Dynamical studies on low molecular weight polyacrylamide aqueous solution

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From quasi elastic light scattering and viscosity measurements we deduce the unperturbed dimensions and dynamical power laws of low molecular weight polyacrylamide in 0.1 N NaCl aqueous solutions.

(Keywords: Diffusion coefficient; viscosity; unperturbed dimensions; polyacrylamide; dilute solution)

INTRODUCTION

Due to their increasing technological importance water-soluble polymers have been extensively studied on a fundamental point of view during these last ten years[1]. However the first studies dealing with polyacrylamide (PAAm) were reported thirty years ago[2,3]. A large discrepancy is found in the literature among the dynamic or static studies which were done on those polymers. Authors have explained this discrepancy putting forward many effects which can arise with this class of polymers. Beside the classical influence of polydispersity[4] and plurimolecular aggregation at high molecular weight[5] many peculiar effects are specific to PAAm: presence of residual charges on the lateral groups of atoms, inter- and intramolecular hydrogen bonds[6], bound water around the amide functions[7], imidation cross-linking of lateral groups leading to inter- or intrachain cross-linking[8]. Furthermore, difficulties which are inherent to physico-chemical measurements in aqueous solutions must be considered.

New investigations on unhydrolysed PAAm had been carried out in our laboratory[9]. Measurements of the molecular weight dependence of the radius of gyration (R_G) has been performed by light scattering on well defined samples in dilute 0.1 N NaCl aqueous solutions. In a high molecular weight range ($10^5 < M_w < 10^7$), an unexpected behaviour was found:

$$\langle R_G^2 \rangle^{1/2} = 0.0749\, M_w^{0.64}\ (\text{Å}) \tag{1}$$

The value of the excluded volume exponent ν_G in this power law is abnormally higher than that generally observed for polymers in good solvents ($\nu_G = 0.60$). Secondly, translational diffusion coefficient D and sedimentation velocity S measurements had been performed[10] in the same range of molecular weight. Both these dynamic quantities depend on the dynamic radius R_D, and, from their molecular weight dependence, the dynamic excluded volume exponent was found to be very low: $\nu_D = 0.53$. These results had been explained on the basis of a 'modified blob' model[11] where the spatial cross-over from Gaussian to excluded volume statistics of the segment distribution function around the centre of mass of the molecule occurs at a large molecular weight value ($M_w = M_\tau \sim 3.10^3$). Furthermore, it has been deduced from this interpretation that the θ temperature should be around -3°C for the PAAm–water system.

In a previous study[12], which was done on PAAm in 0.1 N KBr–D_2O solution at room temperature, we have measured the *Rg versus* M_w variation by neutron scattering. It turns out that no excluded volume effect is observed on static dimensions in a low molecular weight range ($M_w < 3.10^4$). The present paper deals with complementary data on the dynamic properties of the low molecular weight PAAm in 0.1 N NaCl–water solution at room temperature. This investigation includes the synthesis and characterization of the polymer samples. Furthermore, measurements of the molecular weight dependence of the translational diffusion coefficient and intrinsic viscosity is analysed.

In a second paper, we will emphasize the temperature dependence of the molecular dimensions in a temperature range just above the θ temperature which will be determined.

The aim of these two contributions is to confirm the molecular model which had been invoked to describe the behaviour of PAAm in aqueous solutions in the high molecular weight range.

EXPERIMENTAL

Synthesis and characterization of PAAm samples

The classical process for free radical polymerization of PAAm (H_2O_2 or AIBN as initiators in aqueous and DMF solutions) is generally known to lead to high molecular weight samples. As we were concerned with the low molecular weight range, we chose the polymerization method described by Bhadani *et al.*[13]

The PAAm samples were prepared by radical polymerization in dimethylformamide (DMF). To avoid cross-linking induced by water, DMF was distilled over sodium. The acrylamide (Am) was twice recrystallized from acetone. Pure HNO_3 (97%) was used as initiator for the polymerization reaction. The experimental set up was thermostatically controlled during the course of the reaction. The polymerization was stopped after four

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hours at temperature higher than 70°C or after 24 h at lower temperatures. The polymer which is not soluble in DMF, precipitates from the medium. It was washed in DMF and ethanol, dissolved in water, filtered, concentrated and precipitated in a methanol–ethanol mixture (50/50).

A gel chromatography experiment was performed on the polymer in order to get an approximate molecular weight value. From data given in *Table 1*, it turns out that the low molecular weight samples are obtained at high temperatures and low monomer concentrations.

Infra-red spectra of the polymerization products were compared to the acrylamide spectrum. No absorption appeared at 1680 cm^{-1} which is characteristic of an imidiation reaction[8] and the H–N bands of the monomer and polymer were similar. The N/C ratio (0.38) measured by elementary analysis was close to the theoretical value (0.39) expected for pure homopolyacrylamide, without hydrolysed groups or imide functions in the chain.

Fractionation of PAAm samples and molecular weight characterization of the fractions

(1) The polydispersity value of PAAm samples synthesized by free radical polymerization is high and for the purpose of our study, it was necessary to fractionate these samples. Therefore, PAAm were dissolved three times in distilled water at concentration less than 1% (g/100 g) at 25°C. Successive additions of non solvent (distilled ethanol) and decreasing temperature allowed us to collect twenty-one fractions ($9.10^3 < M_w < 4.10^5$) from the three parent polymers.

(2) The weight average molecular weights, M_w, of the fractions were determined by light scattering using a Fica apparatus (wavelength $\lambda = 546$ nm). The 0.1 N NaCl–H_2O (three times distilled) solutions were made optically clean by centrifugation at 19 000 g for about five hours and then directly pipetted into the scattering cells. The previous addition of bacteriostatic (NaN_3, 200 mg l^{-1}) stabilizes the PAAm solutions over a period of ten days. No aggregation effects were observed in the concentration range studied ($C < 2\%$).

(3) The refractive index increments (dn/dc) were determined by two different methods. In the first one, the measurements were performed on a differential refractometer Brice Phoenix, ($\lambda = 546$ nm), on undialysed solutions (0.1 N NaCl) of polymer concentration ranging between 3.10^{-3} and 3.10^{-2} g cm^{-3}. In mixed solvents, the analysis of the refractive index increment data can be affected by the preferential adsorption of one of the component on the polymer. Some authors[14] who have studied 0.2 N NaCl aqueous solutions of PAAm, have found a high discrepancy between the dn/dc values measured under constant chemical potential conditions (diffusion experiments by ultracentrifugation) and those determined directly with a differential refractometer. Consequently, in a second experiment and for two fractions we have calculated the dn/dc values from the integration of the peak given by a differential interferometer (type Optilab, white light) at the output of a g.p.c. column working with 0.1 N NaCl water as eluent. This process is analogous to a dialysis experiment.

