

# Polyacrylamide in water: molecular weight dependence of $\langle R^2 \rangle$ and $[\eta]$ and the problem of the excluded volume exponent

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A commercial sample of polyacrylamide (CALGON) has been carefully purified, analysed and fractionated. With suitable care, the molecular characterization can be carried out by light scattering and viscosity measurements, without disturbances arising from microgels or aggregates. The molecular weight dependence of the radius of gyration and intrinsic viscosity are given by:

$$\langle R^2 \rangle^{1/2} = 7.49 \times 10^{-2} M^{0.64} (\text{\AA})$$

$$[\eta] = 9.33 \times 10^{-3} M^{0.75} (\text{cm}^3/\text{g})$$

The value of the exponent  $\nu = 0.64$  in the  $\langle R^2 \rangle^{1/2}$  equation has been cross-checked by a study of the asymptotic behaviour of the scattering envelope. Such a value is higher than that expected in a good solvent ( $\nu = 0.60$ ) and should lead to a higher exponent in the intrinsic viscosity dependence. However, it agrees more closely with the published dependence of sedimentation and diffusion coefficients.

Water-soluble polymers of high molecular weight have given rise to much interest due to their practical applications and more recently in the preparation of highly viscous solutions in the secondary oil recovery process<sup>1</sup>. One of the most used is partly hydrolysed polyacrylamide. The understanding of the role of charged groups on the different factors which govern the efficiency in their use, particularly in the salt-rich waters encountered in oil fields, requires a complete molecular characterization. However, even for non-hydrolysed polyacrylamide, there is a lack of reliable data in the literature concerning the chain conformation in salt water solutions and its relation to intrinsic viscosity, particularly in the range of molecular weights of interest<sup>2,3</sup>. It is the purpose of this work to obtain and discuss such data, obtained for carefully characterized fractions of low polydispersity.

## EXPERIMENTAL

The polymer studied is a commercial polyacrylamide CALGON (HPAMO).

### Fractionation

The polymer has been fractionated by addition of 70% of methanol to an aqueous solution containing 0.66% of polymer at 20°C. The temperature was decreased in two degree intervals. The yield was only 56% in wt, due to presence of significant quantities of impurities in the commercial sample which had not been purified before treatment. We have obtained two series of fractions, the molecular weights of which range between  $1.6 \times 10^5$  and  $8.1 \times 10^6$  (see Table 3).

### Elemental analysis

The results of elemental analysis of the commercial sample and fractions are reported in Table 1.

The commercial product contains 17.5% salt impurities, essentially NaCl. We have also found small but significant quantities of divalent and trivalent cations, the presence of which can play a role in the association phenomena observed in the solutions of the untreated material. These impurities have been eliminated during the fractionation.

A comparison of the theoretical contents of C, H, N and O, corresponding to the chemical formula of pure polyacrylamide with the experimental results (Table 1) reveals an excess of oxygen and a deficiency of nitrogen and carbon. This has been often observed<sup>4,5</sup> on polyacrylamide and attributed to some retained water and to imide functions. Their percentages have been calculated from C, N and O contents through a graphical procedure, according to this hypothesis, and reported in Table 2. The values, although very scattered, are in agreement with those obtained elsewhere<sup>5</sup>.

In the case of polyacrylamides polymerized by u.v. radiation. Boyadjian *et al.*<sup>5</sup> have shown the presence of insoluble fractions which contain approximately 15% of imide functions. The original Calgon sample as well as our fractions are entirely soluble. Besides, as indicated later light scattering plots do not show the presence of large aggregates.

### Gel chromatography

The experimental set-up consists of: a solvent reservoir maintained at slightly higher temperature than the column in order to de-gas the solution; a glass column (height 40 cm

Table 1 Elemental analysis. Experimental and theoretical values of C, N, H and O contents for polyacrylamide samples

| Sample                   | C(%)  | N(%)  | O(%)  | H(%) | Cl(%) | Na(%) | K(%)  | Ca(%) | Mg(%)  | Fe(%)  |
|--------------------------|-------|-------|-------|------|-------|-------|-------|-------|--------|--------|
| Commercial sample Calgon | 40.15 | 15.46 | —     | 5.96 | 11.3  | 5.04  | 0.017 | 0.021 | 0.0047 | 0.0057 |
| F <sub>11</sub>          | 49.04 | 18.39 | 25.49 | 7.48 |       |       | 0.1   |       |        |        |
| F <sub>12</sub>          | 47.96 | 17.93 | 25.99 | 7.24 |       |       | —     |       |        |        |
| F <sub>13</sub>          | 48.03 | 17.62 | 26.70 | 7.56 |       |       | 0.12  |       |        |        |
| F <sub>14</sub>          | 48.55 | 18.59 | 26.63 | 7.41 |       |       |       |       |        |        |
| F <sub>15</sub>          | 47.27 | 17.15 | 27.65 | 7.79 |       |       |       |       |        |        |
| F <sub>16</sub>          | 47.41 | 17.53 | 26.30 | 7.43 |       |       |       |       |        |        |
| F <sub>2a</sub>          | 48.10 | 17.99 | 25.30 | 7.38 |       |       |       |       |        |        |
| F <sub>22</sub>          | 47.71 | 18.00 | 24.83 | 7.45 |       |       |       |       |        |        |
| F <sub>23</sub>          | 48.62 | 18.46 | 25.44 | 7.37 |       |       |       |       |        |        |
| F <sub>24</sub>          | 48.14 | 18.77 | 25.15 | 7.42 |       |       |       |       |        |        |
| F <sub>25</sub>          | 48.00 | 18.99 | 25.10 | 7.65 |       |       |       |       |        |        |
| Theoretical values       | 50.70 | 19.72 | 22.54 | 7.04 |       |       |       |       |        |        |

