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Structure of polyacrylic acid and polymethacrylic acid solutions : a small angle neutron scattering study

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Abstract. — The intensity scattered from polyacrylic acid and polymethacrylic acid solutions has been measured by small angle neutron scattering experiments. The influence of polymer concentration, ionization degree, temperature and salt content has been investigated. Results are in qualitative agreement with a model which predicts the existence of microphases in the unstable region of the phase diagram. Quantitative comparison with the theory is performed by fitting the theoretical structure factor to the experimental data. For a narrow range of ionization degrees nearly quantitative agreement with the theory is found for the polyacrylic acid system.

Introduction.

Weak polyacid systems have been the subject of numerous theoretical [1-8] and experimental [8-25] works in the last decades. In particular the fact that the properties of these systems result from a delicate balance between hydrophobic and Coulombic interactions was recognized many years ago [10, 11, 20].

Recently new models that take these features explicitly into account have been proposed [3-6]. They consider weakly charged chains with a hydrophobic backbone which is solubilized by a small fraction of ionized monomers. They predict that such a system will undergo a microphase separation transition upon decreasing further the solvent quality because the overall electroneutrality condition would imply a too severe loss of entropy for the counterions if the demixtion would take place on a macroscopic scale [3, 4].

These models have been found relevant in the analysis of small angle neutron scattering (SANS) and quasi-elastic light scattering (QELS) results obtained on poly(acrylic acid) gels [24-26]. Variations of the static and dynamic properties of these gels with the ionization degree, polymer or salt concentrations, and temperature were found in qualitative or even sometimes in quantitative agreement with the theoretical predictions.

(*) URA 851.

However some discrepancies were present and were tentatively associated with perturbative effects due to the presence of permanent crosslinks in the gels. In order to clarify this point, we have performed detailed experiments on semi-dilute solutions of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) chains as a function of the ionization degree, polymer and salt concentrations and temperature. In order to make the comparison with the model more quantitative, the theoretical structure factor has been fitted to the experimental curves by non-linear least squares analysis. Thus parameters of the theory can be obtained experimentally. Their physical significance is discussed throughout this paper.

Theoretical background.

Recent models [3, 4] consider semi-dilute solutions of partially ionized polymer chains slightly below the Flory compensation temperature Θ [27]. Without the presence of electrical interactions, such systems would undergo a macroscopic phase separation but the small fraction of ionized groups ensures the solubilization of the hydrophobic backbone. If the quality of the solvent is further decreased, the phase separation of such systems is predicted to occur now on a microscopic scale and to lead to the formation of microdomains. Due to the overall electroneutrality requirement, a macroscopic phase separation would compell the counterions to follow the polymer chains in the polymer rich phase. It is more favourable for the system to undergo a microscopic phase separation into oppositely charged polymer rich and polymer poor domains. The free energy increase due to the local violation of the electroneutrality condition is balanced by the gain of entropy for the counterions. Assuming the polymer chains to remain nearly Gaussian in the vicinity of the transition, the structure factor of the polymer solution can be calculated by means of the random phase approximation. In terms of reduced variables it reads [3, 4] :

$$G(x) = \frac{1}{4 \pi \ell_B r_0^2 \alpha^2} \frac{x^2 + s}{(x^2 + s)(x^2 + t) + 1} \quad (1)$$

Here ℓ_B is the Bjerrum length, α the fraction of ionized monomers and r_0 is a typical distance given by :

$$r_0^{-2} = \left(\frac{48 \pi \ell_B}{\alpha^2} \right)^{1/2} \alpha \phi^{1/2} \quad (2)$$

where a is the length of the statistical unit and ϕ the polymer concentration. The reduced wavevector x is defined as the product of the length r_0 by the usual wavevector transfer defined in a scattering experiment $q = 4 \pi / \lambda \sin(\theta/2)$, where λ is the wavelength of incident particles in the medium and θ the scattering angle. Similarly s is a reduced ionic strength defined as $s = \kappa^2 r_0^2$, where κ is the usual Debye-Hückel screening parameter and t is a reduced temperature given by :

$$\begin{aligned} t &= -12 r_0^2 h \phi / \alpha^2 \\ h &= -(2 v \tau + 3 w \phi) . \end{aligned} \quad (3)$$

Here $h \phi$ is the usual virial contribution in a Θ solvent, v being the excluded volume, $\tau = (T - \Theta) / \Theta$ the reduced distance to Θ temperature and w the third virial coefficient [27]. In a limited range of polymer concentrations ϕ , ionization degrees α and salt concentrations ϕ_s , the structure factor (1) exhibits a maximum for a non-zero value q^* of the wavevector transfer, given by :

$$q^{*2} + \kappa^2 = r_0^{-2} \quad (4)$$

This corresponds to cases where the system would undergo upon cooling a microphase separation transition with a domain periodicity given by $2\pi/q^*$. The observed peak reflects that concentration fluctuations with wavelength $2\pi/q^*$ are favoured above the microphase separation transition. As the transition is approached the maximum increases without changing its position. Upon increasing salt concentration or decreasing polymer concentration and/or ionization degree, equation (4) shows that the maximum shifts to smaller q values i.e. polymer concentration fluctuations with larger wavelengths are favoured. When the condition $\kappa^2 < r_0^{-2}$ is no longer satisfied, the maximum is pinned at zero q value and, upon cooling, the system undergoes a usual macroscopic phase transition. A sketch of the phase diagram, first described by Borue and Erukhimovich [3], is represented in figure 1. Both studies reported in references [3] and [4] lead to the same expression for $G(x)$ except that in [4] the Debye-Hückel screening parameter is defined by :

$$\kappa^2 = 4\pi\ell_B(\alpha\phi + 2\phi_s) \quad (5a)$$

whereas in [3] it is given by :

$$\kappa'^2 = 4\pi\ell_B(2\alpha\phi + 2\phi_s). \quad (5b)$$

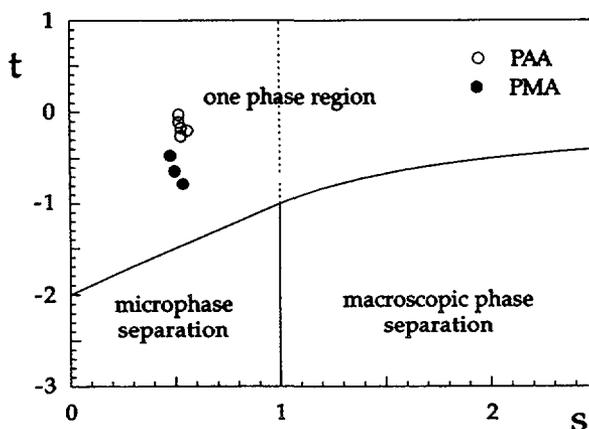


Fig. 1. — Simplified theoretical phase diagram for weakly charged polyelectrolyte chains in a poor solvent. In the stable region, for $s < 1$, the structure factor has a peak for a non-zero q value which shifts to $q = 0$ when $s \geq 1$. In the unstable region, the line $s = 1$ separates the microphase region from the usual macroscopic two-phase region (after Ref. [3]). Data points correspond to samples shown in figure 7.

In a recent theoretical paper [5], Raphael and Joanny made the distinction between quenched and annealed polyelectrolyte systems. In quenched systems, the position of the charges along the chains are fixed while in annealed systems these charges can move along the chains. Because of the smaller mobility of the polymer chains compared to that of the small ions, charges along the chains do not contribute to the electrostatic screening in quenched systems. On the other hand in annealed polyelectrolytes, these charges might be relevant in the estimation of the Debye-Hückel screening parameter which would be given by κ' instead of κ , the usual expression for quenched systems. By now there is no experimental evidence of this theoretical conjecture. Weak polyacids like those studied here might be examples of annealed polyelectrolyte systems.

Experimental section.