The results are given in *Table 2*. The slight discrepancy between the two sets of values shows that dn/dc does not depend on molecular weight and concentration. It can be also deduced that there is no preferential absorption, as later confirmed in section I.B.5. Moreover, these values are in good agreement with those given by Munk *et al.*[14] (dn/dc = 0.172 cm^3 g^{-1}) for PAAm in 0.2 N NaCl but they are higher than that obtained by François *et al.*[9] (dn/dc = 0.164 cm^3 g^{-1}). An average value of 0.180 cm^3 g^{-1} was selected for the M_w determination.

(4) The number average molecular weights were determined from osmometric measurements performed with a Mechrolab Model 502 apparatus.

(5) The g.p.c. experiments were carried out on a home built apparatus. A Cl 2B, 4B, 6B Sepharose mixture (Pharmacia) was used as support and the eluent was a 0.1 N NaCl–H_2O solution. The detection was a differential refractometer (Waters) which was connected to a recorder and calibrated with salt water. *Table 3* gives the characteristics of the standard polyoxyethylene samples (POEH: Hoechst; POEt: Toyo Soda) used to calibrate the g.p.c. columns. No preferential adsorption was revealed by the POE chromatograms. The variation of the elution volume V_e *versus* M_w is shown in *Figure 1* (curve (a)) in a semi-logarithmic representation. It is linear in the intermediate molecular weight range ($10^4 < M_w < 50.10^4$).

Table 1 Synthesis of polyacrylamide: reaction parameters [Am]: acrylamide concentration; [HNO_3]: initiator concentration; M_0: molecular weight of the polymer given by the top of the chromatographic peak

Nomenclature	Temperature of the reaction (°C)	[Am] (kg m^{-3})	[HNO_3] (kg m^{-3})	M_0
PASD3	50.0	399	28	$>10^5$
PASD7	75.0	200	5	$>10^5$
PASD10	91.0	160	8	7.5×10^4

Table 2 Refractive index increment of four PAAm fractions measured on two different refractometers in various concentration range

		PASD3-Z3	PASD3-Z4	PASD7-Z7	PASD10-Z4
M_w		224 000	160 000	51 000	28 000
Concentration range (%)		0.1 → 1.5	0.003 → 0.015	0.005 → 0.025	0.10 → 1.0
dn/dc (cm^3 g^{-1})	Optilab		0.177	0.182	
	Brice Phoenix	0.185			0.179

Table 3 Data for the polyoxyethylene samples M_W: weight-average molecular weight (light scattering); M_n: number-average molecular weight (osmometry) (M_W/M_n)f: polydispersity (Hoechst (POEH) and Toyo Soda (POET) values); (M_W/M_n)chr: experimental polydispersity

Nomenclature		M_W Dalton	M_n Dalton	(M_W/M_n)f	(M_W/M_n)chr
POET	1 200 000	1 200 000		1.12	1.33
POET	660 000	505 000		1.10	1.22
POET	280 000	235 000		1.05	1.05
POET	150 000	150 000		1.04	1.05
POET	73 000	73 000		1.02	1.02
POEH	35 000	31 000		1.00	1.08
POEH	20 000	22 000	22 000	1.00	1.00
POEH	10 000	13 000		1.00	
POEH	3 000	2 950		1.00	

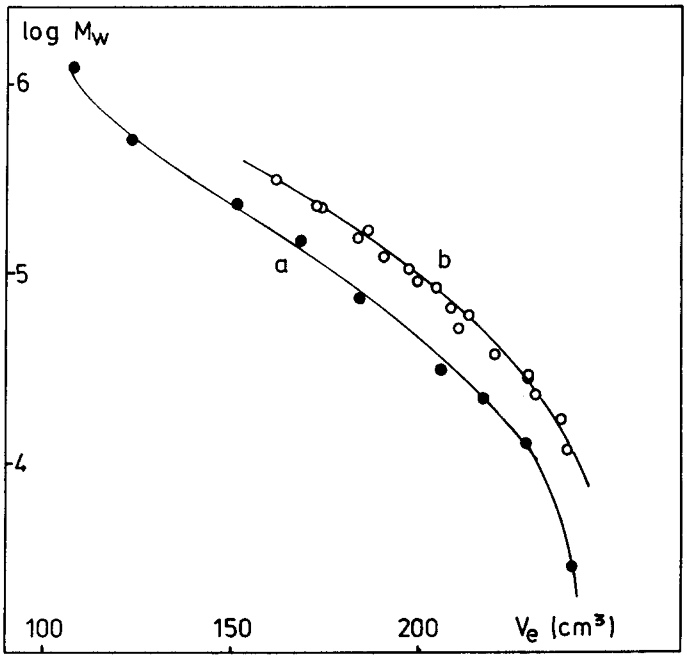

Figure 1 Gel permeation chromatography experiments: plot of log M_w *versus* elution volume V_e for standard polyethyleneoxide (curve a) and for polyacrylamide fractions (curve b)

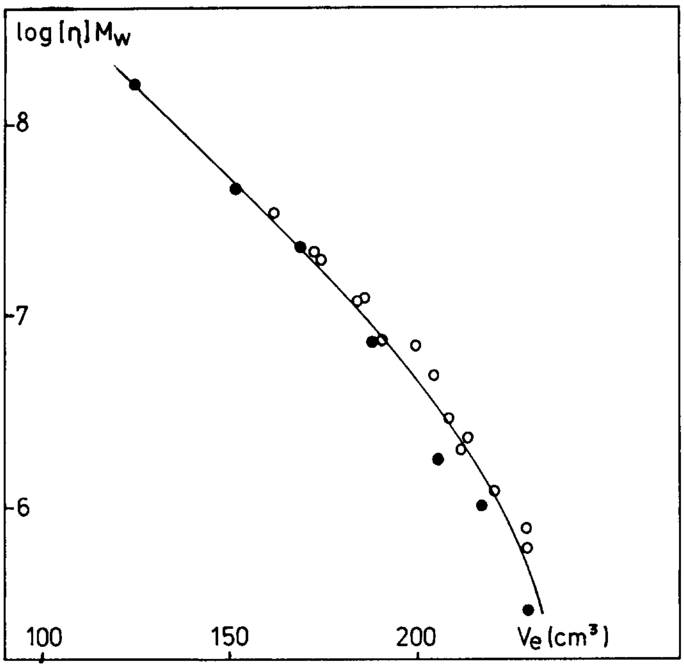

Figure 2 Gel permeation chromatography experiments: Universal calibration, log [η] M_w *versus* V_e, according to Benoit *et al.*[16]. Open symbols: polyacrylamide fractions; full symbols: polyethylene oxide

The polydispersity index of the samples was calculated with respect to the monodisperse POEH 20.000 sample ($M_w/M_n = 1.00$) to take into account the axial diffusion effect.

