



HAL
open science

Distribution of the “ micelles ” in hydrated perfluorinated ionomer membranes from SANS experiments

Bernard Dreyfus, Gérard Gebel, Pierre Aldebert, Michel Pineri, Marielle
Escoubes, Michel Thomas

► **To cite this version:**

Bernard Dreyfus, Gérard Gebel, Pierre Aldebert, Michel Pineri, Marielle Escoubes, et al.. Distribution of the “ micelles ” in hydrated perfluorinated ionomer membranes from SANS experiments. *Journal de Physique*, 1990, 51 (12), pp.1341-1354. 10.1051/jphys:0199000510120134100 . jpa-00212449

HAL Id: jpa-00212449

<https://hal.science/jpa-00212449v1>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
Physics Abstracts
61.12 — 61.40

Distribution of the « micelles » in hydrated perfluorinated ionomer membranes from SANS experiments

Bernard Dreyfus ⁽¹⁾, Gérard Gebel ⁽¹⁾, Pierre Aldebert ⁽¹⁾, Michel Pineri ⁽¹⁾, Marielle Escoubes ⁽²⁾ and Michel Thomas ⁽²⁾

⁽¹⁾ Groupe Physico-Chimie Moléculaire, Service de Physique, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires, 85X, 38041 Grenoble Cedex, France

⁽²⁾ Laboratoires de matériaux plastiques et de Biomatériaux (*), Université Claude Bernard, Lyon I, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

(Reçu le 2 novembre 1989, révisé le 12 février 1990, accepté le 20 février 1990)

Résumé. — L'analyse de la forme et de l'intensité de spectres de diffusion de neutrons aux petits angles d'une membrane ionomère perfluorosulfonée en équilibre avec différents taux d'humidité nous permet de proposer un modèle pour la distribution des « micelles » hydratées au sein de la matrice perfluorée. Le modèle décrit une structure localement ordonnée de ces micelles avec quatre premiers voisins localisés à une distance bien définie dans un gaz complètement désordonné de micelles. L'ajustement des spectres expérimentaux à partir de la fonction de distribution radiale, déduite de cette structure localement tétraédrique, nécessite seulement deux paramètres ajustables. Nous démontrons que la remontée aux petits angles et le pic ionomère sont liés à l'existence des domaines ioniques. Nous montrons qu'il n'est pas nécessaire d'invoquer l'existence de fluctuations aux grandes distances ou des défauts à grande échelle pour interpréter le domaine des petites valeurs de q . Notre modèle permet l'obtention d'un bon ajustement entre spectres expérimentaux et courbes théoriques pour des valeurs de q ($q = 4 \pi \sin \theta / \lambda$) comprises entre 0,02 et 0,26 Å⁻¹ et des fractions volumiques en eau de 6 à 26 %.

Abstract. — The analysis of the shape and intensity of small angle neutron scattering (SANS) curves obtained on a perfluorinated ionomer membrane with different water contents suggests a model for the distribution of the hydrated « micelles » in the perfluorinated matrix. The model describes a locally ordered structure for these micelles with four first neighbours located at a well defined distance embedded in a completely disordered gas of micelles. Only two adjustable parameters are necessary to fit the experimental scattering curves over the whole q range, based on the radial distribution function associated with this locally « diamond-like » (tetrahedral) structure. It is demonstrated that both the zero angle upturn and the ionomer peak are linked with the ionic domain existence. It is shown that there is no need for long range fluctuations or large scale defects to interpret the zero angle domain. Our model is in reasonably good agreement with all the experimental results for q ($q = 4 \pi \sin \theta / \lambda$) ranging from 0.02 to 0.26 Å⁻¹ and for water contents from 6 to 26 % (volume fraction).

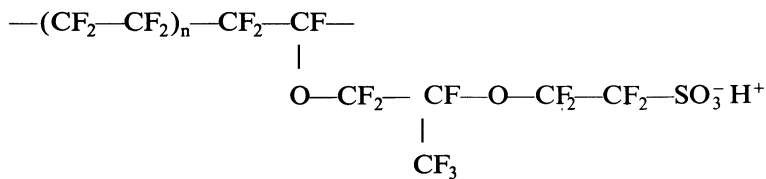
(*) URA 507.