Table 2 Calculated percentages of retained water and imide functions in the fractions of polyacrylamide

| Fraction             | F <sub>11</sub> | F <sub>12</sub> | F <sub>13</sub> | F <sub>14</sub> | F <sub>15</sub> | F <sub>16</sub> |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| H <sub>2</sub> O (%) | 4               | 5               | 5               | 6               | 7               | 6               |
| Imide (%)            | 4               | 4               | 8               | 2               | 7               | 4               |

volume 2 l). The support is an agarose gel (Sephacrose 2B) generally used for proteins and polysaccharides; an injection loop; a peristaltic pump for solvent circulation; a Waters refractometer as detector.

The elution volume was measured with a graduated reservoir. Aqueous NaCl solution (0.1 M), containing sodium azide (0.1%) to prevent microbial growth, is used as solvent.

This technique has been used either in an analytical way to obtain the polydispersity index of our samples or in a preparative way to obtain a larger range of more monodisperse fractions.

For the polydispersity study, we inject approximately 1.5 ml of a 0.1 M NaCl solution containing 10<sup>-3</sup> g/g of polymer. In order to get the calibration curve,

$$\log M = f(V_e)$$

(V<sub>e</sub> = elution volume), we have used the molecular weight measured by light scattering. The nearly linear curve obtained (Figure 1) shows the good efficiency of the support for the separation in the range of molecular weights of interest. The polydispersity ratios, calculated using the classic graphical integration technique, are reported in Table 3. To obtain sufficient concentration for light scattering and viscosimetry measurements in 8 ml fractions, directly sampled out after the detector, larger volumes (~5 ml) of the same solution have been injected. The concentration can be calculated in one of two ways. Either, using the corresponding areas of the chromatograms

$$C_i = C_0 \frac{S_i}{S_t} \cdot \frac{V_b}{V_s}$$

where S<sub>i</sub> is the area corresponding to the sample, S<sub>t</sub> the total area of the chromatogram, C<sub>0</sub> the concentration of the injected solution, V<sub>s</sub> the sample volume, and V<sub>b</sub> the volume of the injection loop. Alternatively, we can use the heights of the chromatogram for each fraction (see dn/dc measurements) directly, after calibration of the refractometer.

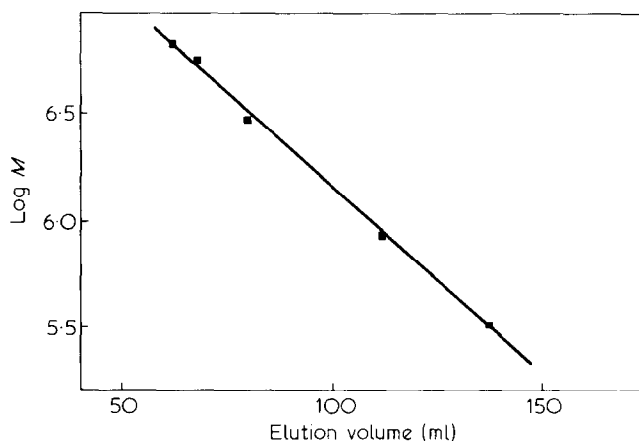


Figure 1 Calibration curve of the gel chromatographic column

We have checked the good agreement between the results obtained with these two methods and generally used the second. The concentration range was between 2 × 10<sup>-5</sup> and 10<sup>-4</sup> g/g.

Light scattering

Preparation of the solution. The polymers were always dissolved, at least 24 h before measurements, at ordinary temperatures and without agitation in order to avoid a possible shear or thermal degradation. The solutions were centrifuged for at least 3 h. For g.p.c. samples, this centrifugation is not necessary, circulation through the g.p.c. columns freeing the solutions from dust.

