# Theta point of polyacrylamide in aqueous solution and temperature dependence of the molecular dimensions

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The molecular weight ($M_w$) and temperature ($T$) dependence of the expansion factor and the second virial coefficient of polyacrylamide (PAAm) in dilute solution are investigated. The theoretical predictions of the blob and of the modified Flory's theory are compared with experimental results on polystyrene. We note similar behaviour for these two polymers which cannot certify in the intermediate region if the volume exponent $\nu$ is higher than the theoretical asymptotic value or not. In addition we give an experimental determination of the theta temperature for PAAm in water $\theta = -8$°C.

**(Keywords: theta point; expansion factor; second virial coefficient; PAAm; dilute solution)**

## INTRODUCTION

In the course of systematical studies on unhydrolysed polyacrylamide in 0.1N NaCl aqueous solutions[1-4], we have shown that the static and dynamic conformational properties, at 25°C, are significantly different according to the molecular weight range investigated. This can be described in terms of a cross-over between the Gaussian statistics and the excluded volume statistics for a rather high value of molecular weight ($4 \times 10^4$). For comparison, in the case of polystyrene[5-7] or poly(methyl methacrylate)[7], the effect due to volume exclusion on the conformation occurs for much lower molecular weight. This finding, either in the classical Flory's theory[8] or in the framework of the more recent theoretical approaches can be related to a low value of the reduced temperature $1-\theta/T$ at $T=25$°C. Starting from a modified 'blob model' François *et al.*[10] were able to interpret the data on the molecular dimensions of polyacrylamide by assuming that the $\theta$ temperature is around $-3$°C.

The first purpose of this paper is an experimental attempt in the determination of the $\theta$ temperature of polyacrylamide (PAAm) in aqueous solutions. On the other hand, we confirm the values of the unperturbed dimensions of polyacrylamide as obtained in previous papers[4,10]. Our discussion will deal with the confrontation of the experimental and theoretical variations of the molecular expansion of the chain as a function of the reduced temperature, by comparing different theoretical approaches. Finally, our aim is also to emphasize the differences in the behaviour of a highly polar polymer in polar solvent and of a more classical non polar polymer such as polystyrene in organic solvent.

## EXPERIMENTAL

A high molecular weight sample (ADIO) from Rhône-Poulenc was used as well as various low molecular weight samples, obtained in our laboratory by fractionation of a free radical polymerized polyacrylamide[4]. In all the cases, we obtained by elementary analysis a N/C ratio close to the theoretical value (0.39) expected for a pure homopolyacrylamide and the potentiometric titration, after ionic exchange, has revealed an hypothetic carboxylic content lower than 0.3% which was not significant according to this technique. The molecular characteristics of the PAAm samples are given in *Table 1*.

Light scattering measurements were performed either on a Fica apparatus (wavelength $\lambda = 546$ nm) or on a home built set up[11] ($\lambda = 632$ nm). The 0.1 N NaCl/$H_2O$ or methanol/0.1 N NaCl/$H_2O$ solutions ($H_2O$ 3 × distilled) were made optically clean by centrifugation at 1900*g* for about five hours and then directly pipetted into tight scattering cells. The temperature was regulated at ±0.1°C. We have previously shown that the effect of preferential adsorption can be neglected and the $A_2$ values determined from the Zimm-plot are not apparent[4,15].

The preferential adsorption was studied by gel permeation chromatography[12] by using an eluent methanol–water (fraction of methanol: 38%). A mixture of Sepharose CL2B and Sephacryl F 300 gels was used as support. The detector was an Optilab 902 interferometer. The calibration of the detector was obtained by eluating water solutions of methanol slightly more concentrated in methanol than the eluent. The polymer samples were dried under vacuum at 50°C during several days in order to avoid the errors due to the presence of hydration water. However, one can expect that a small quantity of residual water will introduce a slight additional error on the preferential adsorption.

**Table 1** Data for polyacrylamide samples. $M_W$: weight average molecular weight (light scattering)[4]; $M_W/M_n$: polydispersity index (gel permeation chromatography)[4]

| Nomenclature | $M_W$ | $M_W/M_n$ |
|---|---|---|
| AD10 | 6.7 $10^6$ | 2.2 |
| PASD3-Z3 | 2.2 $10^5$ | 1.7 |
| PASD3-Z5 | 9.1 $10^4$ | 1.23 |
| PASD3-Z6 | 6.1 $10^4$ | 1.13 |
| PASD7-Z7 | 5.1 $10^4$ | 1.11 |
| PASD10-Z3 | 3.3 $10^4$ | – |

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**Table 2** Values of the second virial coefficient $A_2$ at different temperatures $T$

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | sample: PASD10-Z3 | | | | | |
| $T$(°C) | 4 | 9.5 | 18 | 25 | 28 | 39 | 49 | 60 |
| $A_2 \times 10^4$ (cm$^3$.g.$^{-2}$ mol) | 3.3 | 4.5 | 5.2 | 6.1 | 6.0 | 6.5 | 6.8 | 6.8 |
| | | | sample: PASD3-Z3 | | | | | |
| $T$(°C) | 4.5 | 14 | 24.5 | 25 | 34.5 | 44 | 55.5 | |
| $A_2 \times 10^4$ (cm$^3$.g.$^{-2}$.mol) | 2.0 | 2.4 | 3.0 | 2.8 | 3.0 | 3.1 | 3.2 | |
| | | | sample AD10 | | | | | |
| $T$(°C) | 2.5 | 6.5 | 10 | 18.5 | 26.4 | 3.0 | | |
| $A_2 \times 10^4$ (cm$^3$.g$^{-2}$.mol) | 0.3 | 0.5 | 0.7 | 1.1 | 1.3 | 1.8 | | |