The Tung's relation gives[15]:

$$\left(\frac{\sigma}{a}\right)^2=\left(\frac{\sigma_{chr}}{a}\right)^2-\gamma^2 \qquad (2)$$

where a is the slope of the fitted straight line in *Figure 1(a)*, σ and σ_{chr} are the width of, respectively, the reference and the sample chromatograms and γ is related to the sample polydispersity $(M_w/M_n)_{chr}$ by:

$$\gamma^2=\ln(M_w/M_n)_{chr} \qquad (3)$$

This column is efficient since its axial diffusion coefficient value is found to be 0.32 and its theoretical plate number is about 2580 plates per metre.

The molecular weight dependence of the elution volume, V_e for PAAm fractions is represented in *Figure 1* (curve (b)). The discrepancy between the POE and PAAm curves is easily explained by the differences in the hydrodynamical volumes of the two polymers. Benoît *et al.*[16] have proposed a so-called 'universal calibration' in which $\log[\eta]\cdot M_w$ is plotted *versus* V_e, where $[\eta]$ is the intrinsic viscosity. In this representation, all the experimental points (POE and PAAm) fit better on a single curve although there appears to be an increasing divergence when V_e increases.

The data for the polyacrylamide fractions are given in *Table 4*. For seven of them, the polydispersity index values which were calculated from the chromatograms, using relations (2) and (3) are in good agreement with those obtained directly from the M_w/M_n ratio. One can note that the polydispersity index slightly increases with molecular weight. Therefore, it will be necessary to discuss a possible polydispersity effect on the dynamic dimensions of the polymer.

In the sensitivity limit of the refractometers, the chromatograms do not show preferential adsorption. *Figure 3a* represents the elution peak of a PASD3-Z3 solution on 0.100 N NaCl-H_2O (4.61 10^{-3} g cm^{-3}); no rejection or adsorption peak of salt is observed at high elution volumes. *Figure 3b* is the chromatogram of a solution 0.105 N NaCl in water eluted by water–0.100 N NaCl. The

Table 4 Data for polyacrylamide fractions M_W: weight average molecular weight (light scattering); M_n: number average molecular weight (osmometry); $(M_W/M_n)_{chr}$: polydispersity index (g.p.c.); M_D and M_η: average molecular weights calculated from relations (17) and (21); [η] and D: intrinsic viscosity and diffusion coefficient measured in 0.1 N NaCl-water at 25°C

Nomenclature	$(M_W/M_n)_{chr}$	M_W	M_n	M_n	M_D	[η] (cm³ g⁻¹)	$D \times 10^7$ (cm² s⁻¹)
PASD3-Z2	2	315 000	–	287 000	365 000	108.7	1.58
PASD3-Z3	1.7	224 000	–	208 000	254 000	93.9	1.67
PASD7-Z1	1.7	219 000	–	204 000	248 000	90.9	2.02
PASD3-Z4	1.5	166 000	–	155 000	181 000	74.3	2.23
PASD7-Z2	1.3	154 000	–	148 000	164 000	74.7	2.22
PASD7-Z3	1.2	121 000	–	117 000	126 000	60.1	2.72
PASD7-Z4	1.24	106 000	85 000	102 000	112 000	57.3	2.58
PASD3-Z5	1.23	91.000	–	88 000	96 000	59.8	2.33
PASD7-Z6	1.12	64 000	–	63 000	66 000	45.8	3.93
PASD3-Z6	1.13	61 000	54 000	60 000	63 000	38.3	3.23
PASD7-Z7	1.11	51 000	46 000	50 000	52 000	38.8	3.21
PASD7-Z8	1.10	38 000	34 000	37 000	38 500	31.2	4.34
PASD3-Z7	1.08	29 000	25 000	28 400	29 500	25.5	4.31
PASD10-Z4	1.08	28 000	–	27 700	28 500	21.0	4.85
PASD7-Z9	1.08	27 000	25 000	26 700	27 500	22.8	–
PASD10-Z5	1.05	23 000	–	22 700	23 400	19.8	5.46
PASD10-Z6	1.07	17 000	–	16 800	17 300	16.9	6.92
PASD10-Z7	1.02	12 000	–	11 900	12 200	11.9	–
PASD3-Z8	–	9 000	9 000	8 900	9 200	13.5	8.68

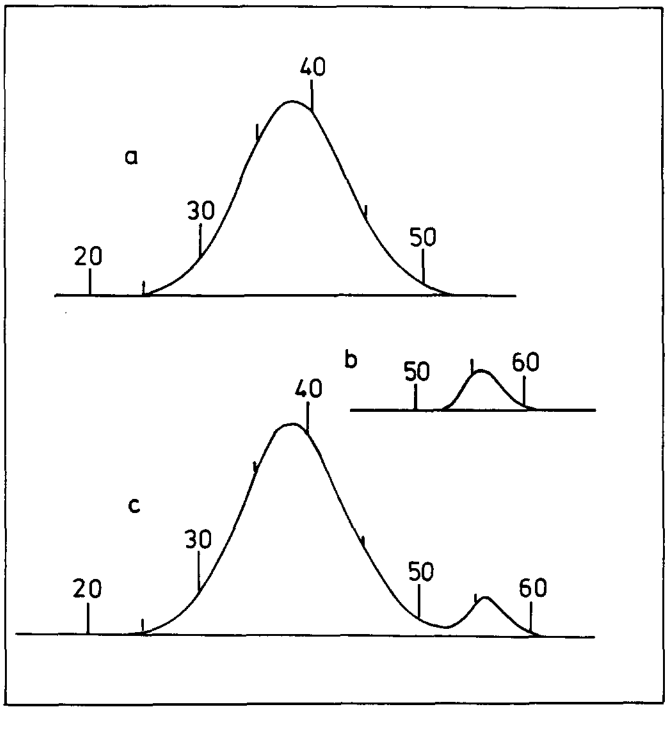

Figure 3 Chromatograms of: (a): 0.100 N NaCl solution of PASD3-Z3 fraction (c=0.46×10^{-2} g cm^{-3}); (b): 0.105 N NaCl solution; (c): 0.105 N NaCl solution of PASD3-Z3 fraction (c=0.46×10^{-2} g cm^{-3}). Eluent: 0.100 N NaCl solution

chromatogram of a PASD3-Z3 in 0.105 N NaCl–H_2O eluted by water–0.100 N NaCl is given in *Figure 3c*. The comparison between these three figures shows without any ambiguity that there is no preferential adsorption, ($\lambda < 0.01$ g/g) as it can be deduced from the (dn/dc) measurement (see *Table 2*).