Samples have been obtained by following the general procedure described in previous papers [24-26]. Solutions of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) with given degrees of ionization, polymer and salt concentrations can be obtained through a radical polymerization of the monomer in the presence of the appropriate amount of sodium hydroxide and sodium bromide. The reaction is initiated by ammonium peroxydisulfate and performed in D_2O , in order to provide a good contrast in SANS experiments. Chemical reagents were used without further purification. Energy dispersive X-ray fluorescence [28] showed that the content of D_2O in multivalent ions was about a few $\mu M/L$. The molecular weight distribution function (mwdf) of the chains obtained in this reaction is known to depend on both the ionization degree and the monomer concentration in the reaction bath because propagation and termination rate constants are dependent on the nature of the radical chain ends [29]. In order to isolate the effects associated with this variation of the mwdf we have followed two different procedures. In the first one we have performed the polymerization reaction directly in the scattering cell, as was done previously for polymer gels, and the samples were studied in the reaction bath. In the second method, a stock solution was synthesized at zero neutralization degree (no sodium hydroxide added) and the final polymer and salt concentrations as well as the neutralization degree were adjusted subsequently in the scattering cell. The neutralization degree f is the molar ratio of sodium hydroxide to monomer concentrations. The effective ionization degree α is defined as the ratio of the number of ionized carboxylic groups to the total number of monomers. For low neutralization degrees it is necessary to take into account the dissociation of the weak polyacids to estimate the total amount of ionized groups. Since we consider here only weakly charged systems we used the dissociation constants of the monomers in water to obtain the ionization degree of the polymer solutions i.e. $k_{AA} = 5.6 \times 10^{-5}$ [30] and $k_{MA} = 2.6 \times 10^{-5}$ [31].

SANS experiments were performed on the spectrometer PACE in Laboratoire Léon Brillouin (Laboratoire commun CEA-CNRS). The temperature was regulated within 0.1 °C. All data were treated according to standard procedures for small-angle isotropic scattering. The spectra were corrected for transmission, sample thickness and electronic noise. Background samples were monomer solutions with the same composition as the polymer solutions. Normalization to the unit incident flux, geometrical factors and detector efficiency corrections were performed by using the incoherent scattering of H_2O , corrected for the scattering of the empty cell. In the whole set of SANS measurements, three different wavelengths of the incident neutrons were used ($\lambda = 5.45, 7.83$ and 8.16 Å). In order to allow the comparison between sets of data obtained with different λ values, the data treated were put on an absolute scale through multiplication by the tabulated values of the differential incoherent cross section per unit volume of H_2O at 25 °C [32]. In this way we obtain an absolute scattering intensity $I(q)$ which is directly proportional to the structure factor of the solution,

$$I(q) = KG(qr_0). \quad (6)$$

The proportionality constant K depends on the contrast between the polymer and the solvent relatively to the incident neutrons. Note that in writing equation (6) we have neglected the contributions to the scattering intensity arising from the small ions. This is justified because their scattering length densities and their concentrations are small compared to those of the polymer chains [33]. The constant K can be estimated from tabulated values of the scattering length densities and the partial molar volumes of the polymerized monomers [34]. We obtained the values 9.6 and 25 barns for PAA and PMA systems, respectively.

In order to make the comparison between experiments and theory more quantitative, we have fitted equations (1)-(6) to our experimental scattering intensities. The non-linear least squares fitting procedure uses three adjustable parameters : the contrast factor K , the length of the statistical unit a that enters both r_0 and t , and the parameter h related to the reduced temperature t . The polymer and salt concentrations as well as the ionization degree are input parameters.

Results and discussion.

ERROR BARS. — The fitting procedure allows us to follow the variation of the parameters K , a and h with the ionization degree, the polymer concentration, the salt content and the temperature. One expects that, upon a variation of all these parameters, the contrast factor K and the statistical unit length a will be invariant while h should depend on C_p and T .

Before the presentation of the results, it is necessary to discuss first the errors that accumulate through the fitting procedure, the preparation of the samples and the SANS experiments.

It is easy to understand how the fitting parameters control the shape of the structure factor and how accurately they can be obtained. In the limit of large scattering wavevectors, equation (1) predicts a q^{-2} decay of the scattering intensity which is consistent with the assumption that the chains remain nearly Gaussian and can be treated within the RPA formalism. Combining (1) and (6) we get :

$$I(q) = K \frac{12 \phi}{(qa)^2}, \quad a^{-1} \gg q \gg r_0^{-1} \quad (7)$$

This q^{-2} decay is in agreement with the general experimental behaviour. Equation (7) shows that the ratio K/a^2 determines the level of the plateau obtained in a Kratky plot $q^2 I(q)/\phi$ as a function of q . In most of our experiments, when the value of the asymptotic exponent is close to the Gaussian value, the level of the plateau i.e. the ratio K/a^2 is generally a constant within a possible 10 % variation. However it seems that the data for different samples are grouped independently of the polymer and salt concentration but that the plateau shifts to higher values when the ionization degree decreases. This is also observed for PMA samples. We will come back to this point later in the discussion.

The determination of the effective statistical unit length a for a given sample is unambiguous since this parameter controls the peak position (Eq. (3)) once the ionization degree and the polymer and salt concentrations are fixed. However the value of a is strongly dependent on the expression adopted for the Debye-Hückel screening parameter (Eq. (5)) and decreases from about 9 Å to about 6 Å when κ' is used instead of κ . This has a major consequence on the K value which drops by a factor larger than 2 because it is fixed by the plateau value in the asymptotic range. While the K values obtained with κ are in a good agreement with the estimated ones this is no longer the case when κ' is used. Thus in the following we have adopted the usual expression κ for the Debye-Hückel screening parameter.

In the fitting procedure the value of the parameter h has no influence on the intensity at large q values or on the peak position. As revealed by a close inspection of equation (1), h determines, together with a , the overall shape of the structure factor in the small q range and in the peak region. Both the peak intensity and the intensity at $q = 0$ depend in a complicated manner on a and h . Thus the h value is particularly sensitive to the number of experimental points in this q region. Due to the peaked shape of the structure factor in these systems and the small scattering intensity at low q values, it is rather difficult to obtain good data points for $q < 10^{-2} \text{ \AA}^{-1}$ within a reasonable amount of time. This implies that h is poorly defined

compared to K and α . Typical relative error bars associated with K , α and h are 5 %, 1 % and 10 to 50 %, respectively (Tabs. I to IV).

Table I. — *Fitting parameters obtained from different experiments on PAA and PMA samples prepared with the same polymer concentration and neutralization degree ($C_p \approx 0.71$ M/l, $\alpha \approx 0.05$). The last column indicates the samples studied in the reaction bath (r.b.) and samples prepared by dilution (dil.). Units are barns for K , Å for α and Å³ for h . See text for the differences between the italic and normal characters.*

Polymer	Date	K	α	h	Preparation
PAA	06/90	10.5 ± 0.3	9.5 ± 0.07	11.0 ± 1.6	r.b.
	01/91	8.4 ± 0.2	8.4 ± 0.05	12.7 ± 1.5	dil.
	05/91	7.8 ± 0.2	9.0 ± 0.04	29.9 ± 1	dil.
PMA	05/91	29.4 ± 0.5	8.5 ± 0.04	26.8 ± 1	dil.
	10/91	22.7 ± 0.7	8.7 ± 0.06	38.2 ± 1.5	r.b.
	02/92	26.5 ± 0.6	8.5 ± 0.05	34.9 ± 1.2	r.b.
	03/92	19.9 ± 0.6	8.0 ± 0.06	39.0 ± 1.3	r.b.

We have to emphasize that the values of the parameters K , α and h are sensitive to the values of the input parameters, especially the ionization degree and the salt concentration. The computation of the actual degree of ionization is a difficult matter since we have to use the dissociation constant of the monomers diluted in H₂O while we study rather concentrated solutions of polymers in D₂O. Concerning the salt concentration, it would be probably better to take into account the ions originating from the dissociation of the initiator (NH₄)₂S₂O₈. However the final state of these ions in the polymerized system is not known since there is only uncertain evidence for the actual incorporation of the sulfate radical-ion group as end-group [37]. Therefore it is not easy to ascribe to them the role of co-ions or of charged functions on the polymer chains. At this point we can only recognize that uncertainties on the actual α and C_s values exist and affect the values of the fitted parameters, especially when the neutralization degree is small. Examples will be given later on.