The preferential adsorption coefficient, $\lambda_0$, is given by the following relationship:

$$\lambda_0 = \Delta\phi_1 V/q = \Delta\phi_1/c \ (\text{cm}^3\ \text{g}^{-1}) \quad (1)$$

where $\Delta\phi_1$ is the difference between the volume fractions of the solvent 1 (methanol) inside and outside the macromolecular coil. It is calculated from the peak surface and the calibration constant; $q$ is the weight of polymer in the injected volume $V$ and $c$ the polymer concentration expressed in g cm$^{-3}$.

The viscosity measurements were performed on an automatic capillary viscosimeter Fica thermostatically controlled at ±0.01°C. A Zimm–Crothers viscosimeter, involving low shear gradients, was used for high molecular weight sample.

## RESULTS

### *Determination of the θ temperature of polyacrylamide in 0.1 N NaCl aqueous solutions*

*Variation of the second virial coefficient* versus *temperature.* In *Table 2*, are given the variations of the second virial coefficient $A_2$, as a function of temperature for two PAAm fractions and for the AD10 sample. These coefficients were calculated from the slope of the straight line representing the variations of the ratio ($c/I$) $I$ = scattered intensity) at zero angle *versus* polymer concentration $c$, in the Zimm representation. In the case of ternary mixtures (mixed solvent), the fluctuation theory shows that the measured molecular weight and second virial coefficient have an apparent value, if one of the solvent is preferentially adsorbed onto the polymer[13,14]. However in our case, for PAAm in 0.1 N NaCl solvent, some previous gel permeation chromatography experiment has shown that such a phenomenon can be considered as negligible[4].

According to the classical Flory's theory[8], the $A_2$ variation *versus* $T$ and $M_w$ is given by:

$$A_2 = 4\pi^{3/2}\mathcal{N}_a B_0\left(1-\frac{\theta}{T}\right)F(y) \quad (2)$$

and

$$y = B_0\left(1-\frac{\theta}{T}\right)\left(\frac{R_G^2}{M_w}\right)_0^{-3/2} M_w^{1/2} \quad (3)$$

where $\mathcal{N}_a$ is the Avogadro's number, $B_0$ is a constant, $(R_G^2/M_w)_0$ represents the local rigidity of the chain in $\theta$ conditions and $F(y)$ is a function which tends to 1 when $y$ tends to zero. Formally, $A_2$ is expected to be a linear function of $1/T$ in the vicinity of the $\theta$ temperature.

By extrapolation of these curves to $A_2 = 0$, one can obtain an approximate value of the $\theta$ temperature $-3°\text{C} < \theta < -7°\text{C}$. By assuming a mean value $\theta = -5°\text{C}$, we have plotted on *Figure 1* the $A_2$ *versus* $(1-\theta/T)$ variations according to relation (2). The curves obtained for the three PAAm samples can be compared to those determined by Berry for polystyrene samples of analogous molecular weights just above the $\theta$ point in decaline[15]. It turns out that the behaviour of these two polymers are very similar. This can justify the extrapolation process used to determine the $\theta$ point for PAAm in aqueous solution. Nevertheless we must take into account the particular nature of the solvent ($H_2O$–0.1 N NaCl) which presents singular variations of its physical properties in the 0°–4°C temperature range. That is the reason why it seemed necessary to approach the $\theta$ conditions by another method.

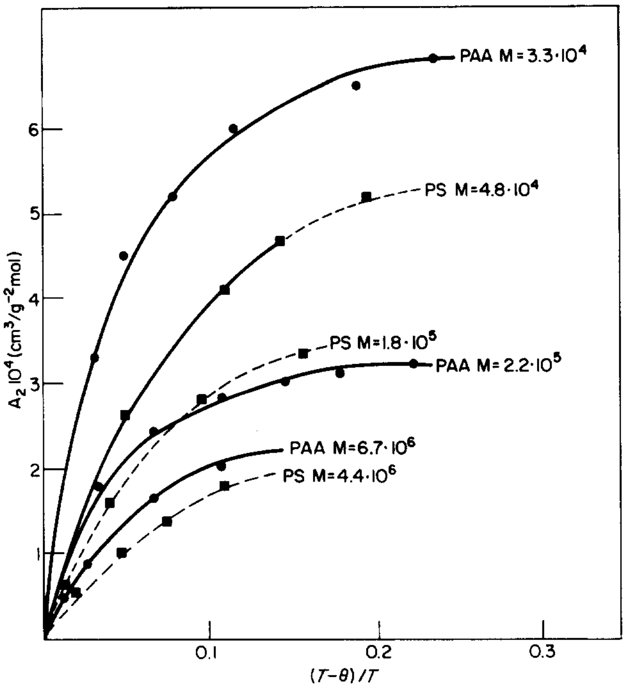

**Figure 1** Comparison between the second virial coefficient $A_2$ *versus* $(1-\theta/T)$ determined respectively with polyacrylamide (full line) and polystyrene (dotted line)[15]