Measurements of intrinsic viscosity [η] *and translational diffusion coefficient* D

The viscosity measurements were performed on an automatic capillary viscosimeter Fica at 25° ±0.01°C. The translational diffusion coefficients were measured by quasi elastic light scattering experiment using a home built apparatus. The optical and mechanical part of this apparatus has already been described[17]. The electronic treatment of the scattered signal was modified[18] compared with the earliest experimental set up. Indeed the scattered signal going through a photon counting system is sent to a minicomputer in a real time experiment. The full homodyne correlation function defined on N channels ($N < 256$) is calculated and accumulated in the computer. Each experimental point is described by the following relation:

$$C(i\Delta\tau)^{\mathrm{exp}} = \frac{1/M \sum_{j=1}^{M} n(t_j)n(t_j+i\Delta\tau)}{\left\{\frac{1}{M}\sum_{j=1}^{M} n(t_j)\right\}^2} \qquad i=1,N \tag{4}$$

where $C(i\Delta\tau^{\mathrm{exp}}$ is the experimental normalized correlation function of the scattered intensity, $\Delta\tau$ is the width of each channel which can range from 1 μs to 1 s, $n(t_j)$ is the number of photoelectron falling on the photocathode of the photomultiplier at time t_j and M is the number of accumulations which were done.

In a first step the final set of data is analysed using a routine least squares exponential fit:

$$C(i\Delta\tau)^{\mathrm{th}} = K_1 \exp - \bar{\Gamma}\tau + K_2 \tag{5}$$

where K_1 and K_2 are constants and $\bar{\Gamma}$ is related to the translational diffusion coefficient D:

$$\bar{\Gamma} = \frac{1}{\tau_c} = 2Dq^2 \tag{6}$$

q is the scattering vector and is given by:

$$q = \frac{4\pi}{\lambda} n \sin\frac{\theta}{2} \tag{7}$$

where n is the refractive index of the solution and θ the scattering angle. In a second step, following an approach inherent in Koppel's work[19] the experimental data are analysed in terms of moments where the logarithm of the normalized correlation function is developed as:

$$\log C(i\Delta\tau)^{\text{th}} = K_3 - \bar{\Gamma}\tau + \frac{1}{2!}\frac{\mu_2}{\bar{\Gamma}^2}(\bar{\Gamma}\tau)^2 \qquad (8)$$

In this expression, K_3 is a constant and μ_2 is the second cumulant of the distribution function of the diffusion coefficients in the case of polydisperse macromolecules.

Three parameters can be defined to control the goodness of a fit. The first one is the standard error of the three unknown parameters of equation (5) which is estimated from the variance–covariance matrix of the parameters[20]. Experimental correlation functions are accumulated until these standard errors are less than one per cent.

The second parameter is the $\mu_2/\bar{\Gamma}^2$ factor which appears in relation (8). All the experiments done on polyacrylamide have given a value of less than 0.1 which can be considered as the standard limit for monodisperse system[21].

Finally a correlation function of the deviation between the experimental points and the theoretical curve can be defined as:

$$Q = 1 - \frac{\sum_{i=1}^{N-1} \Delta C_i \Delta C_{i+1}}{\sum_{i=1}^{N} \Delta C_i^2} \qquad (9)$$

where

$$\Delta C_i = C(i\Delta\tau)^{\text{th}} - C(i\Delta\tau)^{\text{exp}} \qquad (10)$$

This Q coefficient is calculated at the end of each fit and we have verified that for PAAm in water solution its value is almost unity ($Q > 0.7$), which corresponds to a truly monoexponential statistically well defined, experimental function.

The experimental correlation functions were sampled on 250 points lying in the range:

$$4 < \bar{\Gamma}\tau_{\max} < 8 \qquad (11)$$

where

$$\tau_{\max} = N\Delta\tau \qquad (12)$$

For low and high molecular weight PAAm we have ensured that relation (6) is valid over the scanned q vector range (see *Figure 4*). Moreover we have ensured that determination of $\bar{\Gamma}$ or τ_c is independent of the width $\Delta\tau$ of each channel in the range given by relation (11).

Figure 5(a–b) shows the D variation *versus* the polymer concentration for a low and high molecular weight sample. All the measurements were done on one polymer concentration ranging from 2×10^{-2} (g cm^{-3}) for higher molecular weight to 4×10^{-2} (g cm^{-3}) for lower molecular weight fractions.

RESULTS

Intrinsic viscosities[η] and translational diffusion coefficients D are given in *Table 4*. The logarithmic variation of D *versus* M_w is plotted in *Figure 6a*. The experimental points fit with a straight line leading to the following relation:

$$D = 6.4\ 10^{-5} M_w^{-0.48 \pm 0.02}\ (\text{cm}^2\ \text{s}^{-1}) \qquad (13)$$

obtained by least square analysis.