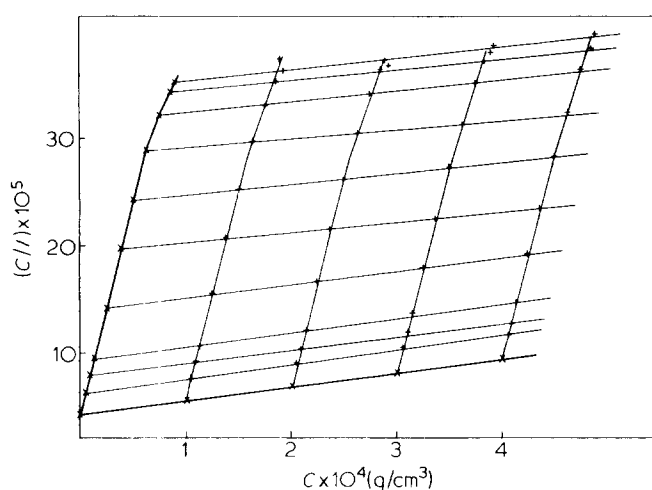
Measurements. The complete Zimm plots have been obtained for fractions 11–16 and 21–25 of the polyacrylamide. Figure 2 shows an example of a Zimm plot. The values of molecular weights M<sub>w</sub>, radius of gyration R<sub>G</sub> and Second Virial coefficient A<sub>2</sub> are reported in Table 3.

For the g.p.c. samples, we have measured the intensity of the scattered light at all angles but for only one concentration. We have taken into account the concentration dependence for the determination of M<sub>w</sub> and R<sub>G</sub>, using the variation of A<sub>2</sub> with M determined on the fractions.

Refractive index increment dn/dc. Using a Waters refractometer, we have measured the dn/dc of HPAMO fractions in 0.1 M aqueous sodium chloride solutions, prepared and centrifuged for the light scattering measurements. The results are reported in Table 4. For the other solvents, formamide or more concentrated salt solutions, we have calculated the cor-

Table 3 Molecular parameters of the fractions of polyacrylamide

| Fraction        | $M_w \times 10^{-5}$ (l.s.) | $\langle R^2 \rangle^{1/2}$ (Å) | $A_2$ ( $10^{-4}$ cm <sup>3</sup> /g <sup>2</sup> ) | $M_w$ (g.p.c.) $\times 10^{-5}$ | $M_w/M_n$ |
|-----------------|-----------------------------|---------------------------------|---|---------------------------------|-----------|
| F <sub>11</sub> | 67                          | 1690                            | 2.2   | 72                              | 1.2       |
| F <sub>12</sub> | 57                          | 1530                            | 2.8   | 57                              | 1.2       |
| F <sub>13</sub> | 29                          | 1040                            | 2.8   | 38                              | 1.3       |
| F <sub>14</sub> | 21                          | 790                             | 2.7   | 18                              | 1.5       |
| F <sub>15</sub> | 8.5                         | 440                             | 2.9   | 8.0                             | 2.0       |
| F <sub>16</sub> | 3.2                         | —                               | —   | 2.7                             | 1.6       |
| F <sub>2a</sub> | 81.7                        | 1990                            | 1.5   | 81                              | —         |
| F <sub>2b</sub> | 61.2                        | 1580                            | 2.6   | 70                              | —         |
| F <sub>2c</sub> | 25.6                        | 1030                            | 2.8   | —                               | —         |
| F <sub>22</sub> | 29                          | 970                             | 2.8   | 37                              | 1.4       |
| F <sub>23</sub> | 9.2                         | 490                             | —   | 6.9                             | 1.35      |
| F <sub>24</sub> | 3.2                         | —                               | —   | 2.2                             | 1.20      |
| F <sub>25</sub> | 1.6                         | —                               | —   | 1.7                             | 1.15      |

Figure 2 Zimm plot obtained with the F<sub>11</sub> fraction of polyacrylamide

responding  $dn/dc$  using the Lorenz–Lorentz relation. It has been shown that this relation (1) leads to very good values of  $dn/dc$  if the following parameters are known:  $n_1$ , refractive index of the solvent;  $R_2$ , specific refractivity of the polymer as calculated from  $dn/dc$  values of the polymer in 0.1 M NaCl solutions;  $\bar{V}_p$ , partial specific volume of the polymer

$$\frac{dn}{dc} = \frac{(n_1^2 + 2)^2}{6n_1} \left( R_2 - \frac{n_1^2 - 1}{n_1^2 + 2} \bar{V}_p \right) \quad (1)$$

The partial specific volume  $\bar{V}_p$  has been measured with an automatic densimeter DMA02 on the F<sub>2</sub> fraction in 0.1 M NaCl solutions and is equal to 0.702 cm<sup>3</sup>/g. The  $dn/dc$  values for each solvent are reported in Table 4.

#### Viscosity measurements

The viscosity measurements have been generally carried out with a Grammain–Libeyre type automatic capillary viscometer<sup>6</sup> (capillary diameter 0.4 mm) and, for zero gradient, with a Zimm–Crothers viscometer<sup>7</sup>, automated and improved by Neimark *et al.*<sup>8</sup>.

In all cases, even for g.p.c. samples, we have diluted the original solutions and extrapolated the results to zero concentration. As these polymers are very sensitive to shear degradation<sup>9</sup> the agitation time should not exceed the minimum time needed for dilution. The specific viscosity is a linear function of  $C$ , in the concentration range studied

( $C < 10^{-3}$  g/cm<sup>3</sup>), not showing the anomalies observed by other authors<sup>10</sup>. On Figure 3, are reported some examples of variation of  $\eta_{sp} = f(C)$ .