1. Introduction.

During the past twenty years ionomers, and especially the perfluorinated ionomer membranes, have been extensively studied [1, 2]. If the aggregation of charges in clusters is nowadays well accepted [3], the size and the distribution of the clusters inside the polymer matrix is still a subject of controversy [4]. The small angle scattering curves generally exhibit the so-called « ionomer peak » and a strong upturn at very small angle which will be called below the « central peak ». Despite the ability of some models to produce a zero angle upturn [5, 6], the overall agreement in the fits has never been obtained [5]. So this upturn has been interpreted as arising totally or partially from physical grounds totally different from those adopted for the ionomer peak such as uncertainties in the measurement, impurities, voids, excess salt precipitates or long-range fluctuations of ion concentration [7]. Therefore most authors have preferred to ignore the upturn and to reproduce only the ionomer peak, often by using numerous parameters [5], so that the agreement is not really very convincing. Recent anomalous small-angle X ray scattering experiments showed that the zero angle upturn and the ionomer peak are strongly correlated [7]. In this paper we propose a structural model which produces. Both the central and the ionomer peak for the first time with correct intensities and widths. Furthermore, the same radial distribution function can describe the complete set of experimental curves over a wide range of water contents. We have been driven [6] to recognize that, for energetic reasons, the structure which allows the smallest extension for the segments of polymers linking two adjacent micelles should have a low compacity (*loose* structure). The structure which allows the smallest distance D between the micelles, for a given concentration of charges, is diamond-like. Of course such a highly ordered structure cannot extend over long distances in these materials which are more likely « amorphous ». The description to which we are led is a locally ordered shell for the first four neighbours embedded in a disordered gas-like state for the more remote micelles.

2. Experimental.

2.1 MATERIAL. — Nafion-117, a perfluorinated ionomer membrane, is commercially available from Dupont de Nemours Company. The membrane is derived from copolymers of tetrafluoroethylene and a perfluorovinyl ether terminating in a sulfonic acid group :



The equivalent weight of this polymer ($\text{EW} = 1\,100 \text{ g/eq}$) defines an average value of n ($n = 6.56$) and the volume associated with one sulfonic group is $V = 913 \text{ \AA}^3$. The density is assumed to be 2 g/cm^3 .

The membrane was immersed in 2 N aqueous HCl for 24 h, in order to ensure a fully acidic form, then washed several times with bidistilled water.

2.2 EXPERIMENTAL SET UP. — The cell especially devised for neutron experiments has been described elsewhere [8]. The membrane is fixed between two brass compartments hollowed by quartz windows transparent to neutrons. The two compartments can be equilibrated to the same pressure with a by-pass. The cell is connected to a secondary vacuum pump

(10^{-4} torr) and to a water thermostated evaporating system. The quantity of polymer in the neutron beam is the same for all the experiments, independent of the degree of swelling.

2.3 WATER SORPTION DETERMINATION. — The water sorption f (weight of sorbed water/weight of « dry » membrane) has been determined from the sorption isotherm at 20°C performed on a sample previously dried under a dynamical secondary vacuum. The water activities P/P_C correspond to the ratio of the partial vapor pressure (P) of water at the temperature of the evaporating system and of the saturated vapor pressure (P_C) at the sample temperature. Under these conditions, 2 % w/w of non-desorbable water still remains in the membrane. The total water volume fraction Φ is defined as :

$$\Phi = \frac{v_{\text{water}}}{v_{\text{polymer}} + v_{\text{water}}} \quad (1)$$

The water and polymer densities are assumed to be constant ($\rho_{\text{water}} = 1 \text{ g/cm}^3$ and $\rho_{\text{polymer}} = 2 \text{ g/cm}^3$).

The residual water is taken into account for the calculation of Φ :

$$\Phi = \frac{2(1.02f + 0.02)}{1 + 2(1.02f + 0.02)} \quad (2)$$

The number of water molecules per sulfonic group, ν , can also be determined :

$$\nu = \frac{1100 \cdot (1.02f + 0.02)}{18} \quad (3)$$

The values of f , Φ and ν are given in table I for each P/P_C used in these experiments.

