

EXPERIMENTAL

Polymerization

Samples of Poly(Acrylic Acid) (PAA) were obtained by polymerizing acrylic acid using solution polymerization [7]. The PAA was prepared using an initiator (ammonium persulfate) and a chain-transfer agent (2-propanol) [8]. The initiation was carried out by means of free radicals that were obtained from the persulfate. The dispersion was thermodynamically unstable and needed continuous agitation to prevent the coalescence and to dissipate the reaction heat. The polymerization required nitrogen to displace the oxygen which acts as an inhibitor of the reaction. The reagents, reactive grade, were: acrylic acid (99.7%, Celanese Mexicana), deionized water, ammonium persulfate (99.7%, J.T. Baker), nitrogen gas (99.9%, INFRA) and isopropanol (99.98%, J.T. Baker). A typical formulation, in molar percent, was:

Raw material	%
Deionized Water	91.94
Isopropylic Alcohol	1.12
Acrylic Acid	6.84
Ammonium Persulfate	0.10

Polymerization was carried at 70 ± 1°C in a stainless steel Parr Reactor of 300 mL with stirrer, control temperature and with nitrogen purge.

The identification of the PAA was made by infrared spectroscopy. The polymers were neither fractioned nor purified, but only dried in an oven for 24 hours to 60°C in order to eliminate water and solvents.

Preparation of Solutions

The dry PAA was dissolved in 1,4-dioxane (99.9%, J. T. Baker) without purifying, as well as in solutions 1.5 M and 0.1 M of deionized water/NaBr (99%, Sigma Chemical). The solutions were filtered using a 0.45 μ nylon filter.

Viscosity of Solutions

The reduced viscosity was calculated from viscosity measurements of the polymer solutions in several concentrations, taking into account the viscosity of the solvent. To calculate the Staudinger index $[\eta]$, the viscosities of the solvent and of solutions of several concentrations must be measured. The polymer solution concentrations can not be too high, since this makes difficult the extrapolation of the viscosity data to infinite dilution. Experience shows that the best solute concentrations are those whose relative viscosity lies between 1.2 to 2.0. The upper limit of relative viscosity (2.0) results from the fact that the relationship between reduced viscosity and concentration becomes increasingly nonlinear with increasing concentration. The lower limit of relative viscosity (1.2) arises from the fact that, at low concentrations, anomalies in the function: relative viscosity = f(concentration), begin to appear. These anomalies are usually considered to be apparatus-dependent and to result from adsorption of macromolecules on the capillary walls. To determine relative viscosity of 1.2 we need an accuracy of ~ ± 1%, the viscosity ratio must be determined to an accuracy better than ± 0.2%, and the viscosities themselves to an accuracy better than ±0.1 %. Capillary viscosimeters are particulary suitable for such determinations. The viscosimeters most widely used in macromolecular science are the ones known as Ostwald, Cannon-Fenske and Ubbelohde. In all those types, the time required for a given quantity of liquid to pass between two marks is taken as an indication of the viscosity. As long as the liquid flow is not infinitely slow, potential energy is partially lost in overcoming frictional forces during flow. Some of the potential energy is also lost through conversion to kinetic energy, which in turn is dissipated through the formation of vortices at the exit of the capillary (Hagenbach Effect). Additionally, a given amount of initial work is employed on forming the parabolic shear rate gradient (Couette Effect). The apparent increase in viscosity caused by these two nonfrictional effects is, according to Hagenbach and Couette, taken into account by incorporating a correction term in the Hagen-Poiseuille equation. Measured times should never be less than 100 s; otherwise the percentage error would increase. Also, the viscosimeter must hang vertically for every reading; otherwise the effective length of the capillary varies from one reading to another. The temperature should be up constant to ~ ± 0.01°C, since a temperature difference of 0.01°C usually means a viscosity change of ~ 0.02%. Solution and solvent almost always have different densities. For viscosimeters whose calibration constant is less than 0.05 cSt/s, it is necessary carry out the correction if the times of flow are below 100 seconds. ASTM D446-89 standard was followed in this case [9].