#### Structure of the solutions

The aqueous solutions of polyacrylamides are suspected to contain fibrous aggregates of very high molecular weight. These aggregates have been observed by electronic microscopy<sup>11</sup> and the disaggregation kinetics studied by viscosimetry<sup>12,13</sup>. This phenomenon is generally attributed to intermolecular hydrogen bonds and is evidenced by an important decrease of viscosity with time. Boyadjian *et al.*<sup>14</sup> have noticed differences of measured molecular weight by light scattering, according to the nature of the solvent and have concluded the presence of aggregates broken up by the effect of salts in pure water but not in formamide. We must, however, note that the discrepancies between their molecular weight values may be due to errors in the  $dn/dc$  values; it is indeed surprising that their quoted  $dn/dc$  values do not vary with salt concentration even in 10% NaCl. This explains the care taken in our  $dn/dc$  determinations.

The molecular weight measurements and conformational studies using light scattering or viscosimetry are only really meaningful if the dispersion of polymer molecules in the solution is well-realized. It is thus essential to carry out some experimental tests in order to show that the solutions prepared according to our solubilization technique do not contain aggregates in the concentration range considered.

First, we have checked the stability of a solution of high molecular weight polymer which does not present sensible aging as described by other authors. More precisely, the viscosity, one week after the preparation of the solution (kept at ordinary temperature, without agitation) remains constant and equal to the viscosity measured after 24 h. The relation  $\eta_{sp} = f(C)$  is always linear, the Huggins constant being approximately 0.3–0.4 which is a usual value.

We have reported in Table 4, the results of light scattering measurements carried out on two fractions F<sub>11</sub> and F<sub>12</sub> in aqueous solutions of different ionic strengths or in formamide. The measured molecular weights are in good agreement within experimental errors and the radii of gyration have values of the same order of magnitude. Besides the Zimm plots (see Figure 2) present a slight curvature at high scattering angles, in opposition to Boyadjian results which show more downward curvature. Our plot, as shown later, can be explained by excluded volume effects, without reference to the presence of aggregates. The good agreement between the radii

Table 4 Comparison of the molecular parameters in different solvents

| Fraction        | Solvent  | $M_w \times 10^{-6}$ | $\langle R_G^2 \rangle^{1/2}$ (Å) | $A_2 \times 10^4$ | $(dn/dc)$ (cm <sup>3</sup> /g) | $\nu$ |
|-----------------|--|----------------------|-----------------------------------|-------------------|--------------------------------|-------|
| F <sub>11</sub> | Pure water                                     | 7.5                  | 1900                              | —                 | 0.165                          | —     |
|                 | Water 0.1M NaCl                                | 6.7                  | 1700                              | 2.1               | 0.164                          | 0.69  |
|                 | Water 0.1M LiCl                                | 6.4                  | 1760                              | 1.9               | 0.164                          | 0.69  |
|                 | Formamide                                      | 6.6                  | 1790                              | 1.3               | 0.095                          | 0.68  |
| F <sub>12</sub> | Pure water                                     | 5.1                  | 2000                              | —                 | 0.165                          | —     |
|                 | Water 3 x 10 <sup>-3</sup> M N <sub>3</sub> Na | 5.4                  | 1551                              | 2.9               | 0.165                          | 0.69  |
|                 | Water 0.1 M NaCl                               | 5.7                  | 1544                              | 2.8               | 0.164                          | 0.67  |
|                 | Water 1M NaCl                                  | 5.5                  | 1482                              | 2.7               | 0.159                          | 0.625 |
|                 | Water 4M NaCl                                  | 5.9                  | 1616                              | 2.9               | —                              | 0.66  |

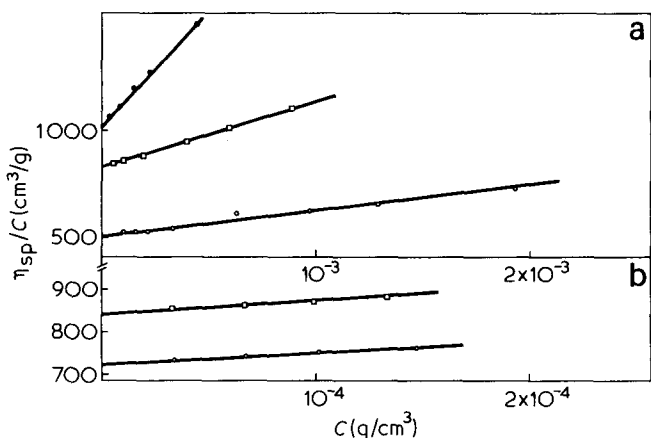


Figure 3 Variation of the specific viscosity of some polyacrylamide samples as a function of the polymer concentration (capillary viscosimeter): (a) measurements on fractions 11; 12; 4; (b) measurements on two g.p.c. solutions samples