Table I. — *Various parameters for the Nafion 117 H⁺ membrane equilibrated with different water vapor pressures : f is the water sorption, Φ is the water volume fraction, ν is the number of water molecules per SO_3 group, I_{inc} is the incoherent intensity, $I(0)$ is the intensity at $q = 0$, D is the distance between micelles, R is their radius, n_0 , n_D and n_R (ν_1) are the numbers of charges per micelle calculated respectively from $I(0)$, D and R . The values in brackets are obtained using $\alpha = 1.095$ instead of 1.122.*

P/P_C	0.07	0.24	0.44	0.58	0.72	0.82	0.85	0.90	0.92	0.95	1
f %	1.35	2.90	4.55	5.80	7.25	8.45	8.95	9.90	10.3	11.1	14.9
Φ	0.063	0.090	0.117	0.137	0.158	0.175	0.182	0.195	0.200	0.210	0.256
ν	2.03	3.02	4.04	4.82	5.72	6.46	6.53	7.36	7.61	8.11	10.46
I_{inc}	0.013	0.017	0.023	0.027	0.032	0.035	0.36	0.039	0.040	0.042	0.055
$I(0)$	0.105	0.195	0.294	0.413	0.577	0.730	0.831	0.963	1.123	1.310	2.09
D	(24.11)	27.17	27.93	28.99	30.44	30.25	31.34	31.97	32.19	33.28	34.44
R	(14.25)	13.89	13.20	13.55	14.17	14.65	14.85	15.06	15.19	15.87	17.27
n_0	(37.0)	41.6	32.1	32.3	32.4	33.4	36.6	35.0	38.4	40.2	38.2
n_D	(16.7)	27.0	28.4	30.8	35.0	33.6	37.2	38.8	39.3	43.0	43.7
$n_R(0)$	(194.2)	124	79.5	72.1	69.4	68.0	70.0	64.7	64.3	68.9	68.7
$n_R(175)$	(50.2)	42.3	32.5	32.6	34.4	35.7	36.9	36.0	36.3	40.0	45.6
σ	153	90	77.1	75.0	72.1	80.2	74.5	73.5	73.7	73.6	85.7

2.4 NEUTRON EXPERIMENTS. — The small-angle neutron experiments have been performed at the Laboratoire Léon Brillouin (L.L.B., Saclay, France) on the PACE spectrometer. The wavelength λ and the sample detector distance D have been fixed at $\lambda = 6.4 \text{ \AA}$ and $D = 1.2 \text{ m}$, respectively giving a q range from $q = 0.02$ to 0.26 \AA^{-1} ($q = 4\pi \sin \theta / \lambda$).

In order to obtain a scattering function $I(q)$ comparable for all the samples, several steps have to be performed. The normalization of the detectors and absolute intensities are obtained through the incoherent scattering of a 1 mm thick test film of pure water. Then the correction for the finite transmission ($\approx 90\text{-}95\%$) has been performed and the scattering of the empty cell subtracted.

The SANS spectra shown in figure 1 corresponding to each P/P_0 have been obtained after sorption equilibrium. It is assumed that thermodynamical equilibrium is reached when no