Ubbelohde viscosimeters are so constructed that, during a measure, the pressure head of the suspended liquid at the capillary outlet is independent of the amount of liquid originally introduced into the viscosimeter. This also means that the solution originally introduced into the viscosimeter can be diluted with a solvent to provide a series of concentrations without being forced, as in the case of the Ostwald viscosimeter, to empty and clean out the viscosimeter after each measurement. Another advantage of the Ubbelohde viscosimeter is that the stress on the suspended liquid exactly compensates the surface tension effects on the upper meniscus, and this is particularly important in the case of surface-active substances. On the other hand, the amount of liquid required for a measure is higher in the Ubbelohde than in the Ostwald viscosimeter.

In our case, we decided to measure viscosities in an Ubbelohde viscosimeter type 1C (constant of calibration 0.03 cSt/s). The viscosimeter was placed in a thermal bath with diluted solutions and the solvent. The viscosimeter containing the liquid was allowed to reach the temperature of the bath [10]. Ten minutes later, we began the experiment and registered 3 readings with a precision of ± 0.1 s. All measures were carried out at 15, 25 and 30 ± 0.1°C. The correction of the viscosity was achieved with a calibration constant smaller than 0.05 cSt/s. The mathematical expression which relates the volume (V) of the bulb, the length (L) of the capillary, the diameter (d) of the capillary, the flow time (t) of the measures, the density of the liquid (ρ) and the calibration constant (C) of viscosimeter, is:

$$\eta = Ct\rho - \frac{E\rho}{t^2}, \tag{16}$$

where E is the kinetic energy factor:

$$E = \frac{1.66V^{1.5}}{L(Cd)^{0.5}} \tag{17}$$

Our viscosimeter had the dimensions: $V = 4\,\text{cm}^3$, $L = 9\,\text{cm}$, $C = 0.03$ cSt/s $= 0.03\,\text{mm}^2/\text{s}^2$ and $d = 0.078\,\text{cm}$. The constant E acquired a value of $30.50\,\text{mm}^2$ s. The expression employed to obtain the viscosity was:

$$\eta = 0.03t\rho - \frac{30.50\rho}{t^2} \tag{18}$$

The reduced viscosity was obtained by using the standard test method ASTM D2857-87 [10]. It consisted in measuring the flow times of several solutions at different concentrations. The relative viscosity (η_r), the specific viscosity (η_{sp}), and the reduced viscosity (η_{red}) were calculated for each of the measurements. The data of reduced viscosity and concentration were ploted in order to obtain the intrinsic viscosity. The ordinate to the origin (concentration zero) of the plot η_{red} *vs.* C represents the intrinsic viscosity.

The molecular weights were calculated from the Mark-Houwink-Sakurada equation for each system. The parameters K and ν of Mark-Houwink-Sakurada equation are absolute values that were obtained from light scattering and reported by Okamoto [11] and Brandrup [6]. Molecular weights of PAA were determined by using:

$$[\eta] = 8.5 \times 10^{-4} M_v^{0.50} \quad \text{1,4-dioxane@30°C} \tag{19}$$

$$[\eta] = 12.4 \times 10^{-4} M_v^{0.50} \quad \text{NaBr 1.5 M@15°C} \tag{20}$$

$$[\eta] = 3.12 \times 10^{-4} M_v^{0.755} \quad \text{NaBr 0.1 M@25°C} \tag{21}$$

Determination of the Molecular Parameters

With the values of $[\eta]$ and M_v, the expansion factor, α_η, was calculated in both theta and no-theta conditions: (Eq. (3)); the parameter associated to the effect of steric hindrance, A, (Eq. (6)); the mean-square average end-to-end distance, $\langle R^2 \rangle$, (Eq. (7)); square average radius of gyration, $\langle S^2 \rangle$, (Eq. (15)); the conformation factor, also called the polymer chain stiffness parameter, σ, (Eq. (13)); and the excluded volume parameter, z, (Eq. (8)), were also all calculated. The parameter B was obtained from the slope of the plots of the models of the Flory-Fox-Schaefgen, (FFS), Eq. (10); Stockmayer-Fixman, (SF), Eq. (11); and Berry, (B), Eq. (12).