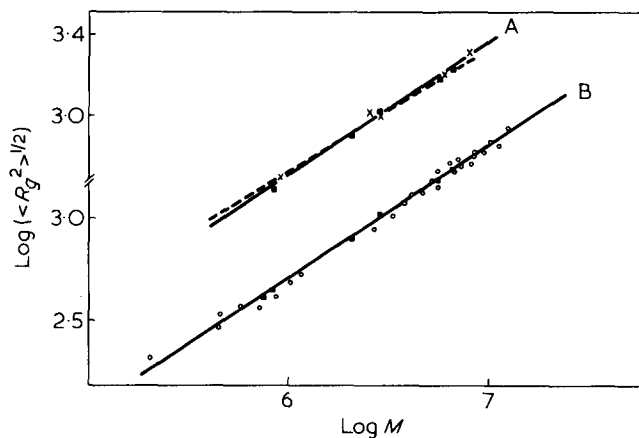


Figure 4 Log-log plot of the mean radius of gyration,  $\langle R_G^2 \rangle^{1/2}$ , versus molecular weight in 0.1 M NaCl water. A, measurements on fractions 11 to 2.5 (study of complete Zimm plots); B, measurements on fractions 11 to 1.6 and 0.4, on g.p.c. samples. — — —, least square fitting with the results forced to a  $M^{0.60}$  law

of gyration obtained directly on fractions and on g.p.c. samples (see Figure 4) constitutes an additional argument for the absence of aggregates in our solutions, for concentrations lower than 10<sup>-3</sup> g/cm<sup>3</sup> and for correctly purified products.

We may note that the initial commercial sample is more difficult to solubilize and the aging effects previously quoted are then observed. It should be of interest to understand this difference and to determine the respective roles played by the presence of di- and trivalent cations or by the previous history of the dry product (precipitation procedure, drying, granularity of the powder etc).

This preliminary study does not show the effect of salt concentration on the macromolecular dimensions of polyacrylamide both for NaCl and bacteriostatic N<sub>3</sub>Na. All our following experiments have been carried out in 0.1 M NaCl solutions with 0.1 wt % of N<sub>3</sub>Na.

RESULTS

Light scattering measurements

The variation of the radius of gyration versus molecular weight is plotted in Figure 4. The values determined from the study of the fractions F<sub>11</sub> to F<sub>16</sub> and F<sub>2a</sub> to F<sub>25</sub> (complete Zimm plots) correspond to the curve A, and those obtained with g.p.c. solution samples (one concentration studied with A<sub>2</sub> correction) are represented on curve B, on which are also reported values of fractions F<sub>11</sub> to F<sub>16</sub>. We can note a very good agreement between the different series of values which are correctly located on a straight log-log plot:

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

obtained from least squares analysis. The values of the second virial coefficient A<sub>2</sub> (Table 3) of the fractions indicate that aqueous 0.1 M NaCl water can be considered as a good solvent for the polyacrylamide, as shown previously by Silberberg et al.<sup>15</sup>. The exponent 0.64 is even higher than the classical excluded volume exponent 0.60, generally considered for a polymer in good solvent<sup>16</sup>. A least squares line obtained by forcing the results to 0.60 dependence has been drawn in Figure 4, and it is clear that the fit is not correct. Moreover, this surprising value 0.64 can be cross-checked from the asymptotic behaviour of scattered light at high scattering angles. Loucheux et al.<sup>17</sup> have shown that, for a high molecular weight polymer in a good solvent, with excluded volume effect, ( $\langle R_G^2 \rangle^{1/2}$  proportional to M<sup>ν</sup>), the scattered intensity, at high scattering angles, is proportional to (sin<sup>2</sup>θ/2)<sup>1/2ν</sup>. A plot of log I versus log[sin<sup>2</sup>(θ/2)] for θ > 105°, therefore leads to a value of 1/2ν = ε for each concentration of polymer as shown in Figure 5. The extrapolation at C = 0 gives, in the case of the F<sub>11</sub> fraction in 0.1 M NaCl (Zimm plot of Figure 2) 1/2ν = 0.76 and ν = 0.66, in good agreement with the value 0.64 previously found.

An additional check can be found by calculation of the polydispersity from the intercept of the asymptote at zero angle which has been shown<sup>17</sup> to be equal to