*Study of the cloud point and θ temperature for PAAm in 0.1 N NaCl–water–methanol muxtures.* In a previous paper[16], we have shown that the mixture (0.1 N NaCl–water–methanol (volume fraction of methanol 40%) is a $\theta$ solvent of PAAm at 21°C and we have determined the unperturbed dimensions of PAAm under such conditions. In the present work, we study the variation of the $\theta$ temperature *versus* methanol concentration, in an attempt to determine the $\theta$ temperature in pure 0.1 N NaCl

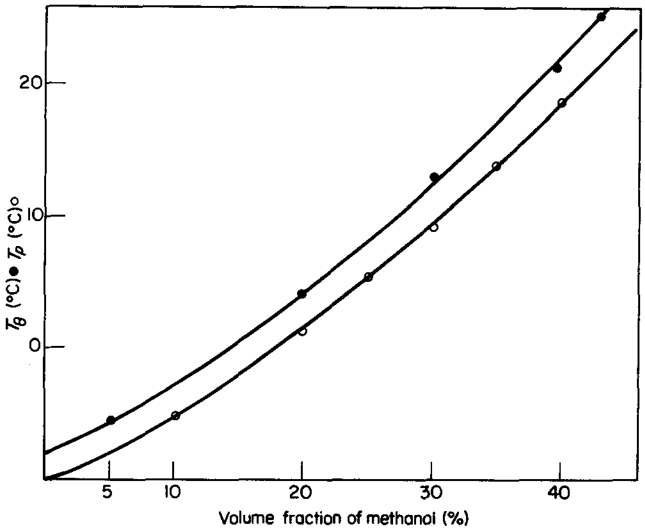

**Figure 2** Plot of the variation of the cloud point $T_p(0)$ and the theta temperature $T_\theta$ (●) *versus* the volume fraction of methanol

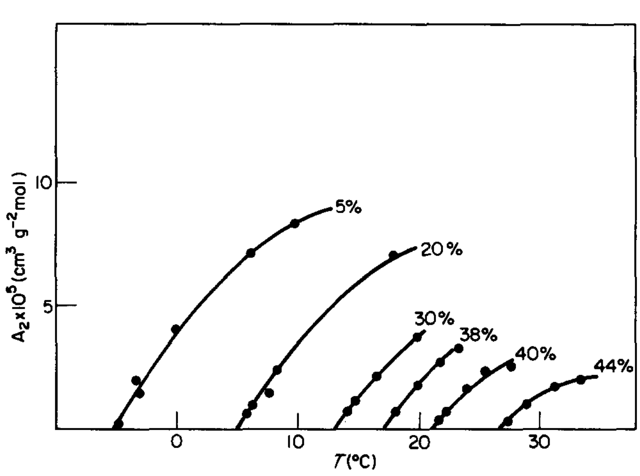

**Figure 3** Plot of the second virial coefficient $A_2$ of the PAAm (AD10) in methanol – pure water mixtures *versus* temperature and volume fraction of methanol

water by extrapolation at zero methanol content.

In a first experimental approach and by using a simple turbidimetric method, we have measured the cloud point $T_p$ of the solutions of the high molecular weight sample (AD10) containing a volume fraction of methanol starting from 5% to 45%. For these tests, the polymer concentration was $3\ 10^{-3}$ g cm$^{-3}$ which is the concentration value at which the $T_p = f(c)$ curve has its maximum, for 40% of methanol content. Results show that $T_p$ is a regular function of the solvent composition (*Figure 2*).

In *Figure 3* we have plotted the $A_2 = f(T)$ variations for various methanol contents, as obtained from light scattering experiments. The temperatures at which $A_2$ becomes zero are reported in *Figure 2 versus* solvent composition. They can be identified with the $\theta$ points, only in absence of preferential absorption effects[13,14].

Our gel permeation chromatography experiments in methanol water mixtures show that water is preferentially absorbed on PAAm. For the high molecular weight sample this adsorption does not exceed 0.104 cm$^3$ per g of polymer. Nevertheless the molecular weight dependence of the intrinsic viscosity was found to be:

$$[\eta] = 0.11\, M^{0.51}\ (\text{cm}^3\,\text{g}^{-1}) \qquad 5\ 10^4 < M < 1.7\ 10^6 \quad (4)$$

for the conditions (21°C and 40% of methanol) where $A_2 = 0$. This power law is well characteristic of the Gaussian statistics and $\theta$ conditions. At last, the radius of gyration of AD10 measured at temperature at which $A_2 = 0$ is $1200 \pm 50$ Å whatever the methanol content is. Such arguments show that a correct value of $\theta$ temperature of PAAm in pure water must be obtained by extrapolation of the values determined at various solvent compositions. This process leads to $\theta = -8$°C in rather good agreement with the previous determination.