In Eqs. (6, (10)–(12)), the constant Φ appears. Theoretical and experimental investigations have shown that Φ does not depend on neither the constitution or the configuration of the polymer nor the chemical nature of the solvent used. As a proportionality factor between the radius of gyration and the hydrodynamic volume, Φ is only related to the expansion of the coil in the relevant solvent, *i.e.*, to the values of α or ε (12). The theoretical calculation leads to:

$$\Phi = \Phi_0(1 - 2.63\varepsilon + 2.86\varepsilon^2) \tag{22}$$

where Φ_0 is the value in the theta state. The parameter ε is determined from:

$$\nu \equiv 0.5(1 + 3\varepsilon) \tag{23}$$

where ν is the power of the molecular weight in the equation of Mark-Houwink-Sakurada. Φ acquires values for two cases: when Φ_0 is related to the radius of gyration, $\langle S \rangle$, then $\Phi_0 = 4.18 \times 10^{22}$ dL/mol cm^3. If one uses the chain end-to-end distance then $\Phi_0 = 2.84 \times 10^{21}$ dL/mol cm^3. For PAA: in theta conditions (1,4-dioxane and NaBr 1.5 M) ν acquires the value of 0.50 and $\varepsilon = 0$ using Eq. (23); using Eq. (22) and assuming that a relationship exists with $\langle R \rangle$, we have $\Phi = \Phi_0 = 2.84 \times 10^{21}$ dL/mol cm^3. In no-theta conditions $\nu = 0.755$, $\varepsilon = 0.17$ and $\Phi = 1.34 \times 10^{21}$ dL/mol cm^3. The values of the constant Φ that were adopted in this study were:

θ system	$\Phi_0 = 2.84 \times 10^{21}$ dL/mol cm^3
non-θ system	$\Phi = 1.34 \times 10^{21}$ dL/mol cm^3

RESULTS AND DISCUSSION

Determination of the Intrinsic Viscosity

The plot of η_{red}-concentration of solutions of PAA in 1,4-dioxane is shown in Figure 1. The plots of η_{red}-concentration of solutions of PAA in aqueous solutions of NaBr (1.5 M and 0.1 M) are shown in Figure 2. Those figures show an interesting behavior of η_{red} of PAA with the solvents. Elias [12] states that, in absence of salts, η_{red} increases sharply with decreasing polyelectrolyte concentration. When the concentration of the salt in the polyelectrolyte increases, the reduced viscosity decreases. The effect is explained in the following fashion: by decreasing the polyelectrolyte concentration, the degree of ionization increases. In the case of polysalts, they form gegenions. The gegenions form an ionic atmosphere around the chains of the polyelectrolyte macromolecule. In very dilute solutions, salt-free solution, the diameter of the ion atmosphere is greater than the diameter of the coiled molecule. The carboxylate ions ($-COO^{-1}$) repel each other, increasing the chain rigidity and expanding the polymer thus increasing the viscosity. At medium concentrations, the gegenions reside partially within and partially outside the polymer coil. At very high concentrations, the gegenions reside more likely within than