$$\frac{1}{2M_n} \frac{\Gamma(1/\nu)2\nu}{[\Gamma(1/2\nu)]^2}$$

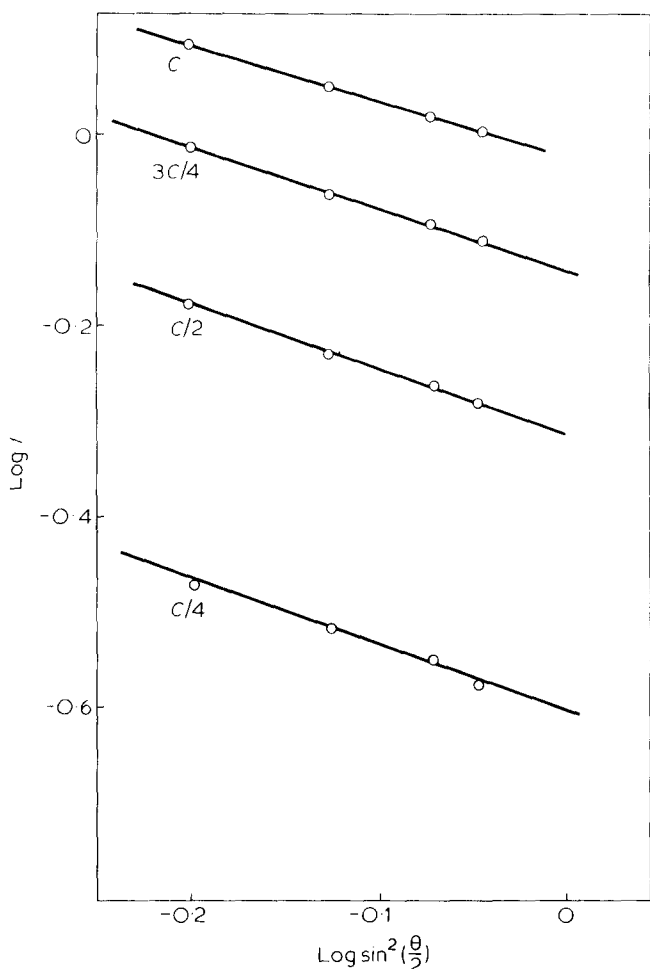


Figure 5 Variation of  $\log I$  versus  $\log[\sin^2(\theta/2)]$  and plot of  $\epsilon = 1/2\nu$  versus concentration for the  $F_{11}$  fraction of polyacrylamide

The angular dependence of the scattered intensity, extrapolated at zero angle, taken on the Zimm plot of fraction 11, has been replotted on Figure 6 as a function of  $(\sin^2\theta/2)^{1/2\nu}$  with  $\nu = 0.50, 0.60$  and  $0.64$ . The values of  $M_w/M_n$  thus obtained are respectively 4.8, 2.0 and 1.3. It seems that only the last value agrees with the g.p.c. result (Table 3).

A similar analysis of the slope and intercept of the asymptote has been carried out for fractions  $F_{11}$  and  $F_{12}$  in different solvents. All the values of  $\nu$  are significantly higher than 0.60. We therefore think that this unexpected result has a firm experimental foundation (Table 4).

### VISCOSITY MEASUREMENTS

Figure 7 gives a log-log plot of  $[\eta] = f(M_w)$ . As for the previous study, we can comment on the good agreement between the two series of experiments (measurements on fractions and on g.p.c. samples). The effect of shear rate appears for  $M_w > 2.5 \times 10^6$  in the same range of degree of polymerization as for polystyrene in a good solvent (benzene)<sup>18</sup>. The use of the zero gradient results in the high molecular weight range improves very much the linearity, providing the following relation:

$$[\eta] = 9.33 \times 10^{-3} M^{0.75} (\text{cm}^3/\text{g}) \quad (3)$$

In Figure 7 we have also drawn curves corresponding to previously published laws of variation of  $[\eta] = f(M)$ :

$$[\eta] = 6.31 \times 10^{-3} M^{0.8} (\text{cm}^3/\text{g})$$

Scholtan *et al.*<sup>2</sup> (0.2 M NaCl-water)

$$[\eta] = 6.8 \times 10^{-2} M^{0.66} (\text{cm}^3/\text{g})$$

Collinson *et al.*<sup>3</sup> ( $5 \times 10^{-3}$  M ferriperchlorate)

The first has been obtained on fractions whose molecular weight has been measured combining sedimentation and diffusion. The coefficient is close to ours; the systematic displacement of the curve can be explained by the use of sedimentation and diffusion which gives a mean molecular weight intermediate between  $M_w$  and  $M_n$ .

The second has been 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. It is therefore of very little significance.

### DISCUSSION

Our results show that, with suitable care, a correct molecular characterization of the polyacrylamide fractions can be carried out. The relation between the radius of gyration and molecular weight:

$$\langle R_G^2 \rangle^{1/2} = 7.49 \times 10^{-2} M^{0.64} (\text{\AA}) \quad (2)$$

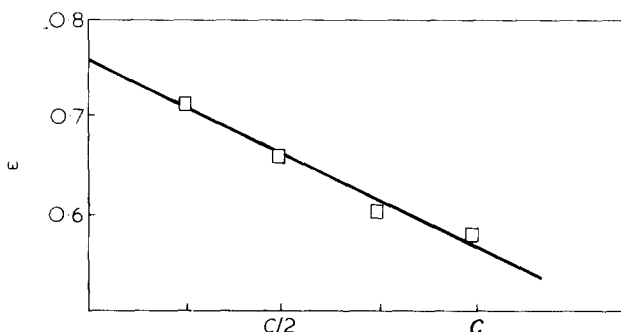


Figure 6 Comparison of the extrapolations at  $\theta = 0$  and  $C = 0$  of the asymptotic part of  $P^{-1}(\theta)$  as a function of  $[\sin^2(\theta/2)]^{1/2\nu}$  with  $\bullet, \nu = 0.5$ ;  $\times, 0.6$  and  $+, 0.64$