When comparing different sets of experiments another source of errors originates in the reproducibility of sample preparation and apparatus configuration. This is illustrated in figure 2 where are reported the structure factors of three different PAA solutions and four different PMA solutions corresponding to the same preparation i.e. $C_p \approx 0.71$ M/l and $\alpha \approx 0.051$. Whereas the overall shapes of the structure factors are well reproduced, the absolute level of the scattering intensity and fine details may vary slightly from one experiment to another. Table I gives the fitting parameters obtained for the structure factors in figure 2. The error bars associated with the reproducibility of the experiments are seen to be somewhat larger than those due to the fitting procedure. This should be kept in mind when comparing different sets of experiments.

These differences in the values of the parameters may most likely originate in the difficulty to prepare small amounts of samples with a good accuracy but one cannot exclude small differences in the general configuration of the spectrometer. Thus as a general rule we have tried to investigate the variation of a given parameter (like polymer concentration, salt content or temperature) within a single set of measurements. This allows one to obtain the general trends in a much better way.

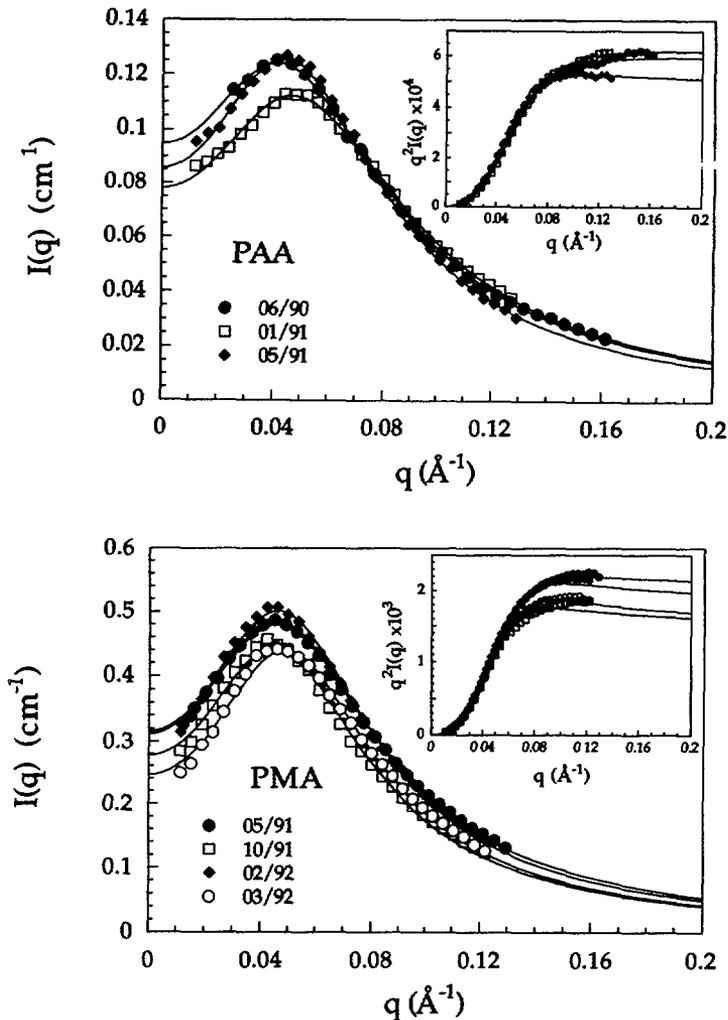


Fig. 2. — Typical reproducibility of SANS measurements and sample preparation ($C_p \approx 0.71$ M/l, $\alpha \approx 0.05$). The insets show the experimental data in the Kratky representation. Solid lines are best fits to the experimental structure factors.

The insets in figure 2 show the Kratky representation of the scattering intensities. In fact the Kratky plot provides a powerful tool to discriminate the samples. Three different behaviours can be distinguished : first either the experimental structure factors show a plateau regime in the Kratky plot or they do not. Most samples belong to the first category except for a few ones which have large ionization degrees (~ 0.1) (PAA solutions) or small ionization degrees (~ 0.02) (PMA solutions). Among the samples which exhibit the q^{-2} decay for large q values, we can further make a distinction according to the shape of their fitting curves. As a general rule, the fitting curves of the PAA solutions show a monotonous behaviour in the Kratky plot (Fig. 2a) while those of the PMA samples show a maximum i.e. the fitting curves reach their plateau values for q values larger than 0.2 \AA^{-1} , well beyond the range ($q \sim 0.1 \text{ \AA}^{-1}$) where the data points start to show a Gaussian behaviour (Fig. 2b). This feature is generally associated

with an uneven repartition of the residues in the whole q range measured in the experiments. This point will be discussed further later on.

To provide a help in the reading of tables I-IV and in the discussion, the parameter values obtained on samples which do not show a q^{-2} decay at high q values are bold-typed, while those corresponding to non-monotonous fitting curves (in the Kratky plot) are italic-typed.

EFFECT OF THE POLYMER CONCENTRATION AND OF THE IONIZATION DEGREE. — Equations (2) and (4) predict that the peak position shifts to higher q values upon increasing the ionization degree and/or the polymer concentration. This is indeed what is observed experimentally. Figure 3 shows the variation of $q^{*2} + \kappa^2$ as a function of $\alpha C_p^{1/2}$ for all PAA and PMA samples investigated. To find the peak position independently of any model, we used a parabolic fitting through a few points around the maximum. In figure 3 the error bars are not too pessimistic evaluations of the real errors which affect the measurements due to the finite resolution in the wavevector definition. These errors are large enough to allow the data points to be satisfactorily described by a straight line in the case of PAA while for PMA the data points are

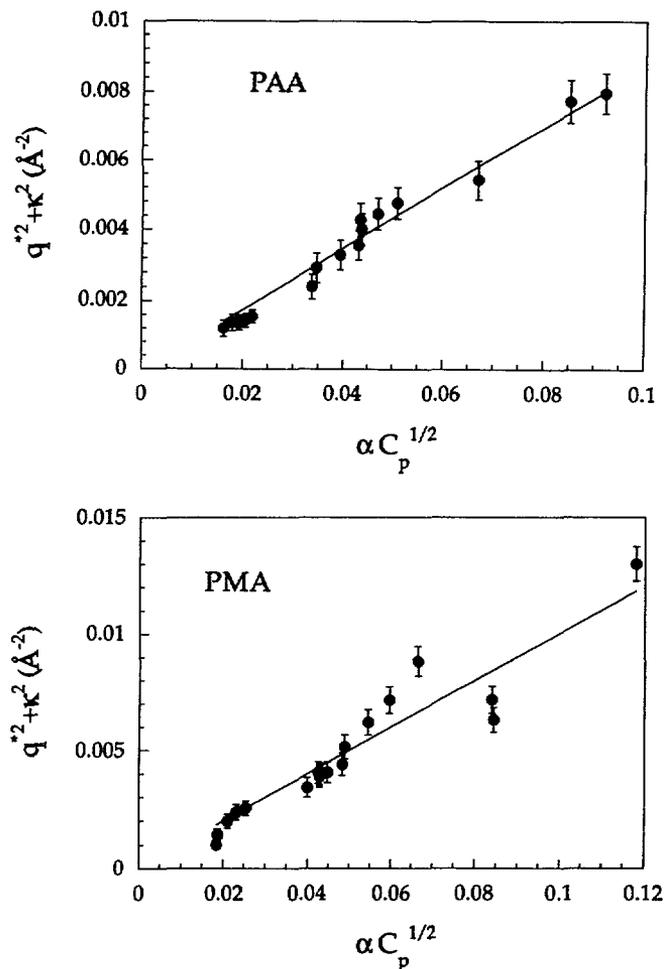


Fig. 3. — Variation of the peak position for PAA and PMA solutions with different polymer concentrations and ionization degrees.

much more scattered. The slopes of the straight lines provide a measure of an average statistical unit length $a \approx 9.3 \pm 0.2 \text{ \AA}$ for PAA and $a \approx 8.1 \pm 0.5 \text{ \AA}$ for PMA.