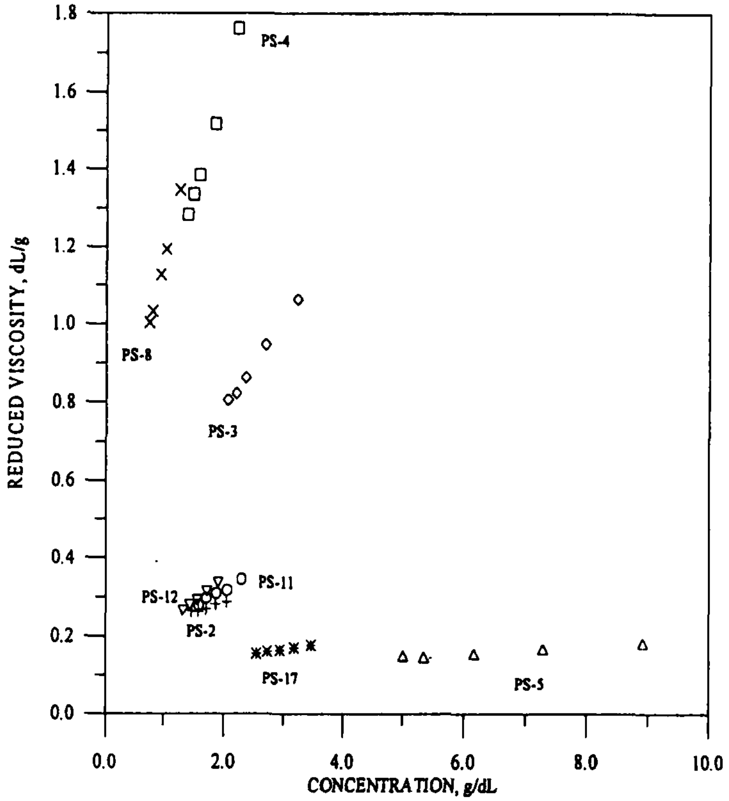

FIGURE 1 Viscosity *vs.* concentration plot for PAA in 1,4-dioxane.

outside the polymer coil; the osmotic effect that this produces caused more water to penetrate the polymer and to expand it. Thus, at low concentrations the electrostatic effect dominates and at high concentrations the osmotic effect dominates. The introduction of salts into the polyelectrolyte solution causes the ionic strength outside the polymer coil to be increased with respect to that inside the polymer coil, and the diameter of the ion atmosphere is decreased. Both effects decrease the diameter of the polymer coil and therefore, reduce the viscosity.

Figure 2 shows the behavior of two degrees of ionization (0.1 M and 1.5 M) of the disolved samples in NaBr. We analized the samples PS-17, PS-18 and PS-19. It can be observed that the disolved polymers in

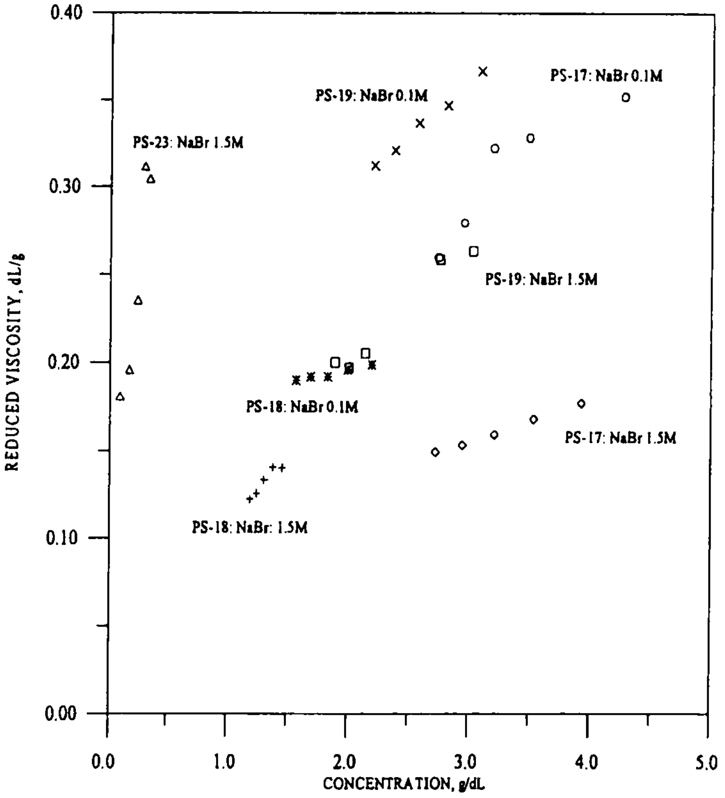

FIGURE 2 Viscosity *vs.* concentration plot for PAA in NaBr solutions.

concentrated solutions (1.5 M) have smaller viscosities that those samples disolved in diluted solutions (0. 1 M). This agrees to the theory because PAA produce an ionic atmosphere and therefore, the reduced viscosity decreases.