### *Unperturbed dimensions of PAAm*

In this work, we obtain the unperturbed intrinsic viscosity of PAAm through relation (4) and the unperturbed static dimensions for one sample $R_{G\theta} = 1200$ Å. By taking into account the arguments developed in our previous paper[4], about the polydispersity effects and the differences between the static and dynamic behaviour, we have calculated the unperturbed dimensions $A$, expressed by:

$$A = \left(\frac{6\langle R_{G\theta}\rangle^2}{M}\right)^{1/2} \quad (5)$$

In *Table 3*, we compare the $A$ value obtained from the different experiments. $A$ is found to be:

$$0.92 < A < 1.02\ \text{Å g}^{-1/2}\,\text{mol}^{1/2} \quad (6)$$

From this result, we can calculate the steric factor $\sigma$ and the characteristic ratio $C_\infty$, by assuming that the length of the C–C bond is 1.53 Å and the C–C–C angle is 113° as given by Yoon *et al.*[17]:

$$2.51 < \sigma < 2.78 \quad (7)$$

$$14.6 < C_\infty < 15.8 \quad (8)$$

For the confrontation of experimental results with theoretical predictions, we will also need the number of monomer units, $n'$, in the statistical element.

$$n' = \frac{A^2 M_0}{(l')^2} \quad (9)$$

where $M_0$ is the molecular weight of the monomer and $l'$ is the length of a segment:

$$l' = 2.55\ \text{Å} \quad (10)$$

We find:

$$9.2 < n' < 11.3 \quad (11)$$

**Table 3** Comparison of the $A$ values obtained in different works

| Ref. | Method | Experimental law | $A$ (Å) |
|---|---|---|---|
| Ref. 16 | light scattering in $\theta$ solvent | $R_{G_\theta} = 0.39\ M^{0.5}$ | 0.95 |
| Ref. 4 | Stockmayer–Fixmann on $[\eta]$ data | | $0.92 < A < 1.03$ |
| Ref. 4 | translational diffusion coefficient of low molecular weight sample | $D = 6.4 10^{-5}\ M^{-0.48}$ | 1.02 |
| this work | light scattering in $\theta$ solvent (one sample) | | 0.92 |
| | intrinsic viscosity in $\theta$ solvent | | 0.92 |

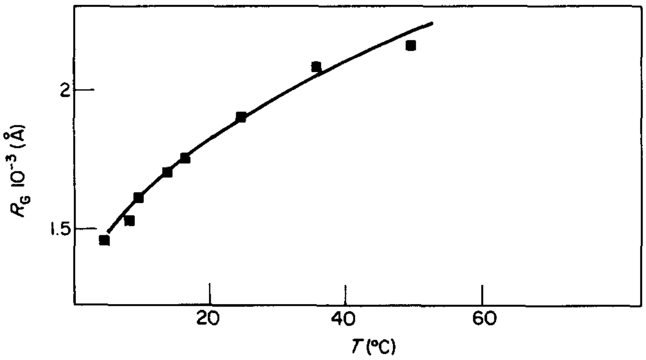

**Figure 4** Plot of the radius of gyration $R_G$ *versus* temperature for two different molecular weights: (a) (■) $M_w = 6.7 \times 10^6$; (b) (●) $M_w = 2.2 \times 10^5$; in 0.1 N NaCl aqueous solutions

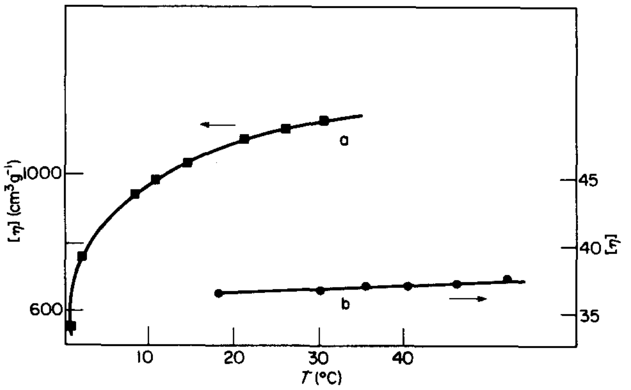

**Figure 5** Plot of the intrinsic viscosity variation $[\eta]$ against temperature for the same molecular weight: (a) $M_w = 6.7 \times 10^6$; (b) $M_w = 2.2 \times 10^5$; in 0.1 N NaCl aqueous solutions

### *Temperature dependence of intrinsic viscosity and radius of gyration*

In *Figures 4* and *5*, we have plotted the variations of $R_G$ and $[\eta]$ as a function of temperature for PAAm in 0.1 N NaCl aqueous solutions. The continuous increase of the molecular dimensions as well below as above room temperature confirms that this temperature is not too far from the $\theta$ conditions.

Moreover, heating up to 200°C solutions of high molecular weight sample in pure water and in water of very high salinity (4 M NaCl and 4 M $CaCl_2$) does not induce phase separation. Contrary to many water soluble polymer solutions which have a LCST[18,19] (lower critical solution temperature) below 100°C, polyacrylamide solutions are very stable, and the chain expansion is an increasing function of temperature at least up to 100°C.

## DISCUSSION

This discussion tends to present a quantitative comparison between the theoretical predictions and the experimental data for the molecular weight and temperature dependences for polyacrylamide in aqueous solutions. Some years ago, Ackasu *et al.*[20] have done the same parallel by collecting all the data available on polystyrene solutions. In fact, our main purpose is to demonstrate that the conformational behaviour of polyacrylamide does not differ significantly from that of a more classical non polar polymer. Indeed the discrepancies between the experimental findings and the theoretical predictions are for polyacrylamide of the same order of magnitude than for polystyrene.

It is the reason why in a first step we limit our analysis to two different theoretical approaches, the classical Flory's theory[8] and the more recent 'blob' theory for polymer statistics[9].