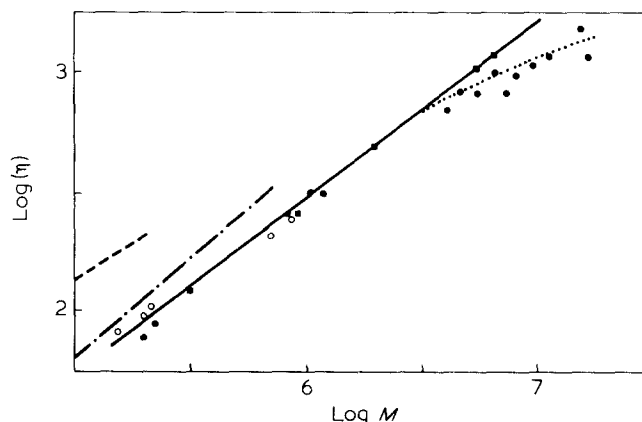


Figure 7 Log-log plot of the intrinsic viscosity of some samples of polyacrylamide in 0.1 M NaCl water.  $\circ$ , measurements made with a capillary viscosimeter on fractions  $F_{11}, F_{12}, F_{14}, F_{15}, F_{23}$  and  $F_{24}$  ( $\times$ ), and on some g.p.c. solution samples.  $\square$ , Measurements made with a Zimm Crothers viscosimeter on fractions  $F_{11}$  and  $F_{12}$ . - - - - -, Results of Scholtan *et al.*<sup>2</sup>; - · - · - ·, Results of Collinson *et al.*<sup>3</sup>

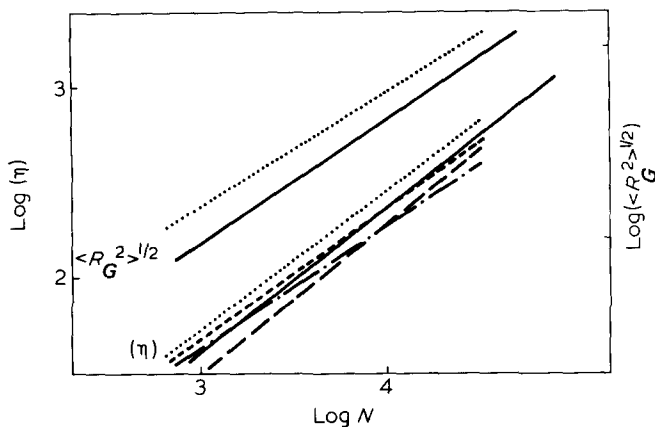


Figure 8 Comparison of the dependence on the degree of polymerization of  $[\eta]$  and  $\langle R_G^2 \rangle^{1/2}$  of the polyacrylamide in 0.1 M NaCl water (—) with those found for other vinyl polymers in good solvents. For  $\langle R_G^2 \rangle^{1/2}$ : - - - -, polystyrene in benzene<sup>19</sup>; — — — —, poly( $\alpha$  methylstyrene) in toluene<sup>20</sup>. For  $\eta$ : - - - -, polystyrene in benzene<sup>21</sup>; — — — —, poly(methyl methacrylate) in benzene<sup>22</sup>; - · - · - ·, poly(vinyl acetate) in acetone<sup>23</sup>; - - - -, poly(methyl acrylate) in benzene<sup>24</sup>; - · - · - ·, poly(vinyl alcohol) in water<sup>25</sup>

gives a very satisfactory account of the experimental results over a broad range of molecular weight. The exponent  $\nu = 0.64$  is larger than the value of 0.60 originally proposed by Flory for polymers in good solvents and recently confirmed, after much discussion, in the framework of the renormalization group theory of polymer solutions<sup>16</sup>. Our experimental value has been cross-checked by an analysis of the whole scattering envelope and has to be considered as highly significant.

The corresponding viscosity relation, obtained from values extrapolated at zero shear gradients to take in account non-Newtonian effects, is (in the same range of molecular weight):

$$[\eta] = 9,33 \times 10^{-3} M^{0.75} \quad (3)$$

A simple comparative plot of our results with those obtained on other vinyl polymers in good organic solvents, plotted according to the degree of polymerization (Figure 8), shows no anomalous behaviour for polyacrylamide water solutions.

In particular, we relied only on the intrinsic viscosity, neither the exponent of its molecular weight dependence,  $a$ , nor the absolute values of  $[\eta]$  reveal any particularity.

There are not so many direct determinations of the  $\langle R^2 \rangle^{1/2} \propto M^\nu$  law by light or neutron scattering methods. The value  $\nu = 0.60$  has, however, been found both for polystyrene (PS) in benzene<sup>19</sup> and poly  $\alpha$ -methylstyrene in toluene<sup>20</sup>.