We extrapolated each linear behavior to concentration zero to obtain the intrinsic viscosity [η]; the values are shown in Table I, where the values of [η] obtained for several synthesized samples are described. We observe (samples PS-19, PS-17, PS-23 and PS-18) that the Staudinger Index for polymers in NaBr 0.1 M are higher than the intrinsic viscosity of polymer in NaBr 1.5 M. MHS equation shows a value of $\nu = 0.755$, it means that dilute NaBr solutions are good solvents an therefore the theory agrees with the experiment.

TABLE I Intrinsic viscosity of polymer solutions, dL g^{-1}

	$[\eta]_\theta$		$[\eta]$	
	Dioxane	*NaBr* 1.5 *M*	*NaBr* 0.1 *M*	α_η
PS-19	–	0.0716	0.1752	2.447
PS-17	–	0.0940	0.1330	1.415
PS-23	0.0800	0.1090	–	1.363
PS-18	–	0.1240	0.2705	2.181
PS-5	0.0991	–	–	–
PS-12	0.1020	–	–	–
PS-11	0.1330	–	–	–
PS-2	0.1925	–	–	–
PS-13	0.2800	–	–	–
PS-3	0.3341	–	–	–
PS-8	0.4763	–	–	–
PS-4	0.4870	–	–	–

Expansion Factor

Equation (3) was used to obtain this factor. The results are shown in Table I. The expansion factor (α_η) is the relationship between the dimensions of the disolved chain in any solvent (perturbed conditions) and the dimensions of the polymer in any theta solvent (non-perturbed conditions) at given temperature. If the polymers are in a good solvent, (α_η) is higher than 1.0. This means that the perturbed dimensions exceed to the non-perturbed dimensions. In our case, the expansion factors (Tab. I) yield valves higher that one, independently of the solvent used; this agrees with the value ν from the of Mark-Houwink-Sakurada equation. This value for NaBr 0.1 M is 0.755 and is close to 0.9. When solvent has a value of 0.9, this means that it is an excellent solvent. If ν is near to 0.5, this means that the electrostatic phenomena cause a precipitation of the polymer.

Determination of the Molecular Weight

We obtained the molecular weights in order to compare them when we have used 3 different MHS equations. Four samples were selected (PS-19, PS-17, PS-23 and PS-18). 1,4-dioxane @ 30°C and aqueous solution of NaBr 1.5 M@15°C are in theta conditions and aqueous solution of NaBr 0.1 M is in non-theta conditions. The molecular weights, M_v, were calculated by using Eqs. (19)–(21). One could observe the difference between the different equations (Tab. II); these

TABLE II Molecular weights of Poly(Acrylic Acid), g $gmol^{-1}$

	1,4-dioxane *@ 30°C*	*NaBr* 1.5 *M* *@ 15°C*	*NaBr* 0.1 *M* *@ 25°C*
PS-19	–	3,333	4,380
PS-17	–	5,740	3,040
PS-23	8,858	7,727	–
PS-18	–	9,960	7,780
PS-5	13,593	–	–
PS-12	14,400	–	–
PS-11	24,500	–	–
PS-2	51,289	–	–
PS-13	108,000	–	–
PS-3	154,495	–	–
PS-8	313,995	–	–
PS-4	328,262	–	–

are not very big, especially when considering that the samples were neither purified nor fractional. We could say that the molecular weight obtained with system PAA-1,4-dioxane is reliable.