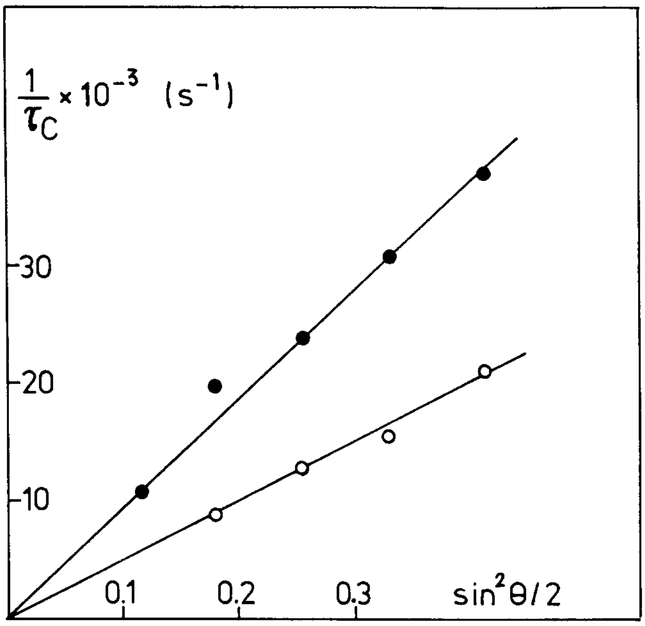

Figure 4 Variation of the reciprocal relaxation time as a function of $\sin^2 \theta/2$, for two fractions. Open symbols: PASD7-Z2 (M_w=154 000), full symbols PASD7-Z6 (M_w=61 000)

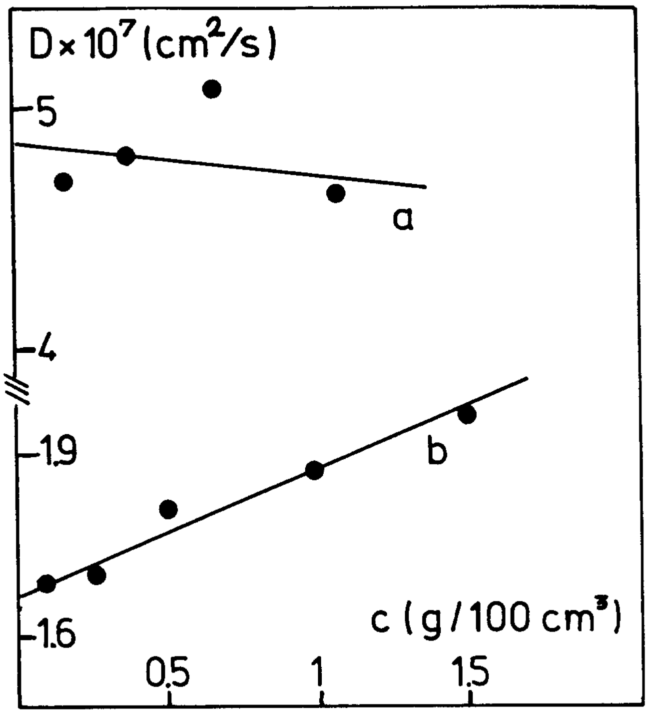

Figure 5 Polymer concentration dependence of the translational diffusion coefficient D. (a): PASD10-Z4 (M_w=28 000); (b): PASD3-Z3 (M_w=224 000)

These experimental points are very scattered. This is due to the low signal to noise ratio at such low concentration and molecular weight ranges. Thus, it is impossible to obtain an accuracy <4% on the exponent value ν_D of the power law. For comparison, we have drawn two straight lines corresponding to 0.6 and 0.5 exponent values. It turns out that the fit could also be compatible with $\nu_D = 0.5$ which is characteristic of the Gaussian statistic. Nevertheless, an exponent value $\nu_D = 0.6$ leads to a straight log–log plot which cannot fit the experimental points.

Furthermore, the polydispersity effect can be evaluated

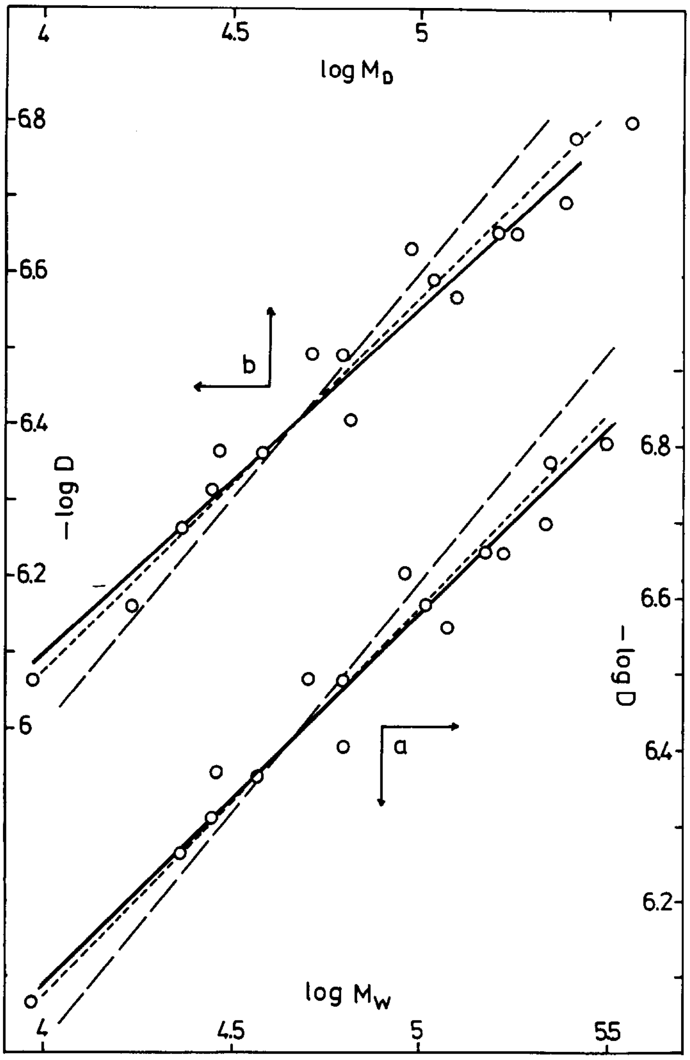

Figure 6 Log–log plots of diffusion coefficient D *versus* M_w (a) and M_D (b). Full lines correspond to relations (13) curve a and (18) curve b. Dotted lines correspond to lower laws with $\nu_D = 0.6$ and $\nu_D = 0.5$

knowing that, in a quasi elastic light scattering experiment, the z average values, D_z, of the translational diffusion coefficient is measured. This average value is defined by:

$$D_z = \frac{\sum c_i M_i D_i}{\sum c_i M_i} \tag{14}$$

where c_i, M_i and D_i are the concentration, molecular weight and diffusion coefficient of the species i[22]. *Figure 6b* is a log–log plot of D *versus* M_D, where M_D is the average molecular weight given by:

$$M_D = \left[\frac{\sum c_i M_i^{1-\nu_D}}{\sum c_i M_i}\right]^{-1/\nu_D} \tag{15}$$

If we assume a classical molecular weight distribution of the Wesslau type[23]:

$$c_i = k \exp\left[-\frac{1}{2\gamma^2}\ln^2\frac{M_i}{M_0}\right] \tag{16}$$

where M_0 is the molecular weight given by the top of the peak and γ is defined by relation (3), M_D is then given by:

$$M_D = M_0 \exp\frac{\gamma^2}{2}(2-\nu_D) \tag{17}$$

The M_D values calculated with $\nu_D = 0.5$ are listed in *Table 4*. A least square fit of the variation of the diffusion coefficient with the M_D molecular weight leads to the relationship:

$$D = 5.4 \times 10^{-5} M_D^{-0.46} \, (\mathrm{cm^2\,s^{-1}}) \tag{18}$$

Taking into account the scattered nature of the experimental points, the discrepancy with respect to relation (13), where $\nu_D = 0.48$, is within the experimental error.