A different insight is provided by fitting equations (1)-(6) to the experimental structure factor. The results are given in table II. Contrary to what is expected, the fitted values of both K and a vary with the polymer concentration and ionization degree.

As stated above, the value of a is mainly given by the peak position. In a previous paper [24] it was already observed that, in PAA gels, equations (2) and (4) could not properly describe the polymer concentration dependence of the peak position. It was found that the effective value of the statistical unit length was slightly decreasing when the polymer concentration was increasing. This behaviour is not observed in the PAA solutions prepared by dilution of a reaction bath : for a given ionization degree, K and a are nearly independent of the polymer concentration and one can define mean values of K and a .

On the other hand, the PMA solutions seem to show the same trend as PAA gels. It must be noted in this respect that i) PMA solutions have been synthesized directly at the concentration where they have been studied and ii) at PMA concentrations larger than 10 %, physical gels may form [11]. One or both of these features are likely to be at the origin of the observed behaviour. They may as well explain the results in figure 3b since the data which show the largest departure from the straight line do correspond to the most concentrated samples.

Another important feature in PMA samples is the non-monotonous behaviour of the fitting curve in the Kratky representation. As mentioned previously, the Gaussian behaviour is recovered at much higher q values than in the experimental data. This might be due to the repartition of the data points which are usually centered around the maximum. However this is also the case for PAA samples whose fits describe the experimental points correctly in the whole q range investigated. This seems to show that the shapes of the structure factors are qualitatively different in PAA and in PMA samples and that equations (1)-(6) are not able to describe adequately the intensity scattered from the PMA samples in both the peak region and the intermediate regime. Thus the fitting parameters obtained from these samples are probably not as significant as for PAA solutions and their variation with α and C_p may simply reflect the inadequacy of the theoretical structure factor to describe the data.

If we now turn to the effect of ionization degree on PAA solutions, table II shows that the mean values a and K defined for a given ionization degree exhibit an opposite variation as α increases. This is not surprising : as shown in figure 4, in the asymptotic q range, the scattering intensity is nearly independent of α , which means that the ratio K/α^2 has to be nearly a constant. Thus the variations of both quantities are correlated in the fitting procedure. However the physical meaning of these variations is not clear. We expect a negligible change of the contrast factor K if we increase the neutralization degree from 0.02 to 0.05. This is at variance with the variation obtained, nearly a factor of 2. Moreover the decrease of a as α becomes larger is rather surprising. If any variation, one would expect an increase associated with a stiffening of the chains for larger ionization degrees.

Here again, for the smallest ionization degrees, one might think of a fitting artefact because the peak has shifted to smaller q values and is not well defined in the scattering experiment. Thus one would prefer to keep the values for K and a fixed. In order to check the sensitivity of the fits to a variation of the adjustable parameters we have fitted the experimental results obtained for one sample with $\alpha \approx 0.02$ by fixing the parameters K and a to the values obtained at $\alpha \approx 0.05$ and letting only h as an adjustable parameter. The results reported in figure 5 show that the quality of the fit has significantly deteriorated. The choice of setting the K and a parameters to their values obtained for $\alpha \approx 0.05$ may appear somewhat arbitrary. However the quality of the fits is in general better for this ionization degree, the fitted K values are then closer to those estimated from the tabulated values of the scattering length densities (for PAA,

Table II. — Variation of the fitting parameters as a function of the polymer concentration and neutralization degree. For a better clarity, the presentation of the data is split according to the polymer type, sample preparation and date of the experiment. See text for the differences between *italic*, **bold** and normal characters.

PAA reaction bath, 06/90.

$C_p \sqrt{f}$	0.05			0.1		
	K	a	h	K	a	h
0.42				14.9 ± 0.5	14.6 ± 0.14	104 ± 6
0.70	10.5 ± 0.3	9.5 ± 0.07	11.0 ± 1.6	7.1 ± 0.2	9.5 ± 0.04	73.5 ± 1.6

PAA reaction bath, 01/91.

$C_p \sqrt{f}$	0.02			0.05			0.1		
	K	a	h	K	a	h	K	a	h
0.42	13.6 ± 0.3	10.7 ± 0.08	-9.5 ± 1.5	11.7 ± 0.2	11.1 ± 0.06	8.4 ± 2.3	20.1 ± 1.2	15.0 ± 0.3	-29.5 ± 20

PAA dilution, 01/91.

$C_p \sqrt{f}$	0.05			0.1		
	K	a	h	K	a	h
0.44	10.8 ± 0.4	9.6 ± 0.07	27.3 ± 2.5	10.3 ± 0.4	9.7 ± 0.08	93 ± 6
0.71	8.4 ± 0.2	8.4 ± 0.05	12.7 ± 1.5	6.6 ± 0.2	8.8 ± 0.04	76 ± 3

PAA dilution, 05/91.

$C_p \sqrt{f}$	0.02			0.05			0.1		
	K	a	h	K	a	h	K	a	h
0.57	13.1 ± 0.3	10.7 ± 0.07	7.6 ± 0.8	10.1 ± 0.2	9.7 ± 0.06	33.6 ± 1.6			
0.71	13.8 ± 0.5	10.7 ± 0.11	5.1 ± 1.1	7.8 ± 0.2	9.0 ± 0.04	29.9 ± 1			
0.85	14.2 ± 0.4	10.9 ± 0.1	1.6 ± 0.9	7.6 ± 0.2	8.8 ± 0.04	22.3 ± 1.1	10.3 ± 0.2	9.3 ± 0.03	54.1 ± 1.7
1.00	13.4 ± 0.4	10.7 ± 0.11	0.4 ± 0.9	7.4 ± 0.2	8.7 ± 0.04	21.5 ± 0.8			

PMA dilution, 05/91.

$C_p \sqrt{f}$	0.02			0.05			0.1		
	K	a	h	K	a	h	K	a	h
0.59	102 ± 4	15.9 ± 0.23	-36 ± 3.2	32.8 ± 0.7	9.4 ± 0.05	34.0 ± 1.4	30.9 ± 1.2	10.4 ± 0.08	143 ± 4
0.71	49.1 ± 0.9	10.6 ± 0.07	-12.4 ± 0.9	29.4 ± 0.5	8.5 ± 0.04	26.8 ± 1	22.6 ± 0.7	9.0 ± 0.05	107 ± 3

Table II (continued).

PMA reaction bath, 10/91.

$C_p \sqrt{f}$	0.02			0.05			0.1		
	K	α	h	K	α	h	K	α	h
0.93	37.2 ± 0.5	8.3 ± 0.03	-2.1 ± 0.4	24.6 ± 0.4	7.5 ± 0.03	28.5 ± 0.6			
1.2	25.6 ± 0.3	7.7 ± 0.03	-0.7 ± 0.3	19.1 ± 0.3	7.0 ± 0.02	26.8 ± 0.4			
1.4	28.3 ± 1	7.7 ± 0.08	-3.2 ± 0.8	14.2 ± 0.3	6.5 ± 0.02	24.6 ± 0.4	8.8 ± 0.3	7.1 ± 0.04	74.6 ± 1
1.7				9.6 ± 0.2	5.8 ± 0.02	21.7 ± 0.3			

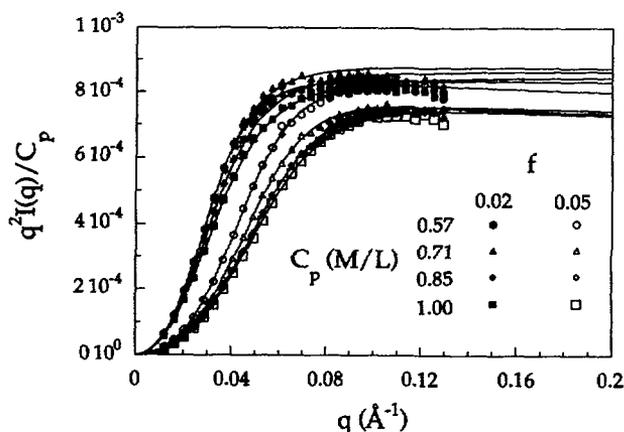


Fig. 4. — Kratky representation of the intensities scattered from PAA solutions prepared by dilution of a stock solution. Solid lines are best fits to the data.