The relation between exponents  $a$  and  $\nu$  is the object of much debate. From the Kirkwood theory, in the limit of non-free draining, Flory and Fox have proposed the well-known relation:

$$[\eta] = \phi_0^{3/2} \frac{\langle R_G^2 \rangle^{3/2}}{M} = \phi_0^{3/2} \frac{\langle R_0^2 \rangle^{3/2}}{M} \alpha^3 \quad (4)$$

where  $\langle R_0^2 \rangle^{1/2}$  is the unperturbed radius of gyration and  $\alpha$  the chain expansion factor. Taking  $\alpha \propto M^{\nu-1/2}$  leads to the relation

$$a = 3\nu - 1 \quad (5)$$

from which one would expect  $a = 0.8$  for 'classical' polymers in good organic solvents ( $\nu = 0.6$ ) and  $a = 0.92$ ; in our case ( $\nu = 0.64$ ), to be compared with the experimental value of 0.75.

However, despite its wide use, relation (5) is seldom verified, even in the 'classical' cases where an experimental value of  $a < 0.8$  is generally found. The theoretical foundation of equation (4) has been extensively discussed by Yamakawa<sup>22</sup>. In particular it has been proposed that the expansion factor  $\alpha_\eta^3$  to be used in the Fox-Flory equation is different from the value  $\alpha_R^3$  characteristic of the radius of gyration, due to non-uniform expansion. In the non-free draining limit, Kurata and Yamakawa<sup>23</sup> have proposed the semi-empirical relation.

$$\alpha_\eta^3 = \alpha_R^{2.43}$$

which seems to fit essentially the experimental data in the small  $\alpha$  region. The use of this relation leads in our case to:

$$a = 2.43(\nu - 0.5) + 0.5 = 0.84$$

still higher than our experimental result.

It is interesting to consider the molecular weight dependence of other hydrodynamic quantities. Accordingly the molecular weight dependence of the sedimentation coefficient  $S$  and of the translatory diffusion coefficient  $D$  are:

$$S \propto M^{1-\nu} \quad D \propto M^{-\nu}$$

with  $\nu = 0.64$

$$S \propto M^{0.36}; \quad D \propto M^{-0.64}$$

to compare with the experimental results reported by Scholtan<sup>2</sup>

$$S = 8.17 \times 10^{-15} M^{-0.31}$$

$$D = 8.46 \times 10^{-4} M^{-0.69}$$

which suggest an even higher value of  $\nu = 0.69$ .

None of the assumptions formulated at the moment is likely to explain a small value of  $a$ . Assuming partial draining, Tschoegel<sup>24</sup> has calculated the variation of the parameter  $\phi$  of the Fox-Flory equation as a function of the hydrodynamic interaction parameter  $h$  for a model with excluded volume effects where  $h$  is taken proportional to  $M^{1-\nu}$ .  $\phi(h, \nu)$  is always an increasing function of  $h$  and therefore partial draining can only result in an apparent increase in  $a$ .

Unfortunately, except for some well known vinyl polymers, there have been very few systematic studies of the molecular weight dependence of radius of gyration, viscosity sedimentation and diffusion on a set of fractions in the same range of molecular weight. We can note, however, that several 'abnormal' exponents are reported for such water-soluble polymers, such as poly(vinyl alcohol)<sup>25</sup> ( $[\eta] \propto M^{0.68}$ ,  $S \propto M^{0.30}$ ) but the data are insufficient to draw any conclusion.

What particular type of chain statistics and hydrodynamic interactions could explain our results is presently an open question. We cannot, from our experiments in the high molecular weight range and in a good solvent, extrapolate the unperturbed dimensions and obtain absolute values of the expansion parameter  $\alpha$ .

However, we should mention two possible chemical

reasons for a special type of chain statistics.

(i) Chemical analysis has shown the presence of a small amount of imidization. Intermolecular reactions would make the high molecular weight fractions branched. Intramolecular reactions would introduce loops. However, there have been suggestions that imidization occurs between neighbouring groups.

(ii) Polyacrylamide can suffer a small amount of unexpected hydrolysis and therefore carry a few charged groups. Potentiometric titrations reveal a possible content of acid groups smaller than 1% for all our fractions. The influence of a very small number of charges on the chain statistics in the absence of added salt has recently been recognized theoretically<sup>26</sup>. But long range effects should be completely screened in the presence of 0.1 M NaCl and moreover we do not find significant differences with measurements in pure water or  $10^{-3}$  M  $\text{N}_3\text{Na}$  (sodium azide)

Considering the reliability of our experimental evidence concerning the peculiar behaviour of these water-soluble polymers we feel encouraged to pursue these studies. Among the possible methods, neutron scattering of fractions in the low and intermediate molecular weight range in  $\text{D}_2\text{O}$  could provide:

(A) the radius of gyration—molecular weight relation, an estimation of the unperturbed dimensions through a Stockmayer—Fixman type extrapolation and therefore the absolute values of  $\alpha$  in the high molecular range. The discovery of  $\theta$  or quasi  $\theta$  solvents would also be of much value in this respect;

(B) the shape of the scattering envelope and in particular, from the asymptotic behaviour (as for light scattering from high  $DP$  fractions) the exponent  $1/2\nu$ .

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