### *Theoretical recalls*

Let us recall the original Flory equation:

$$\alpha_s^5 - \alpha_s^3 = \gamma z \tag{12}$$

which relates the $\alpha_s$ (the linear expansion factor) to the excluded volume parameter, $z$:

$$z = (3/2\pi)^{3/2}(v/l^3)N^{1/2} \tag{13}$$

$N$ is the number of beads in the equivalent statistical chain, $l$ is the statistical length and $v$ is the usual binary cluster integral which is approximated as[21]:

$$v = v_\infty(1 - \theta/T) \qquad \text{for } T > \theta \tag{14}$$

In this expression $v_\infty$ can be considered as a constant.

The simplest 'blob' theory[9] assumes that the pair correlation function jumps from a Gaussian to an excluded volume statistic for a critical number of beads $N = N_\tau$. The mean square distance between two segments $i$ and $j$ should then be written:

$$\langle r_{ij}^2 \rangle = |i-j| l^2 \qquad \text{for } |i-j| \leqslant N_\tau \tag{15}$$

$$\langle r_{ij}^2 \rangle = N_\tau \left( \frac{|i-j|}{N_\tau} \right)^{2\nu} l^2 \qquad \text{for } |i-j| \geqslant N_\tau \tag{16}$$

The value of $N_\tau$ is assumed to be proportional to $(l^3/v)^2$ and is related to the reduced temperature $\tau = (1 - \theta/T)$ by:

$$N_\tau = \beta \tau^{-2}$$

$\beta$ will be the adjustable parameter for the comparison of theory and experiment.

Introduction of relations (15) and (16) in the expressions of the radius of gyration $R_G$ and the hydrodynamic radius $R_H$:

$$R_G^2 = \frac{l}{2N^2} \sum_i \sum_{j \neq i} \langle r_{ij}^2 \rangle \tag{17}$$

$$R_H{}^{-1} = \frac{l}{2N^2} \sum_i \sum_{j \neq i} \left\langle \frac{l}{r_{ij}} \right\rangle \tag{18}$$

leads to the following equations:

$$\alpha_s^2 = x^2(3 - 2x) + 6x^{1-2\nu} \left( \frac{1 - x^{2\nu+1}}{2\nu + 1} - \frac{1 - x^{2(\nu+1)}}{2(\nu+1)} \right) \tag{19}$$

$$\text{and} \quad \alpha_H = \frac{4}{x^{1/2}} \left[ 2(3 - x) + 3 \left( \frac{x^{\nu-1} - 1}{1 - \nu} - \frac{x^{\nu-1} - x}{2 - \nu} \right) \right]^{-1} \tag{20}$$

$\alpha_s$ is defined as $R_G/R_{G\theta}$ and $\alpha_H$ as $R_H/R_{H\theta}$ ($R_{G\theta}$ and $R_{H\theta}$ are the static and hydrodynamic dimensions in the $\theta$ conditions); $x$ is $(N_\tau/N)$.

By using the dynamic argument that the intrinsic viscosity is a measure of the weighted average relaxation times, Weill and Des Cloizeaux[22] end this equation

$$[\eta] \alpha \frac{R_G^2 R_H}{M}$$

Therefore, the viscosimetric expansion factor $\alpha_\eta$ can be easily expressed as:

$$\alpha_\eta^3 = \alpha_s^2 \alpha_H$$

and calculated from relations (19) and (20). In the good solvent limit:

$$\alpha_s = 0.923\,(N/N_\tau)^{0.1} \tag{21}$$

$$\alpha_H = 0.747\,(N/N_\tau)^{0.1} \tag{22}$$

$$\alpha_\eta = 0.860\,(N/N_\tau)^{0.1} \tag{23}$$

By identifying the asymptotical limit of Flory's expression:

$$\alpha_s^5 = \gamma z \tag{24}$$

with expression (21), Ackcasu and Han[20] deduced a relation between $N/N_\tau$ and the parameter $z$:

$$N/N_\tau = Cz^2 \tag{25}$$

where $C$ is a numerical proportionality constant which is:

$$C = \gamma^2/0.923^{10} \tag{26}$$

where $\gamma = 2.60$ in the original Flory's theory and 1.276 in its modified version[21].

Such an identification allows to compare the two types of theory and the experiment with an unique parameter ($N/N_\tau$) which can be obtained[20] in terms of $M_w$ and T;

$$\frac{N}{N_\tau} = \frac{\tau^2 M_w}{\beta n' M_0} \tag{27}$$

If $n'$ can be evaluated from unperturbed dimensions, $\beta$ is the only adjustable parameter for a quantitative comparison.

*Comparison between theory and experiments*

From the comparison done by Ackcasu *et al.*[20] and more recently by Kanda *et al*[23], between theories and polystyrene data, the following remarks can be made:

(i) The blob theory predicts significantly lower values of the chain expansion than the experimental data in the transition region centred around $N/N_\tau \sim 1$. The inadequacy of the blob theory in this region is attributed[10,20] to the discontinuous jump from the Gaussian to excluded volume statistics for $N = N_\tau$.

(ii) The radius of gyration data show that the region of power law is reached as early as $N > 10N_\tau$, as expected from the blob theory[9]. On the contrary, the Flory theory predicts a lower approach to the asymptotic behaviour. In the present work, we use some additional data on polystyrene in the vicinity of the $\theta$ point[23–26] with respect to those considered by Ackcasu and Han[27,28]. Nevertheless we did not consider the data of this polymer in benzene, considering as unknown the value of the $\theta$ point for this system.