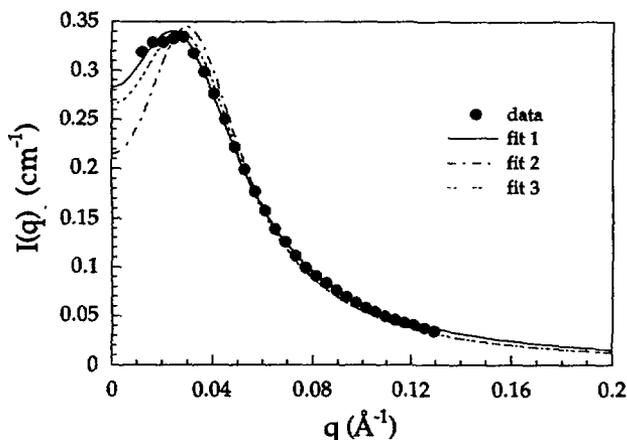


Fig. 5. — Sensitivity of the fits to the number of free parameters and to the values of input parameters. Data from a PAA solution with $C_p \approx 0.71$ M/l and $f = 0.02$. Fit 1 is a normal fit with three free parameters whose final values are $K = 13.8$, $\alpha = 10.7$, $h = 5.1$; input parameters are $\alpha = 0.023$, $C_s = 0$. Fit 2 is a fit with K and α fixed to the values obtained for $f = 0.05$; h is the only free parameter with final value $h = 18.6$; input parameters are $\alpha = 0.023$, $C_s = 0$, $K = 7.6$, $\alpha = 8.83$. Fit 3 follows the same procedure as fit 2 but α and C_s have been modified to evaluate the errors due to the estimation of the true ionization degree and the presence of ionic monovalent impurities; the final value $h = 19.4$ is obtained; input parameters are $\alpha = 0.026$, $C_s = 2.5$ mM/l, $K = 7.6$, $\alpha = 8.83$.

$K_{\text{fit}} \approx 7.6$ barns instead of 9.6 barns, for PMA $K_{\text{fit}} \approx 29$ barns instead of 25 barns) and the fitted a values are nearly the same as the averaged ones obtained from figure 3 (PAA $a \approx 8.8 \text{ \AA}$, PMA $a \approx 8.5 \text{ \AA}$).

Two main reasons could be invoked to explain the poor quality of the fit when a and K have fixed values.

i) The ionization degree has been calculated assuming that the pK of the polymer was that of the monomer in protonated water. While the assumption of same pK for the polymer and the monomer is likely to be reasonable because of the low dissociation degrees considered here, the second assumption that the pK is the same in D_2O and H_2O might not be as well justified and would induce larger errors on solutions with small neutralization degrees. Also as mentioned before the use of simple dissociation equations in rather concentrated solutions may be questioned.

ii) Even a very small quantity of ionic impurities in D_2O might affect the results significantly, the lower the ionization degree the higher the perturbation. As seen in the experimental section, the deuterated water that we used contained only very small traces of multivalent ions. However one cannot rule out a contamination of the monomers or the sodium hydroxide by multivalent impurities that might play a non-negligible role. Moreover as discussed before the initiator used during the polymerization introduces uncertainties in the actual ionization degree and the salt concentration.

These effects are illustrated in figure 5 where the experimental structure factor has been fitted by still keeping the values of a and K obtained for $\alpha \approx 0.05$ but assuming that the sample contained 2.5 mM/l of a monovalent salt or that the actual ionization degree was $\alpha = 0.026$ instead of 0.023. One can see that the quality of the fits is reasonable which makes us think that either one or both of the above reasons might be responsible for the observed anomalous effect of the ionization degree.

Thus the variations of the fitted contrast factor and statistical unit length with the ionization degree do not necessarily invalidate our interpretation of the results. From the data in figure 3 the definition of an average statistical unit length, independently of the ionization degree, seems to be meaningful within the experimental accuracy. For all the reasons mentioned above, slight departures of the experimental peak position from the value predicted by equations (2) and (4) may occur and be reflected by a different fitted value for the statistical unit length. Because of the strong coupling between the squared statistical unit length and the contrast factor introduced by the intensity level in the large q range, a small variation in the fitted a induces a larger relative change in the fitted K .

However, from a different point of view, one has also to remember that the theory of the microphase separation for these systems has been worked out within rather well defined limits. These imply that there are not too many charges in the system, otherwise electrical interactions become dominant, but also that enough counterions are present so that their entropic contribution to the free energy is relevant. For the polymer concentration range investigated here, these conditions might be satisfied only for an ionization degree around 0.05. This would also be a possible explanation for the poorer quality of the fits when the ionization degree departs from the value 0.05. It is likely that deviations from the experimental conditions where the model is valid will show up sooner in the shape of the structure factor (i.e. in the fitting parameters) than in the peak position (Eq. (4)). In this respect, it can also be remarked that an asymptotic decay with an exponent b different from -2 has been observed mainly on PAA solutions with $\alpha \approx 0.1$ ($b < 2$) and on PMA solutions with $\alpha \approx 0.02$ ($b > 2$). This could be linked to the stronger hydrophobicity of PMA chains and might illustrate how delicate the balance between hydrophobic and electrostatic forces is. However the number of these observations is too limited to conclude definitely.

Finally, considering the small variation of the plateau value with the ionization degree (Fig. 4), it can be remarked that equation (7) holds for Gaussian chains, independently of any model. Thus, if we assume that K does not vary with α , the decrease in the plateau value as α increases should be reflected by an increase of the statistical unit length with the ionization degree, which is consistent with a stiffening of the chains. However, changing the a value according to the plateau value does not help to improve the fits since the peak position is then incorrectly described.

In the conditions where $\alpha \neq 0.05$ and K and a are variable, the quantity h acts probably as an additional free parameter which allows a better fit of the data without any real physical meaning. However when the neutralization degree is around 0.05, the situation might be different and it might be worth considering the variations of h .

Figure 6 shows the concentration dependence of the fitting parameters obtained on PAA samples with ionization degree $\alpha \approx 0.05$ (Tab. II). K and a are constant while, as expected from equation (3), h decreases for larger polymer concentrations although the predicted linear behaviour is not followed, likely due to the rather high concentrations investigated here. From table II, it is difficult to see any clear difference between the samples studied in the reaction bath and those obtained by dilution of a stock solution. It would be necessary to perform a more systematic investigation to reach any definite conclusion on this point. In the following we are focusing on samples with $\alpha \approx 0.05$ to investigate temperature and salt effects.

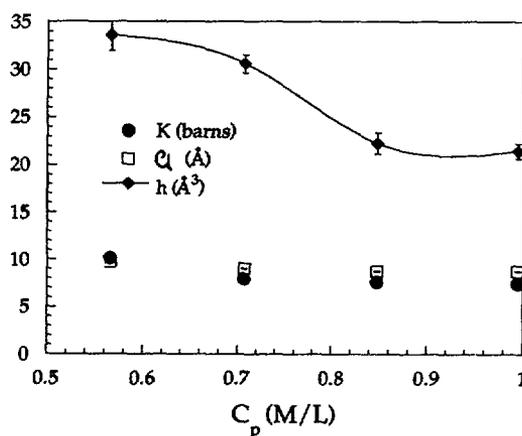


Fig. 6. — Effects of polymer concentration on the fitting parameters of PAA solutions prepared by dilution of a stock solution. For all the solutions, the neutralization degree is 0.05. The solid line is a guide for the eye.