Calculation of the Molecular Parameters

Several theories allow to estimate the values of the molecular parameters of polyelectrolytes from the value of the Staudinger index and from the viscosimetric molecular weight, M_v. All theories analyze the behavior of $[\eta]$ and M_v in order to calculate the parameter K and the parameter B based on approximately closed expressions for the expansion factor. The values in *italic letters* of Table III represent the

TABLE III Experimental and *calculated* intrinsic viscosity, dL g^{-1}

	$[\eta]_\theta$, *dL/g*		$[\eta]$, *dL/g*
	Dioxane	*NaBr* 1.5 *M*	*NaBr* 0.1 *M*
PS-19	–	0.0716	0.1752
PS-17	–	0.0940	0.1330
PS-23	0.0800	0.1090	–
PS-18	–	0.1240	0.2705
PS-5	0.0991	*0.1446*	*0.4119*
PS-12	0.1020	*0.1488*	*0.4302*
PS-11	0.1330	*0.1940*	*0.6423*
PS-2	0.1925	*0.2808*	*1.1226*
PS-13	0.2800	*0.4085*	*1.9767*
PS-3	0.3341	*0.4874*	*2.5810*
PS-8	0.4763	*0.6948*	*4.4089*
PS-4	0.4870	*0.7104*	*4.5593*

intrinsic viscosities calculated by using the molecular weight obtained with 1,4-dioxane for the samples in NaBr 1.5 M and NaBr 0.1 M.

Using the values of $[\eta]$ (experimental and calculated) and the molecular weight of each system, the plots of the FFS, SF and B models were constructed. These plots provide interesting information from their slopes and ordinates to the origin. Using the constants Φ and Φ_0 and the slopes, we calculated the values of K and B for the three solvents. Tables IV – VI show the values obtained from FFS, SF and B theories of K. In non-perturbed conditions, parameter K gives values of 8.5×10^{-4} dL/g for 1,4-dioxane and 12.4×10^{-4} dL/g for NaBr 1.5 M; these values agree with the values reported by Brandrup [6] and Okamoto [11]. However, in perturb conditions or non-theta

TABLE IV PAA molecular parameters in 1,4-dioxane @ 30°C

$[\eta] = 8.5 \times 10^{-4} M^{0.5}$

$Io = 2.84 \times 10^{21}\ dL\ gmol^{-1}\ cm^{-3}$

	K $dL\ g^{-1}$	B cm^{-3}	A cm	σ
FFS	8.453×10^{-4}	29.03×10^{-31}	6.677×10^{-9}	1.839
SF	8.452×10^{-4}	73.73×10^{-31}	6.677×10^{-9}	1.839
B	8.453×10^{-4}	44.52×10^{-31}	6.677×10^{-9}	1.839

TABLE V PAA molecular parameters in NaBr 1.5 M @ 15°C

$[\eta] = 12.4 \times 10^{-4} M^{0.5}$

$Io = 2.84 \times 10^{21}\ dL\ gmol^{-1}\ cm^{-3}$

	K dL/g	B cm^3	A cm	σ
FFS	12.37×10^{-4}	114.5×10^{-31}	7.581×10^{-9}	2.089
SF	12.37×10^{-4}	288.9×10^{-31}	7.581×10^{-9}	2.089
B	12.38×10^{-4}	175.4×10^{-31}	7.581×10^{-9}	2.089

TABLE VI PAA molecular parameters in NaBr 0.1 M @ 25°C

$[\eta] = 3.12 \times 10^{-4} M^{0.755}$

$I = 1.34 \times 10^{21}\ dL\ gmol^{-1}\ cm^{-3}$

	K dL/g	B cm^3	A cm	σ
FFS	5.017×10^{-4}	7.042×10^{-26}	7.208×10^{-9}	1.986
SF	14.86×10^{-4}	2.530×10^{-26}	10.35×10^{-9}	2.852
B	6.835×10^{-4}	6.845×10^{-26}	7.990×10^{-9}	2.201

conditions, K does not agree with the value of 3.12×10^{-4} dL/g reported by Brandrup [6]. We obtained three differents values (5.017×10^{-4} for FFS theory, 14.86×10^{-4} for SF theory and 6.835×10^{-4} dL/g for Berry theory); in this case we could say that the FFS theory is closer ($K = 5.017 \times 10^{-4}$ dL/g) to the value reported by Brandrup [6]. These results lead to conclude that the linear expansion factor of the mean radius of gyration (α_s) is not related to α_η by $\alpha_\eta^3 = \alpha_s^{2.43}$.