On *Figures 6a* and *b*, we have plotted the experimental variations of log $\alpha_s$ *versus* log $N/N_\tau$ for polystyrene and polyacrylamide respectively. $N/N_\tau$ is calculated with two different values of the adjustable parameter $\beta = 0.47$ and 8.8. We take for polyacrylamide the $\theta$ value $T = -8°\text{C}$. It turns out that the discrepancies between the experimental data and the theoretical curves are exactly of the same order of magnitude for polyacrylamide and for polystyrene, if we consider the same value of $\beta$. The previous remarks on the inadequacy of the blob theory to predict the experimental behaviour in the region $N \sim N_\tau$ are confirmed, while the Flory's expression does not give a good account for $N > 10N_\tau$. In this range, for polystyrene as well as for polyacrylamide, the asymptotical value of the exponent of relation (21) is reached.

One obtains a rather good fit in this asymptotical region between experimental data and 'blob' model for $0.47 < \beta < 8.8$. On *Figures 7* and *8* we compare the experimental and theoretical variations of $\alpha_H$ and $\alpha_\eta^3$ *versus* $N/N_\tau$, by keeping $\beta = 0.47$ and plotting together the literature data for polystyrene and our results for polyacrylamide. At first the similarity in the behaviour of both these polymers is definitively confirmed. Secondly $\alpha_H$ cannot be represented by a unique power law $N^{\nu_H}$ in the molecular weight and temperature range currently investigated. Indeed the numerical value of $\nu_H$ obtained by interpreting the experimental data simply by a power law would depend on the range of molecular weight used in the experiment and would be lower than $\nu_H = 0.6$. At last, a unique value of $\beta$ leads to the same fit of the static and hydrodynamic dimensions and this constitutes an additional argument for the theory developed by Weill and des Cloizeaux[22].

It also turns out from this confrontation that the 'blob' concept ($N_\tau$) must only be considered as a simplified hypothesis in the blob model but not as a real picture of polymer chain in solution. Nevertheless, the experimental results show that for $N/N_\tau < 1$ and $N/N_\tau < 4$ *Figure 7*, $\alpha_s$ and $\alpha_H$ respectively are nearly close to unity ($\alpha < 1.05$). It will be then very difficult to separate a state of very low excluded volume from a truly Gaussian region, according to an accuracy not lower than 10% in the radius of gyration and translational diffusion coefficient measurements.

In fact many authors have defined molecular weight range where the behaviour of polystyrene and poly(methyl methacrylate) chain was Gaussian. In the course of a neutron scattering[3] study of the radius of gyration for polyacrylamide at room temperature no significant volume exclusion effect appears in the low range molecular weight $M < 2.8.10^4$. In the case of the hydrodynamical dimension measurements this effect is expected to occur at a higher molecular weight range and accordingly we found a statistical exponent $\nu_H = 0.5$ till $M = 3.10^5$. In addition, with the adjustable parameter $\beta = 0.47$, we found a blob dimension corresponding to $M_\tau = 3.10^4$.

Looking forward at *Table 3* leads to emphasize on the value of the unperturbed dimensions of polyacrylamide and polystyrene[8]. In fact there is no great difference between these two polymers according to the unperturbed effective bond length $a$ which is respectively 705.7[20] and 696.8 Å.

Nevertheless the experimental results show that $\alpha_s$ is nearly close to unity in the domain where $N$ equals $N_\tau$. Above this domain $\alpha_H$ increases very slowly ($\alpha_H \sim 1.05$ for $N/N_\tau < 4$). In this low molecular weight region the accuracy in the radius of gyration and translational diffusion coefficient measurements are not lower than 10%. Then it seems very ambitious to distinguish between a very low excluded volume region ($N \geqslant N_\tau$) and a Gaussian behaviour ($N < N_\tau$). In fact on a 'more classical system'