TEMPERATURE EFFECTS. — Figure 7 shows the variations with temperature of the structure factors of PAA and PMA solutions with $C_p \approx 0.71$ M/l and $\alpha \approx 0.05$. As predicted by the model, the position of the peak is, within the experimental accuracy, independent of temperature. The amplitude of the peak decreases upon increasing the temperature in PAA whereas it shows the reverse behaviour for PMA systems. This is also expected since the phase diagram of the PAA-water system in acidic conditions is characterized by an upper consolute solubilization curve while, in PMA-water solutions under the same conditions, a lower consolute solubilization curve is observed. The temperature dependence of the peak amplitude

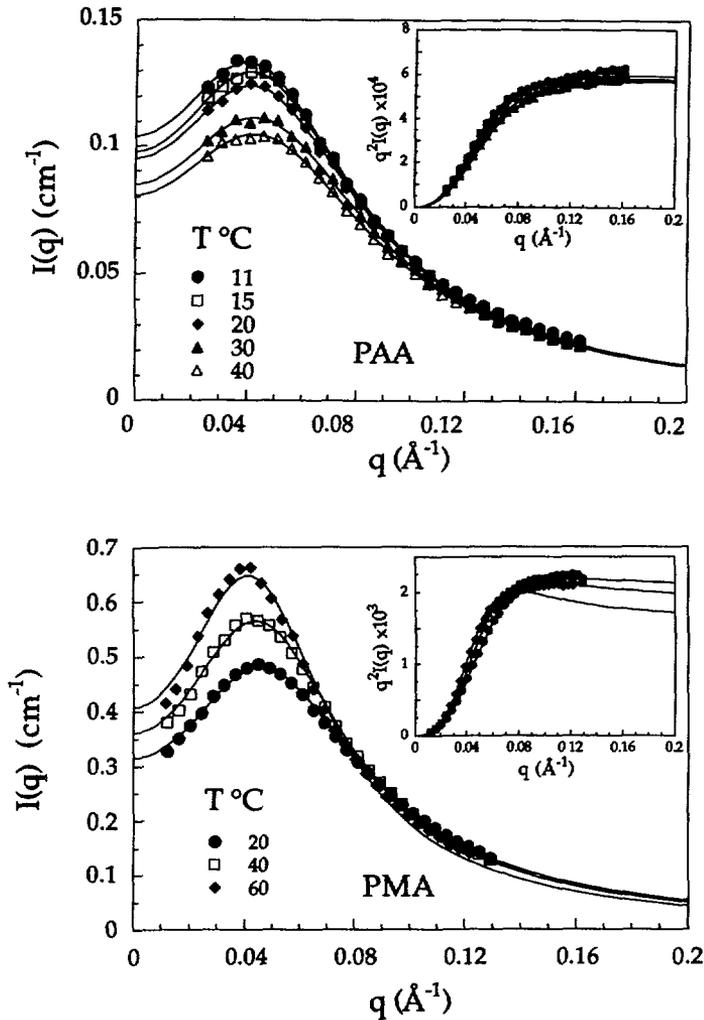


Fig. 7. — Temperature variation of the intensity scattered from PAA (above) and PMA (below) solutions with $C_p \approx 0.71 \text{ M/l}$ and $\alpha \approx 0.05$. Insets show the Kratky representation of the data. Solid lines correspond to the fitted theoretical intensities.

can be analyzed from equation (1) that predicts the following behaviour for the inverse peak intensity :

$$S^{*-1} = 4 \pi \ell_B r_0^2 \alpha^2 (2 - s + t) \tag{8}$$

which can be written as :

$$S^{*-1} = S_0^{*-1} + 2 v \tau \tag{9}$$

where :

$$S_0^{*-1} = \frac{4 \pi \ell_B \alpha^2}{(q^{*2} + \kappa^2)^2} (2 q^{*2} + \kappa^2) + 3 w \phi \tag{10}$$

is temperature independent. Figure 8 shows that, within a good approximation, the peak intensity varies linearly with the temperature.

Table III gives the parameters of the fits reported in figure 7. From these values, one can also obtain the couples of values (s , t) for each sample. The corresponding points are represented in

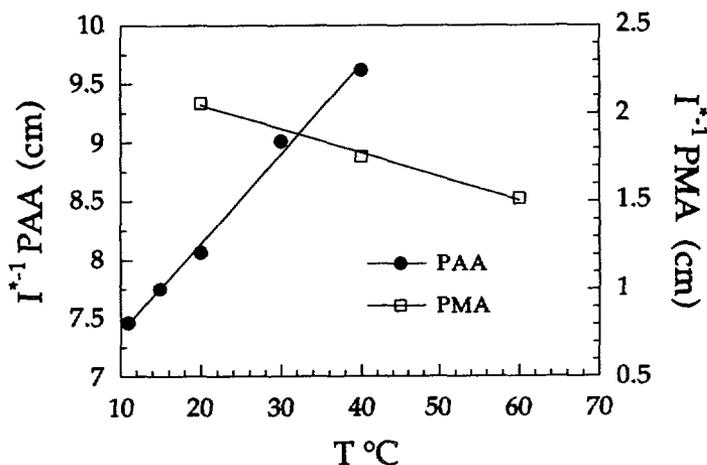


Fig. 8. — Variation of the inverse peak intensity as a function of the temperature for the samples in figure 7. Straight lines are best fits to the experimental data.

Table III. — *Temperature variation of the fitting parameters. For the PMA samples with $C_p = 0.706$ M/l, the experiments were performed at two different dates: May 91 (for $T = 20$ °C and $T = 40$ °C) and October 91 (for $T = 60$ °C). All the measurements on the sample with $C_p = 1.43$ M/l were done in October 91. See text for the differences between *italic*, **bold** and normal characters.*

PAA $C_p = 0.702$ M/l, $\alpha = 0.0515$, 06/90.

T (°C)	K	a	h
11	11.2 ± 0.3	9.9 ± 0.08	13.7 ± 1.8
15	10.2 ± 0.3	9.5 ± 0.06	17.1 ± 1.3
20	10.5 ± 0.3	9.5 ± 0.07	11.0 ± 1.6
30	9.7 ± 0.3	9.3 ± 0.08	6.7 ± 1.8
40	9.7 ± 0.2	9.2 ± 0.06	1.7 ± 1.5

PMA May (05) and October (10) 91.

$T \setminus C_p, \alpha$	$C_p = 0.706, \alpha \approx 0.022$			$C_p = 0.706, \alpha \approx 0.051$			$C_p = 1.43, \alpha \approx 0.021$		
	K	a	h	K	a	h	K	a	h
20 (05)	49.1 ± 0.9	10.5 ± 0.06	-12.4 ± 0.9	29.4 ± 0.5	8.5 ± 0.04	26.9 ± 1	28.3 ± 1	7.7 ± 0.08	-3.2 ± 0.8
40 (05)	43.4 ± 0.7	10.2 ± 0.05	7.3 ± 0.5	29.5 ± 0.6	8.9 ± 0.04	38.6 ± 1	29.3 ± 0.7	8.4 ± 0.05	7.1 ± 0.3
60 (10)	35.9 ± 0.4	9.5 ± 0.03	19.3 ± 0.3	28.4 ± 1	9.5 ± 0.07	50.4 ± 1.5	29.9 ± 0.8	8.9 ± 0.06	13.4 ± 0.2

the phase diagram (Fig. 1). It can be seen that for the PAA samples the values of t become increasingly negative upon decreasing the temperature whereas for PMA samples the opposite behaviour is observed. The microphase transition temperature would correspond to a point on the straight line of equation $t = s - 2$. Figure 9 shows the temperature evolution of the fitting parameters for PAA and PMA solutions with $C_p \approx 0.71$ M/l and $\alpha \approx 0.05$.