In *Figure 7* we compare our data with other literature data[10,24,25]. In the same molecular weight range, our results significantly differ from those of Sholtan[24] worked out from ultracentrifugation experiments in pure water at 20°C. The anomalously high value of the exponent of the power law found from these data ($\nu_D = 0.69$) may be due to the presence of some charged groups on the polymer inducing a polyelectrolyte behaviour particularly pronounced in water without added salt. No chemical characterization of the sample is discussed in the Sholtan paper[24].

Around $M = 10^5$, our data overlap those of Schwartz *et al.*[10] and Patterson *et al.*[25], obtained for a higher molecular weight range. In both cases, the authors have observed no change in $[\eta]$ and R_G with NaCl concentration up to 4M, which conflicts with the results of Klein *et al.*[4] and Munk *et al.*[14] but indicates that their samples do not exhibit a polyelectrolyte effect. Nevertheless, the slope of the log–log plot of D *versus* M_w is significantly lower in the molecular weight range investigated in this work than in the higher molecular weight range. We conclude from these diffusion coefficient

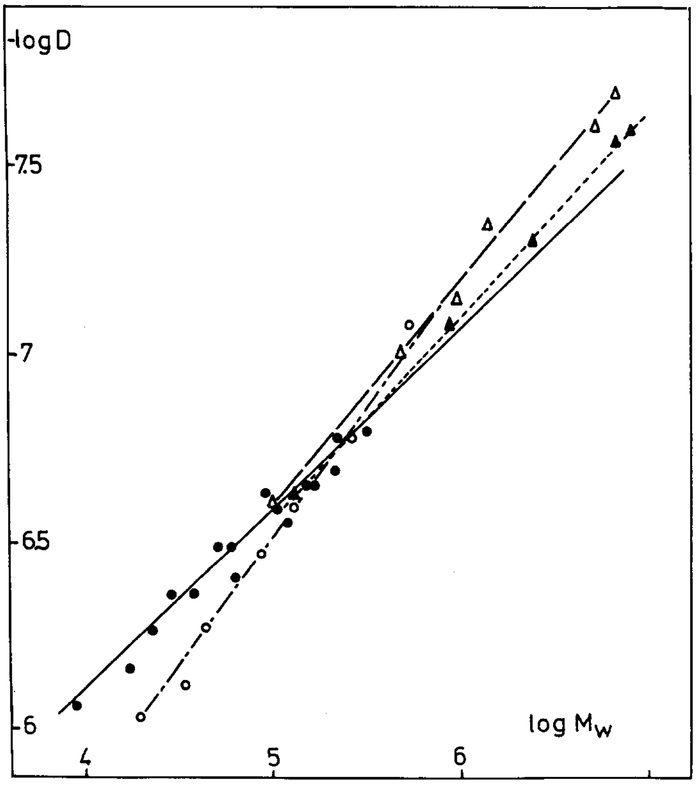

Figure 7 Translational diffusion coefficient measurements: (●): this work; (○): ref. 24; (△): ref. 25; (▲): ref. 10

measurements that PAAm of low molecular weight have a nearly Gaussian dynamic behaviour but, unfortunately, in our experimental conditions, the method does not allow us to get a more precise value of the ν_D exponent.

The intrinsic viscosity data (*Figure 8*) lead to a Mark–Houwink expression:

$$[\eta]=0.024\,M_w^{0.65\pm0.01}\,(\mathrm{cm^3\,g^{-1}}) \qquad (19)$$

The average viscosimetric molecular weight, M_η, is given by:

$$M_\eta=\left[\frac{\sum c_i M_i^a}{\sum c_i}\right]^{1/a} \qquad (20)$$

and can be calculated, in a Wesslau distribution hypothesis, from:

$$M_\eta=M_0\exp a\frac{\gamma^2}{2} \qquad (21)$$

where a is the exponent of the Mark–Houwink power law. *Table 4* shows that M_η slightly differs from M_w even for polydispersity index equal to 2, if we take $a=0.65$. The power law in M_η is then:

$$[\eta]=0.025\,M^{0.66\pm0.01}\,(\mathrm{cm^3\,g^{-1}}) \qquad (22)$$

which is very close to relation (19).