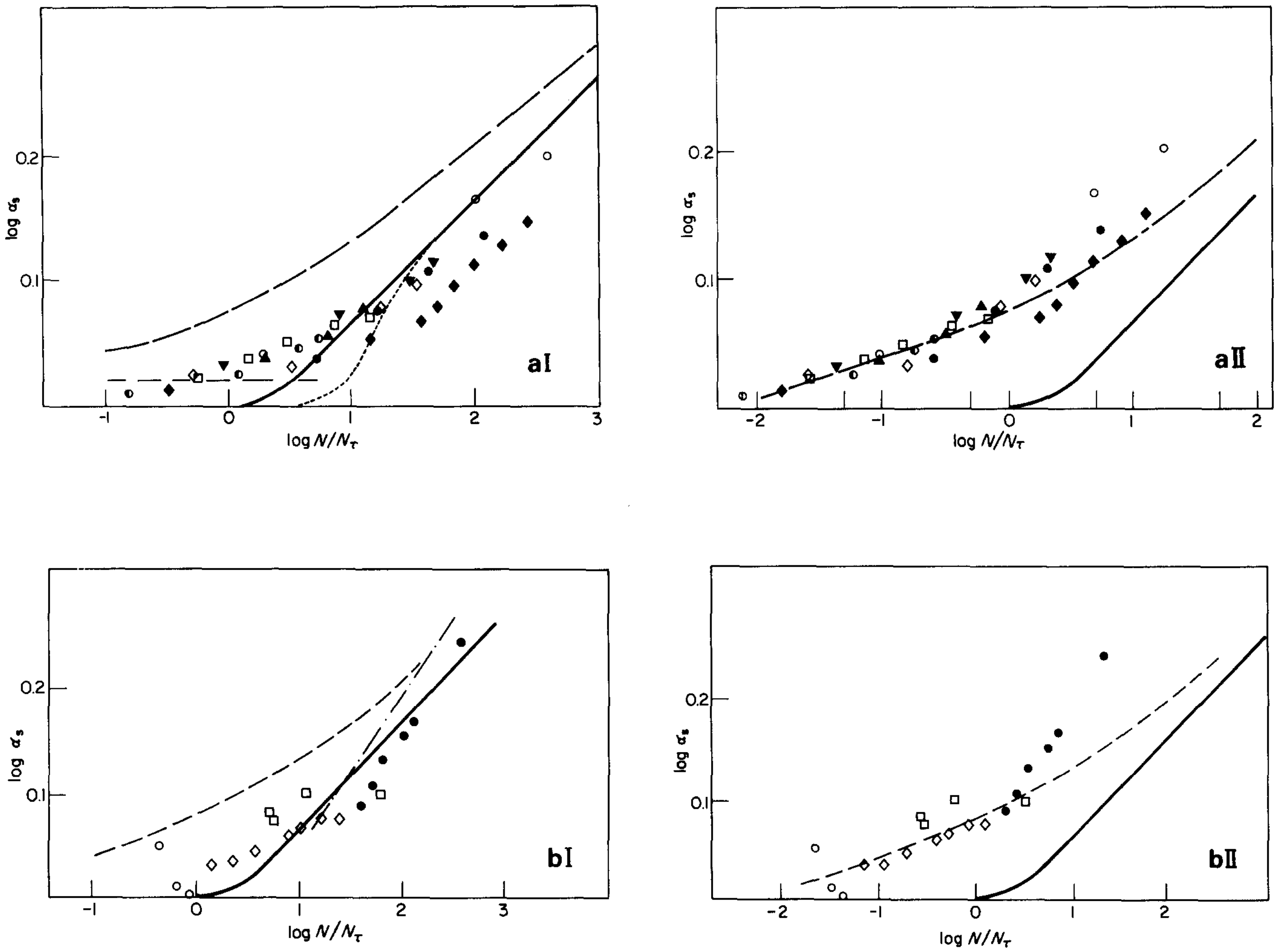

**Figure 6** Plot of the experimental variation of log $\alpha_s$ *versus* $N/N_\tau$ for polystyrene (a) and PAAm (b) in various solvent with well-known theta point and two different values of the adjustable parameter $\beta$: (I) $\beta=0.47$; (II) $\beta=8.8$.
Symbols of *Figures 6a* (Polystyrene):
(1) Cyclohexane (●) $M_w=8.1\times10^6$ [23]; (○) $M_w=43.6\times10^6$ [28]; (▲) $M_w=3.2\times10^6$ [27]; (▼) $M_w=3.2\times10^6$ [27] (◆) $M_w=1.9\times10^6$; (□) $M_w=1{:}11\times10^6$ [25]; (◐) $M_w=7\times10^5$ [26]
(2) Ethyl-acetate (+) $M_w=8.1\times10^6$ [23].
(3) Cyclopentane (×) $M_w=5\times10^6$ [23].
Symbols of *Figures 6b* (Polyacrylamide):
(1) 0.1 N NaCl aqueous solution: (●) $M_w=6.7\times10^6$, (×) $M_w=2.2\times10^5$; (○) from ref. 3; (□) from ref. 33; (-----) from $R_G=f(\log M)$ at 25°C[1].
Common Symbols: (——) Blob model[9]; (-----) François *et al.* model[10]; (– – –) Akcasu *et al.*[31]

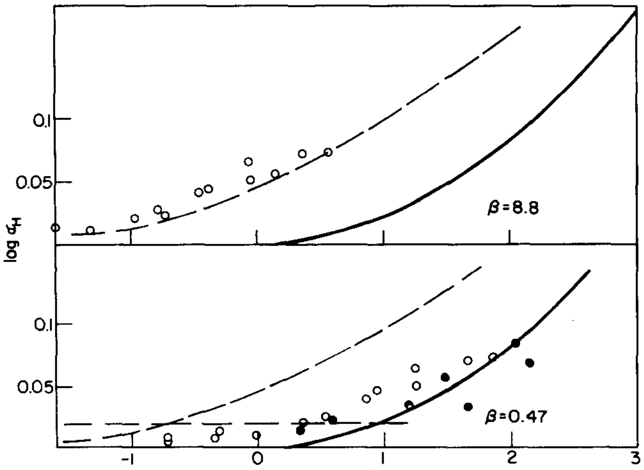

**Figure 7** The logarithm plot of the $\alpha_H$ variations against $N/N_\tau$ for two values of the adjustable parameter $\beta$: (○) Polystyrene[32]; (●) PAAm[2]; (——) blob model[9]; (– – –) Akcasu *et al.*[31]

such as polystyrene or poly(methyl methacrylate) in good (organic) solvent, many authors have found a Gaussian domain in a low molecular weight range. In the course of a neutron scattering study[3] on polyacrylamide ($M<3\cdot10^4$) in aqueous solution ($D_2O$) 0.1 N KBr) we could assimilate the $R_G$ variations *versus* $M$ to a power law with an exponent value $\nu_G$ of 0.5. In a preceding paper dealing with hydrodynamical dimension measurements, it was shown that $\alpha_H$ remains constant in a larger molecular weight range ($\alpha_H=0.5$; $M<3.10^5$).