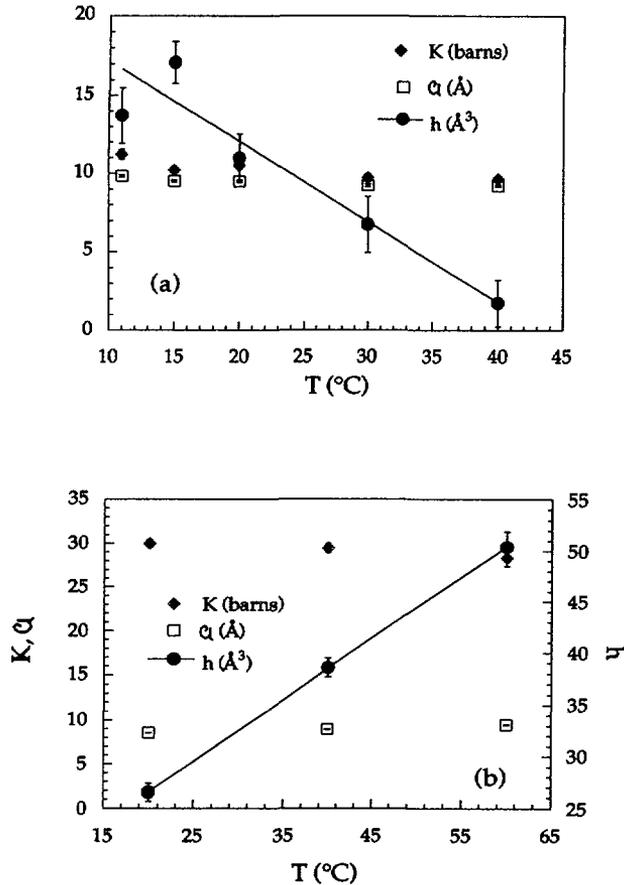


Fig. 9. — Temperature variation of the fitting parameters corresponding to the solid lines in figure 7.

For PAA samples, h would change its sign for a temperature between 40 °C and 45 °C. From the definition of h , one expects that this change of sign occurs at a temperature close to the θ temperature. The θ temperature of PAA in protonated water containing 0.2 M/l HCl has been measured by Silberberg *et al.* [10] and was found to be equal to 14 °C. Recent light scattering measurements [35] confirm this value and show that in deuterated water, in the presence of the same quantity of DBr, the θ temperature is around 27 °C. Such a large difference in the θ temperature between protonated and deuterated water might be due to the presence of H bonding.

It is interesting to note that our light and neutron scattering experiments provide an estimate of the same quantity, i.e. the θ temperature, through measurements performed under very different conditions. In the light scattering measurement, the θ temperature is obtained by

following the temperature evolution of the second virial coefficient in dilute solutions of the polymers. A strong acid is added in order to minimize the effects of charges. However this acid is liable to modify also the solvent thermodynamic quality. On the other hand, the neutron scattering experiment provides a value for the Θ temperature through the temperature evolution of the overall structure factor shape as quantified by a fit to a theoretical model. The measurements are performed in rather concentrated solutions with no acid added. Thus the only minor difference in the Θ temperatures obtained by the two methods appears as a rather surprising agreement that could be considered as a strong support to the theoretical model.

Finally it can be noted that, in PAA systems, the observation of a maximum in the whole temperature range of the experiment ($11\text{ }^\circ\text{C} < T < 40\text{ }^\circ\text{C}$) is consistent with a Θ temperature between $40\text{ }^\circ\text{C}$ and $45\text{ }^\circ\text{C}$, deduced from the temperature evolution of h , and one could expect this maximum to disappear for temperatures above $50\text{ }^\circ\text{C}$.

In the case of PMA samples, light and neutron scattering results do not compare as favourably as above. The Θ temperature in diluted protonated water-PMA samples with 0.2 M HCl added was found to be $55\text{ }^\circ\text{C}$ by the light scattering technique [35]. Measurements in the deuterated system under acidic conditions indicate a Θ temperature slightly below $50\text{ }^\circ\text{C}$ [35]. On the other hand, the fits to the SANS curves suggest the Θ temperature to be below $20\text{ }^\circ\text{C}$ in the samples with $\alpha \approx 0.05$. Only the PMA samples with $\alpha \approx 0.02$ would indicate a Θ temperature between $20\text{ }^\circ\text{C}$ and $40\text{ }^\circ\text{C}$ but we have seen earlier that the fit to the theoretical model is less reliable for this ionization degree range.

At the present time, the most likely explanation for these differences might be found in the complex nature of the interactions in systems with LCST behaviour. For this type of systems, changes in experimental conditions such as the introduction of a strong acid may trigger large differences in the experimental behaviour. Then the description of the vicinity of the transition temperature by a simple expression such as equation (3) might be no longer justified. Further work is needed to clarify that point.

One has also to remember that, for PMA samples, the fitting procedure gives curves with a characteristic decrease in the high q region and an uneven repartition of the residues. As suggested above, this might indicate that the theoretical structure factor is not well suited to describe the intensity scattered from these systems. Therefore the information on the Θ temperature obtained from the variation of h with temperature is probably not as reliable as in PAA systems.

SALT EFFECTS. — The structure factors of PAA and PMA solutions in the presence of various amounts of salt are reported in figure 10. The behaviour already reported for PAA gels [24, 25] is observed here on the solutions. Upon a small addition of salt, the maximum in the structure factor shifts to smaller q values while the peak intensity becomes larger. As more salt is added, the peak disappears and the maximum of the intensity, which is now observed at $q = 0$, increases continuously.

The salt dependence of the peak position is given by equations (2) and (4) or equivalently by :

$$q^{*2} = q^{*2}(\phi_s = 0) - 8 \pi \ell_B \phi_s \quad (11)$$

while the variation of the inverse peak intensity with the salt concentration is given by equation (8) and can be rewritten as :

$$I^{-1}(q^*) = I^{*-1} = I^{*-1}(\phi_s = 0) - \frac{2 \pi \ell_B \alpha^2 \phi_s}{3 K \phi} \quad (12)$$

Figure 11 shows the variation of q^{*2} and I^{*-1} as a function of salt concentration for the PAA

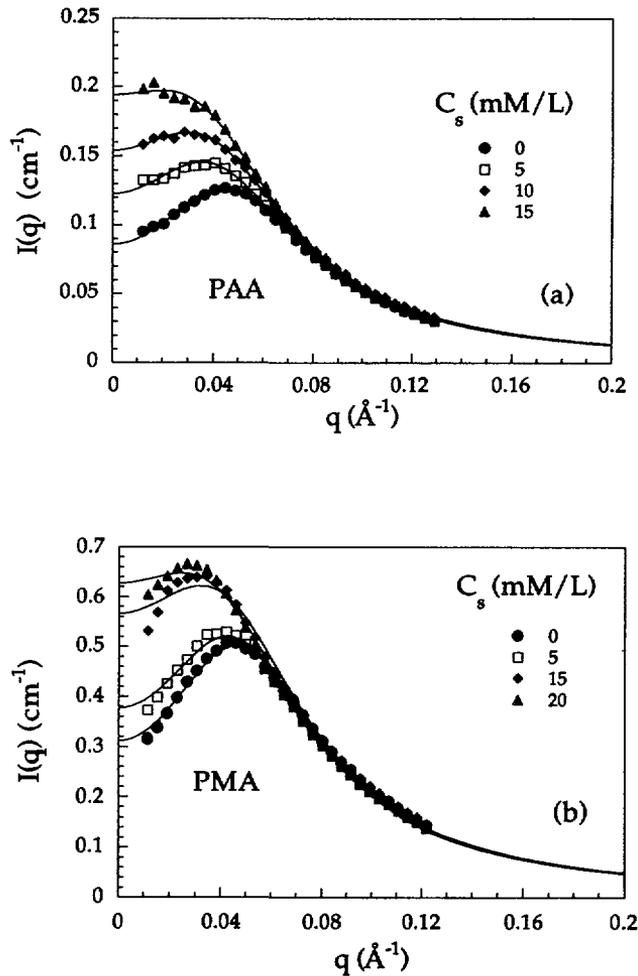


Fig. 10. — Salt effects on the structure factors of PAA (above) and PMA (below) with $C_p \approx 0.71$ M/l and $\alpha \approx 0.05$. Solid lines are fits of the theoretical intensities to the experimental data.

and PMA samples. The linear dependence on the salt concentration predicted by equations (11), (12) is seen to be qualitatively well obeyed. However a closer inspection of the data shows some features that are not consistent with these equations.

From equation (11), the shift of the peak position with the added salt concentration is expected to be the same for both PAA and PMA samples as shown in figure 11a where the experimental $q^{*2}(\phi_s = 0)$ were used to draw solid lines with slope given by equation (11). While the data obtained with the PAA samples are rather well described by equation (11), the predicted shift is much stronger than the observed one in the case of PMA samples. This behaviour is associated with a weak but systematic decrease of the fitted a value in the PMA samples (cf. Tab. IV) which shows that equation (4) is not very well obeyed for these samples.