The parameter B that is associated to the excluded volume and show different values in theta and non-theta state. However, we saw that the magnitude of B indicates the stage of swelling of the polymer; for example, in 1,4-dioxane we observe values between 29×10^{-31} and 73×10^{-31} cm^3 whereas, in NaBr 1.5 M we observe values between 114×10^{-31} and 288×10^{-31} cm^3. This indicates that water is swelling the PAA. If we compare the values of NaBr 1.5 M to values in NaBr 0.1 M, we better observe the effect of water in the swelling of polymer, since the latter values are higher that the values of NaBr 1.5 M. On the other hand, we observe that estimates of the parameter B depend appreciably on the functional form of α_s used and also on the relation assumed for α_s and α_η. In addition, Noda [13] states that the parameter B may be expressed as a function of various terms due to the nonelectrostatic and electrostatic interactions; where electrostatic interactions depend of the charge density and the inverse square root of the added salt concentration.

The parameter associated with steric hindrance, A, in 1,4-dioxane shows the same values in the three theories (6.677×10^{-9} cm). The other theta solvent gives the same values in the three theories (7.581×10^{-9} cm). This agrees with theory because A depends on $[\eta]_\theta$ In other words, A depends on the concentration of sodium ions in the polyelectrolyte because later values are higher than 1,4-dioxane. In non-theta solvent, we obtained different values of A (7.208×10^{-9} for FFS theory, 10.35×10^{-9} for SF theory and 7.99×10^{-9} cm for Berry theory) because we obtained different values of K; in theory, the parameter A should have similar values in all three theories; furthermore parameter A should be higher than parameter A in theta state. However, only SF plot and B plot agree with the last point.

Tables IV–VI show the conformation factors, σ, which were calculated by using Eqs. (13) and (14). In a non-perturbed system, they agree with values reported by Brandrup [6] for 1,4-dioxane (1.83) and for NaBr 1.5 M (2.38); our values are 1.839 for 1,4-dioxane and 2.089 for NaBr 1.5 M. This means that the polymer is more flexible in NaBr 1.5 M than 1,4-dioxane because $\langle R \rangle$ in aqueous solution is higher that in organic solution. For a perturbed system, there are no values reported in the literature.

Values of $\langle R^2 \rangle$ and $\langle S^2 \rangle$ were calculated according to Eqs. (7) and (15). Figure 3 shows the behavior of $\langle S^2 \rangle$ with the molecular weight in the three systems. The plot is in a logarithmic scale in order to better appreciate the behavior of the three systems. We can appreciate that radii of gyration of NaBr 0.1 M are higher than those of the other systems and that the radius of gyration in 1.5 M NaBr is higher than those in 1,4-dioxane. This is due to swelling effects.