Comparing experimental results and theoretical model and whatever the model (smooth[20] or crude transition in the cross-over region) it seems necessary to define an intermediate domain in between the small and large molecular weight regions. In this intermediate domain Ullman[29] introduces a smooth variation of the local excluded volume exponent. Considering the exponent value of the $R_G$ *versus* $M$ power law this modification leads to a larger value than the asymptotical one ($\nu_G$ intermediate $>0.60$). This semi-empirical model describes

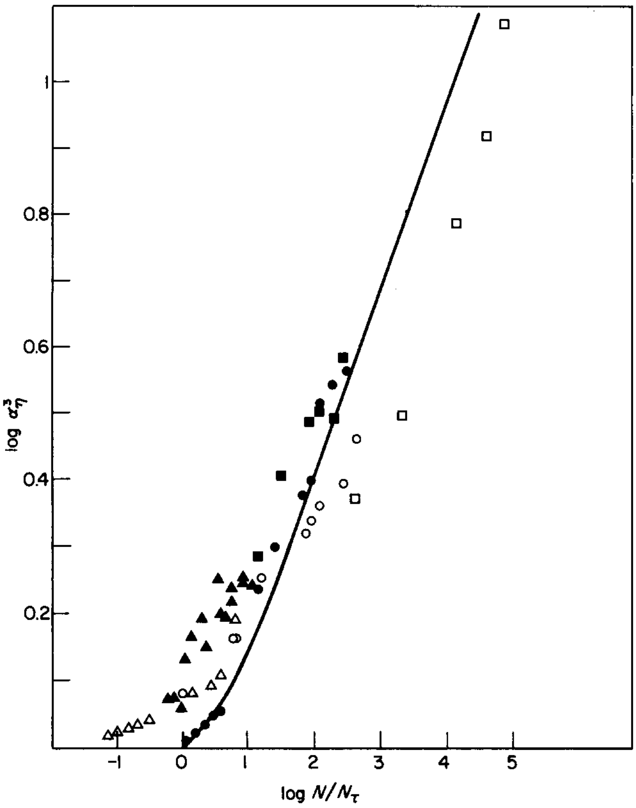

**Figure 8** The logarithm plot of the viscosimetric expansion factor $\alpha_\eta^3$ *versus* $N/N_\tau$ ($\beta$=0.47) for polystyrene (open symbols) and PAAm (full symbols). (△) $[\eta]=f(T)$[23]; cyclohexane – PS, $M_w=10^5$, $M=1.1\times10^6$; (○) $[\eta]=f(T)$[28]; cyclohexane – PS, $M_w$ from $4\times10^5$ up to $4.3\times10^7$; (□) $[\eta]=f(M)$[28]; benzene–PS, $M_w$ from $4\times10^5$ up to $4.3\times10^7$; (●) $[\eta]=f(T)$ this work, 0.1 NaCl–water, $M_w$ from $10^5$ to $6.6\times10^6$; (▲) $[\eta]=f(M)$[4], 0.1 NaCl–water, $M_w$ from $9\times10^3$ up to $3.2\times10^5$; (■) $[\eta]=f(M)$[1], 0.1 NaCl–water, $M_w$ from $0.16\times10^6$ up to $6.7\times10^6$; (——) Blob model[9]

a cross-over behaviour of the static expansion factor $\alpha_s$ which was already found by François *et al.*[10] on polyacrylamide ($3\times10^5<M<10^7$) in 0.1 N NaCl aqueous solution.

The experimental curve of *Figure 6bI* shows an intermediate region where the excluded volume exponent is higher than 0.60. Further investigations are however necessary.

## CONCLUSION

The experimental results presented were obtained by special considerations concerning the cross-over domain for polyacrylamide, the theta point ($T=-8°C$) in 0.1 N NaCl aqueous solution, and the static and dynamic unperturbed dimension calculated from elastic and quasi-elastic light scattering and intrinsic viscosity. We pay attention on the polydispersity effect on all the molecular weight determination and reduced its influence by narrow fractionated samples, all over a large range of molecular weight from $10^4$ to $10^7$ daltons.

This study leads us to consider a low molecular weight region with a translational diffusion coefficient $D$ and radius of gyration $R_G$ behaviour of a Gaussian type power law ($\nu=0.5$), and a high molecular weight region with an asymptotical volume exclusion type ($\nu=0.6$) for the molecular weight dependency power low for $D$ and $R_G$. In between a large cross-over domain is centred around $M_\tau=32\,000$ determined by the semi-empirical blob model improvements of François *et al.*[10]. A review of different blob theory improvements and its comparison with experiment is aimless for the small value of the expansion factor for which a lack of accuracy stop significant conclusion. Nevertheless in this case a Flory type behaviour is not acceptable. All the improvements tend to the same asymptotical value for the expansion factor. In fact the experiment can better be described in the case of the intermediate domain by a power law exponent of $R_G$ crossing its asymptotical line leading to a decrease of $\nu_G$ to 0.6 at infinite molecular weight. Others SANS experiments in this intermediate region *versus* temperature should give more information on this cross-over[30].

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