As already emphasized above, the fitted K and a parameters are strongly correlated. Although they may vary with the salt concentration, the ratio a^2/K keeps nevertheless rather constant values. Thus if we calculate mean values for this ratio we obtain $(10.0 \pm 0.4) \times 10^8$ and $(2.8 \pm 0.2) \times 10^8$ respectively for the PAA and PMA samples with added salt (Tab. IV).

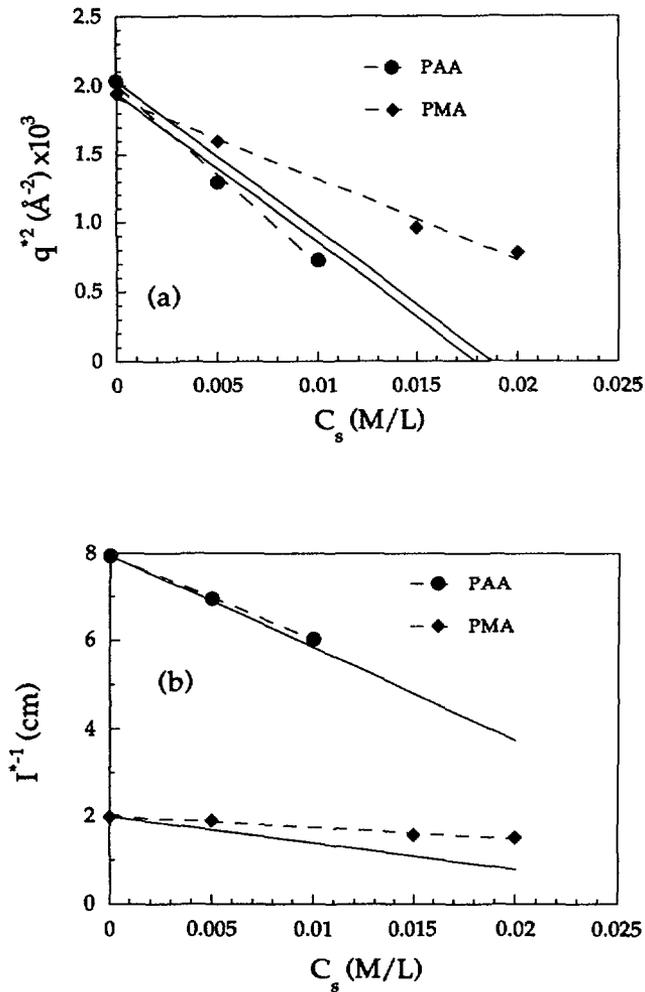


Fig. 11. — Influence of the salt concentration on the peak position (above) and the inverse peak intensity for PAA and PMA solutions in figure 10. Solid lines correspond to the predicted slopes (see text) and dashed lines to the best linear fits.

These numbers have been used in equation (12), together with the experimental $I^{*-1}(\phi_s = 0)$, to obtain the predicted salt dependence of I^{*-1} for the PAA and PMA samples. They are shown in figure 11b as solid lines. Again the agreement with the experimental behaviour is found to be worse for the PMA solutions. However, even for the PAA samples, a best fit line through the data would yield a slope slightly different from the predicted value.

Table V gives a summary of the predicted and observed slopes that characterize the dependence of the peak position and intensity on the molar salt concentration C_s . Again a quantitative agreement with the model is nearly achieved for PAA samples while for PMA samples, although the qualitative linear decrease with salt content is obeyed, clear discrepancies from the predicted slopes are evident. This is to be correlated with the poor agreement between the fitted structure factors and the experimental data (Fig. 10b) and with the stronger sensitivity of the fitting parameters to the salt concentration for these samples (Tab. IV).

Table IV. — *Effect of salt on the fitting parameters. Experiments on PAA solutions were performed in May 91 on diluted samples while PMA solutions were studied in the reaction bath in February 92. For both sets of experiments $C_p \approx 0.71$ M/l and $\alpha \approx 0.051$. See text for the differences between italic and normal characters.*

Polymer	C_s	K	a	h
PAA	0	7.8 ± 0.2	9.0 ± 0.04	29.9 ± 1
	0.005	8.4 ± 0.2	9.2 ± 0.05	26.9 ± 1.2
	0.010	8.1 ± 0.2	8.8 ± 0.05	25.8 ± 0.8
	0.015	7.8 ± 0.3	8.7 ± 0.1	25.9 ± 1.4
PMA	0	26.5 ± 0.6	8.5 ± 0.05	34.9 ± 1.2
	0.005	22.4 ± 0.7	8.0 ± 0.06	34.4 ± 1.3
	0.015	20.4 ± 1.3	7.5 ± 0.1	29.4 ± 1.9
	0.020	18.9 ± 1.2	7.3 ± 0.2	26.7 ± 1.6
	0.030	28.8 ± 2.5	8.7 ± 0.3	13.6 ± 2.5

Table V. — *Comparison between the predicted and measured slopes that characterize the salt effects on the peak position and intensity (data from Fig. 11).*

	Peak position		Peak intensity	
	Predicted	Measured	Predicted	Measured
PAA	0.108	0.13 ± 0.01	210 ± 10	192 ± 5
PMA	0.108	0.059 ± 0.004	59 ± 5	25 ± 3

Conclusions.

In this paper the variations of the static structure factor of weak polyacid solutions have been measured as a function of the polymer concentration, ionization degree, temperature and salt concentration.

Two different polyacids have been investigated : one with a UCST behaviour (PAA) and the other one with a LCST behaviour (PMA). All the results obtained so far agree qualitatively with a recent model which predict the ability of these systems to form microphases in the unstable region of the phase diagram.

The main signature of this feature is the presence in the scattering intensity of a maximum at a finite wavevector value. The amplitude of this maximum has been found to increase as the transition temperature is approached. For both systems, the position of the peak as a function of the ionization degree and polymer concentration is correctly predicted by the theory.

A quantitative comparison with the theory was made possible by fitting the theoretical structure factor to the experimental data, using three free parameters of the model : the contrast factor K , the statistical unit length a and the virial term h .

For PAA solutions, the fitting curves compare very well with the experimental data when the ionization degree is about 0.05. When α departs from this value, the quality of the fits remains

good but the contrast factor and the statistical unit length are unphysically dependent of α . This is most likely due to departures from the rather severe conditions under which the model is derived. However, for smaller α , errors due to the estimation of the true ionization degree or to ionic impurities in the chemical reagents cannot be ruled out. Getting rid of these errors would probably improve the agreement between theory and experiment but is very difficult to achieve for all sources of small errors since classical methods for purification and analysis in aqueous systems hit prohibitive costs in D₂O. When $\alpha \approx 0.05$, K and a are, within the experimental accuracy, independent of the temperature and of the polymer and salt concentrations. Then, as expected, the virial term h decreases with the temperature and polymer concentration and is independent of the salt content. The salt concentration dependence of the amplitude and position of the peak is nearly in quantitative agreement with the model.

For PMA solutions, the agreement between the fitting curves and the experimental structure factors is much less satisfactory than for the PAA systems. For most samples, the fitting curves exhibit in the Kratky representation a decrease in the high q range before levelling off, in contrast with the behaviour of the experimental data points. Also an uneven repartition of the residues is observed in the whole q range. This seems to show a qualitatively different shape of the structure factors in PAA and PMA systems. Therefore a detailed analysis of the parameters K , a and h was not pursued further for PMA solutions. Finally the salt effects on the peak characteristics have been found to be markedly different from the quantitative predictions, in contrast with the behaviour observed on PAA solutions.

These differences between the PAA and PMA systems might be due to the very complex interactions which are present in the latter systems. These complex interactions are at the origin of the LCST behaviour of PMA solutions. As reported long ago [36], they are also responsible for a conformational transition of PMA chains in the small ionization degree range. Nevertheless it is remarkable that the qualitative behaviour of PMA systems still agrees with the model.

Thus we believe we have now a good qualitative understanding of the microscopic structure of these systems and this will provide us with a useful guideline in the investigation of their dynamical properties.

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