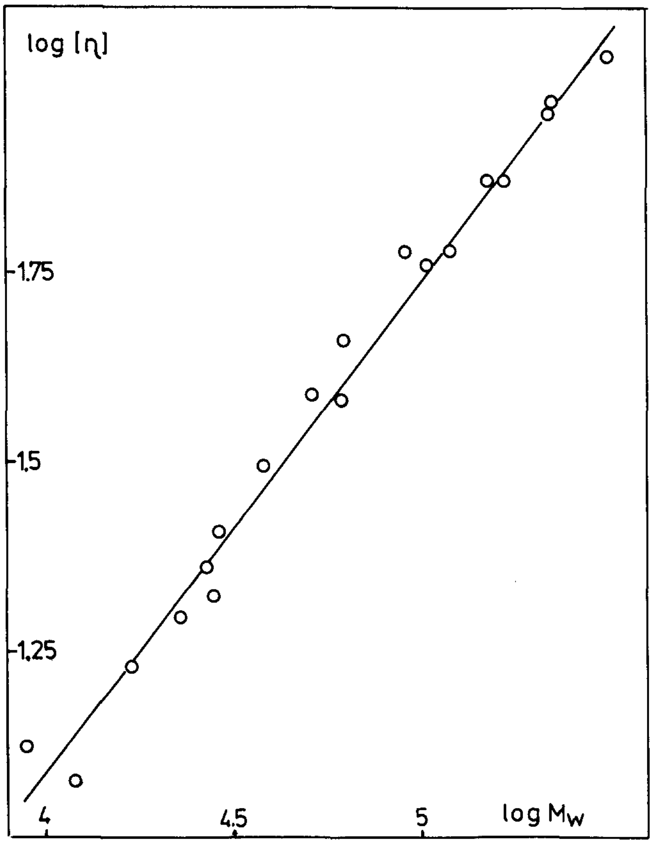

Figure 8 Log–log plot of the intrinsic viscosity *versus* M_w

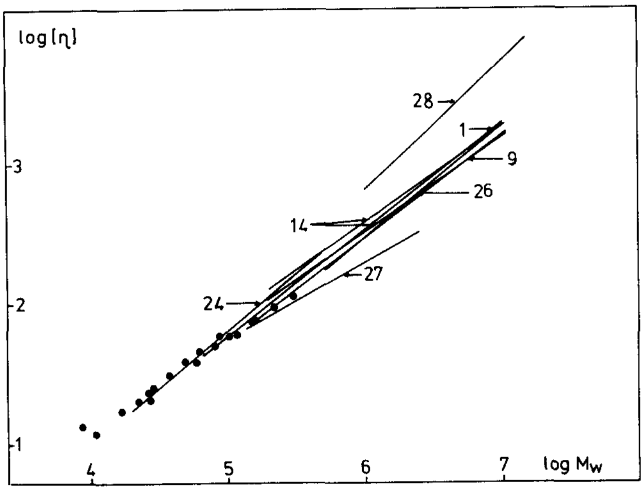

Figure 9 Intrinsic viscosity measurements; full symbols: this work; full lines correspond to power laws given in the indicated references

Figure 9 compares the viscosimetric data of *Table 4* with other results obtained in pure water or in different salinity and temperature conditions[1,9,14,24,26–28]. If we expect the results of refs. 27 and 28, there is a rather good agreement between the different data whatever the salt content is. No molecular weight dependence of $[\eta]$ in the low range molecular weight ($M_w<10^5$) were available for comparison with relation (22). The Mark–Houwink exponent of this relation is much lower than the exponent which was obtained in the higher molecular weight range. Precisely, François *et al.*[9] have found:

$$[\eta]=9.3\times10^{-3}\,M_w^{0.75}\,(\mathrm{cm^3\,g^{-1}}) \qquad (23)$$

for $10^5<M_w<10^7$ in 0.1 N NaCl, this relation being in good agreement with those recently published by Kulicke *et al.*[1]:

$$[\eta]=10^{-2}\,M_w^{0.755} \qquad \text{(in pure water)} \qquad (24)$$

and

$$[\eta]=1.94\times10^{-2}\,M_w^{0.7} \qquad (\text{in } 0.1\ \mathrm{M}\ Na_2SO_4) \qquad (25)$$

for $4.10^4<M<10^7$.

DISCUSSION

The viscosimetric and diffusion coefficient measurements which were performed in this study show the tendency for low molecular weight polyacrylamide ($M_w<10^5$) in water – 0.1 N NaCl to behave as statistical chains with low excluded volume effects. Let us recall that a previous neutron scattering experiment[12] has revealed that the static expansion coefficient of PAAm of low molecular weight ($M_w<3.10^4$) approaches unity, in close agreement with the present dynamic observations.

Furthermore a comparison of the Mark–Houwink relations for polyacrylamide in water, ethyleneglycol and formamide was recently done by Klein *et al*[29]. In the high molecular weight range three different relations fit the experimental points. In the low molecular weight range ($M_w<150\,000$) and whatever the nature of the solvent is, all the experimental points fall into one line in a log–log plot. The slope of this line is close to 0.50. Such an observation confirms the conclusion of the present work. In a forthcoming paper, we will discuss the compatibility of this result with the model proposed by François *et al.*[11] in order to explain the polyacrylamide behaviour in the high molecular weight range. Such a discussion can only be fruitful if the θ temperature of polyacrylamide in water is well known.

Nevertheless, from the present results, we can determine the static and dynamic unperturbed dimensions of PAAm.

Therefore the static results on polyacrylamide in 0.1 N NaCl aqueous solution have shown that, depending on the molecular weight range, two power laws can describe the R_G variations as a function of M_w ($M_w < 3.10^4$ see ref. 12; $M_w > 3.10^4$ see relation (1) and ref. 9).

The dynamic results show the same type of behaviour but the cut off between the two power laws appears at higher molecular weight ($M_w < 4.10^5$ this work; $M_w > 4.10^5$ see ref. 10). These results agree with theoretical predictions[30,31] according to the fact that the dynamic parameter is much more sensitive than the static parameter to the correlation between segments at small distance along the chain of a polymer.

The perturbation of the dynamic dimensions by the excluded volume effect occurs for much higher molecular weight. Then, we can assume that expression (13) is relevant to the unperturbed dynamic dimensions.

Indeed, considering the relation between D and the hydrodynamic radius R_H:

$$R_H = \frac{kT}{6\pi\eta_0 D} \tag{26}$$

where k is the Boltzman constant, T the absolute temperature and η_0 the viscosity of the solvent, it can be deduced from relation (13):

$$R_H = R_{H0} = 2.43\, n_m^{1/2} \tag{27}$$

where n_m is the degree of polymerization and R_{H_0} the unperturbed hydrodynamic radius.

The unperturbed radius of gyration R_{G_0} was found by Schwartz *et al.*[32] to be:

$$R_{G0} = 3.29\, n_m^{1/2} \tag{28}$$

The hydrodynamic theory of Kirkwood and Riseman[33] predicts, for monodisperse flexible non draining coils, a ratio $R_{H_0}/R_{G0} = 0.665$. The same result is obtained in a more recent theory[34] for the θ conditions but a smooth decrease is predicted in good solvents $R_H/R_G = 0.537$. The experimental value of this ratio for polyacrylamide is found to be 0.74 from relations (27) and (28). This value is higher than that predicted by the theories but in looking at static and dynamic unperturbed dimension ratio for polystyrene, Schmidt *et al.*[35] have obtained $R_{H0}/R_{G0} = 0.79$. The same discrepancy with respect to the theoretical predictions is found for polystyrene and polyacrylamide. This confirms that the flexibilities of the two polymers are of the same order of magnitude as shown in a previous paper[32].