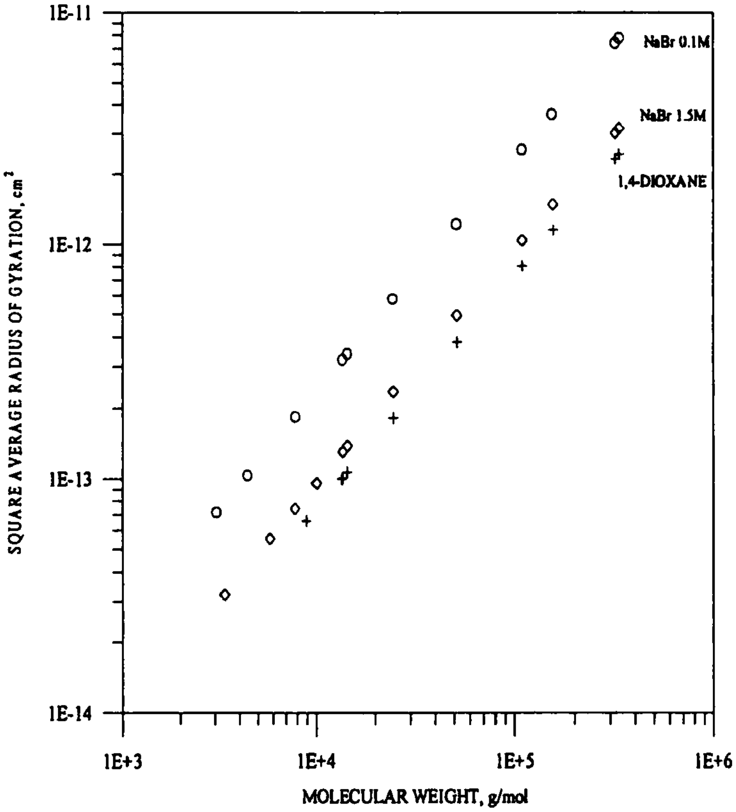

FIGURE 3 $\langle S^2 \rangle$ of PAA in aqueous and no-aqueous systems.

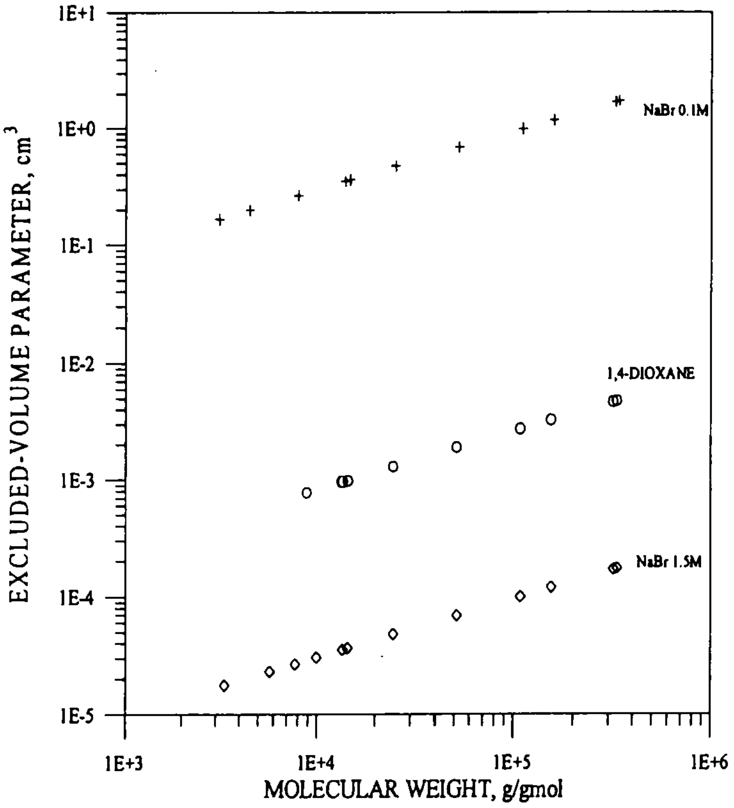

FIGURE 4 Excluded volume parameter of PAA in aqueous and no-aqueous system.

Figure 4 shows the behavior of the excluded volume parameter with the molecular weight, and was calculated with Eq. (8). The plot is in a logarithmic scale to appreciate the behavior of the three systems. We can observe that each molecule in a very dilute solution in a good solvent will tend to exclude all others from the volume which it occupies, therefore swelling the polymer.

CONCLUSIONS

Many authors in the literature who calculate the molecular parameters of polymers, in particular, polyelectrolytes, have shown a strong disagreement between the available theories and the experimental values. In all cases, the calculated expansions are much larger than the experimental expansions. The discrepancy is explained by assuming that the effective charge density of the macromolecule is much smaller that the calculated value. FFS, SF, B theories and others allow to estimate the molecular parameters in non-perturbed conditions. In perturbed conditions, it is possible that the short range interactions could be affected by the ionic resistance of the saline solutions in which the polymers are dissolved. On the other hand, we have determined which theory is best for a particular case. In our case, since we compared the values of the SF theory (in theta and non-theta state) to the other theories, we have adopted these values and work with them in order to produce a realiable thermodynamical characterization. However, the fundamental thermodynamics of polymers is still an open field for research and discussion.

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