Among the different methods which have been proposed to determine unperturbed dimensions from viscosity measurements one of the most used is the Stockmayer–Fixman's plot[36] where $[\eta]/M^{1/2}$ is plotted as a function of $M^{1/2}$. Such a plot is given from our results in *Figure 10a*, where the data of *Table 4* are transferred. The extrapolation at zero molecular weight leads to:

$$0.10 < \frac{[\eta]}{M^{1/2}} < 0.14\ (\mathrm{cm^3\ mole^{0.5}\ g^{-1.5}}) \tag{29}$$

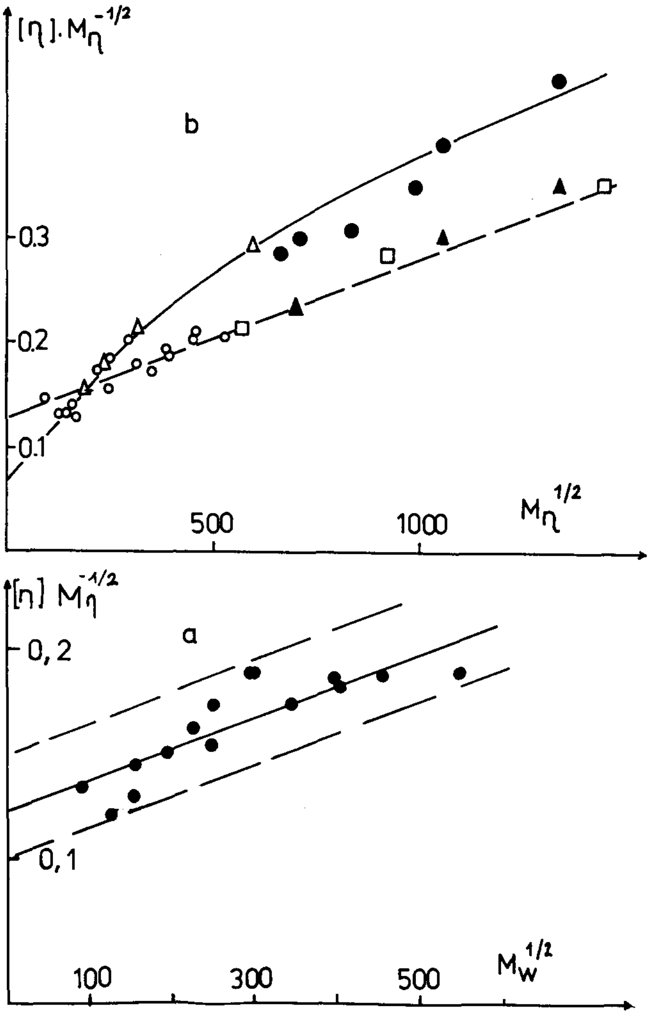

Figure 10 Stockmayer–Fixman plot. (a): (●) full symbols: this work – full lines correspond to a least square regression; (b): full line gives a picture of results found in pure water in ref. 26 (●) and 29 (△); dotted line gives a fit of different results obtained in 0.1 M NaCl solutions ((○): this work, (▲) ref. 9, and in 0.5 M NaCl solutions ((□): ref. 26

It has been shown[31] that the classical Fox Flory expression[37] between the intrinsic viscosity and the static radius of gyration:

$$[\eta] = \phi' \frac{R_G^3}{M} \tag{30}$$

($\phi' = 6^{3/2}\,\phi$, with $\phi = 2.5\ 10^{23}$ universal Flory's constant), must be replaced by:

$$[\eta] = \phi' \frac{R_G^2 R_H}{M} \tag{31}$$

Then, in θ conditions, by introducing in relation (31) the experimental ratio $R_{H_0/R_{G0}} = 0.74$, one obtaines:

$$\frac{[\eta]}{M^{1/2}} = 0.74\ \phi' \frac{(R_{G0}^2)^{3/2}}{M^{3/2}} \tag{32}$$

The value of $[\eta]/M^{1/2}$ determined from relations (28) and (32) is 0.16, in fair agreement with the experimental determination (relation (29)).

The unperturbed dimensions of PAAm in water were calculated by Kurata *et al.*[38] and Winston *et al.*[39] from the viscosity data of Collinson *et al.*[40]. A high value of $[\eta]/M^{1/2}$ was found: 0.278 cm^3 $mole^{0.5}$ $g^{-1.5}$). But we must emphasize that the experimental basis of this determination[40] is of very little significance. In this work, the molecular weight is derived from kinetic arguments starting from the relation between the viscosity of the final polymer as a function of the monomer concentration and inferring the molecular weight of this final polymer from the kinetic constants. Moreover, no information is given in this paper about the polydispersity of the samples.

In *Figure 10b*, we have reported in a Stockmayer representation some viscosity data of more significance[9,26,29]. In order to take into account the polydispersity differences of the samples used in these works the M_η values are considered instead of the M_w values. M_η are calculated from the polydispersity index given by the authors. In spite of a high scattering of the experimental points, all these data are compatible with unperturbed dimensions corresponding to relation (29) (*Figure 10a*). This relation is, on the other hand, in good agreement with the data of Misra *et al.*[41] ($[\eta]/M^{1/2} = 0.160$). Nevertheless, from the data reproduced in *Figure 10b*, Kulicke *et al.*[1] (full line) gives for $[\eta]/M^{1/2}$ the value 0.079 cm^3 mole $^{0.5}$ $g^{-1.5}$, assuming that, in the explored molecular weight range, the Stockmayer–Fixman curve must exhibit a downward curvature. This is not apparent when we consider the results of the present work and those previously obtained by Schwartz *et al.*[32], which can fit on a single straight line. We can note that the results of these authors, for PAAm in 0.5 M NaCl are in very good agreement with François *et al.*[9] data (PAAm in 0.1 M NaCl) while their data for pure water significantly show a higher expansion of the polymer coil in the absence of added salt. It seems that the samples which were used in these works[26] are not pure homopolyacrylamide but contain some carboxylic groups; the polyelectrolytic character of the samples is well demonstrated considering on the one hand the high value of the viscosity and sedimentation coefficient of the power laws ($a = 0.80$ and $\nu_D = 0.68$) and, on the other hand, the great influence of the salinity of the solvent on the molecular dimensions.

CONCLUSION

Low molecular weight well defined samples were obtained by fractionation of a polymer synthesized by radical polymerization ($10^3 < M_w < 3.10^5$). We pay attention to the excluded volume effect on the polymer chain conformation studied by viscosity and inelastic light scattering measurements. By taking into account the polydispersity effects on such measurements, we have determined the power law of the molecular weight dependences of the intrinsic viscosity $[\eta]$ and translational diffusion coefficient D. The exponents of these power laws indicates the tendency of low molecular weight polyacrylamide ($M < 3.10^5$) to behave as statistical coil without excluded volume effect in agreement with the previous predictions of François *et al.*[11].

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