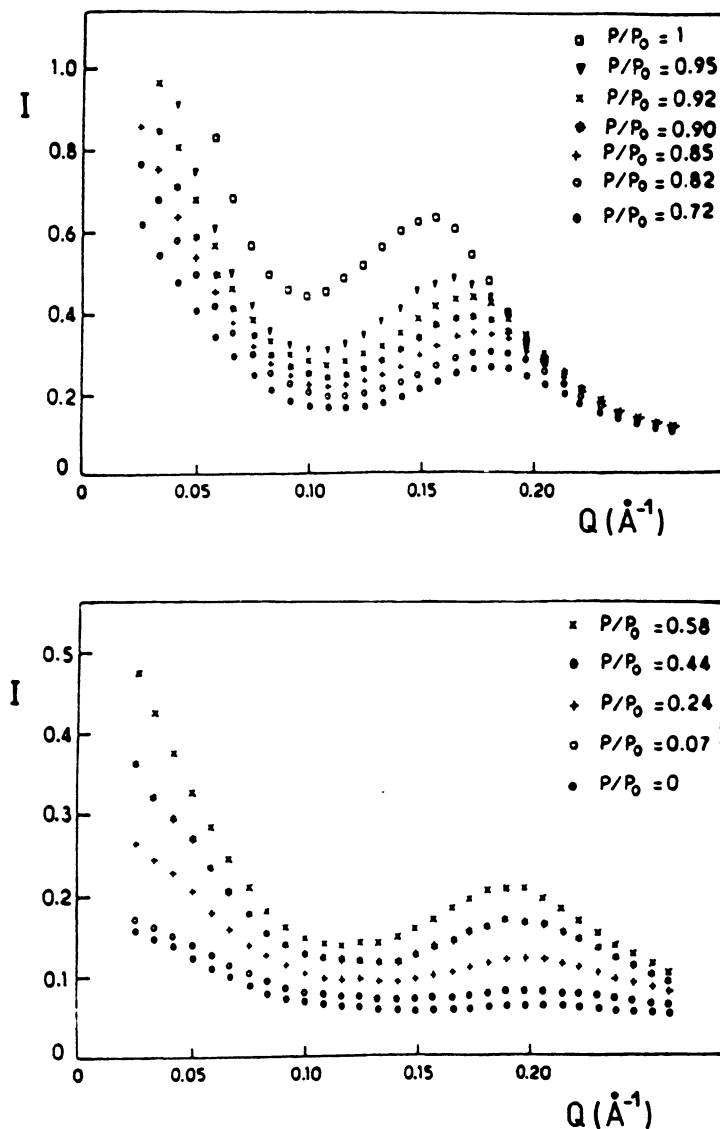


Fig. 1. — SANS spectra of Nafion 117 H equilibrated with different water pressures.

change is observed between successive spectra recorded every 15 min. This usually occurs after around 60 min.

3. Analysis of the results.

3.1 THE SCATTERED INTENSITY $I(q)$. — For a system of N identical scattering objects (micelles) distributed in space, $I(q)$ can be expressed as follows [9]:

$$I(q) = N |F(q)|^2 S(q). \quad (4)$$

In equation (4), q is the scattering vector, $|F(q)|^2$, the structure factor, is the scattered intensity of an isolated object and $S(q)$ is an interference term related to the distribution of the different objects in space, assuming that the diffracting objects are isotropic, or at least with no correlation in their orientations:

$$S(q) = 1 + \frac{1}{V} \int_0^\infty \frac{\sin qr}{qr} (P(r) - 1) 4 \pi r^2 dr. \quad (5)$$

V is the average volume offered to each object in the sample, $P(r)$ is the radial distribution function and is related to the conditional probability of finding one particle in a volume dv_1 and another one in the volume dv_2 at a distance r from the first one. This probability is written as [9]:

$$p_{1,2} dv_1 dv_2 = \frac{dv_1}{V} \frac{dv_2}{V} P(r). \quad (6)$$

When r becomes infinite, the correlation is negligible and $P(r) = 1$. This limiting value has been subtracted in (5). This mathematical trick induces a peak in $S(q)$ with a width inverse of the overall size of the sample usually unobservable. $P(r)$ measures the correlation of the distribution of the micelles; it is related to the distribution of a cloud of points in space and therefore must obey some rules, since it is highly improbable to find an actual distribution of points corresponding to an arbitrary function $P(r)$. One condition is that $S(q)$ from (5) has to be positive for each q value; if it is not, it only means that the trial function $P(r)$ has no physical meaning and cannot be materialized.

Assuming one micelle at the origin, $(P(r) - 1)$ is related to the algebraic excess of the micelle density at distance r . When $(P(r) - 1) < 0$ the particle at the origin exerts a repulsion on the other micelles (and *vice versa*) at a distance r .

For $q = 0$, (5) can be written:

$$S(0) = 1 + \Delta z \quad (7)$$

where Δz is the algebraic total number of micelles attracted around the one at the origin. Numerous models only consider a hard-core repulsion between the micelles. Then $P(r)$ is equal to zero when $r \leq r_C$ and equal to 1 for $r > r_C$ where r_C is the size of the hard-core hole. In these models Δz is negative and, if it is larger than one, it gives a negative $S(0)$.

The two functions $F(q)$ and $S(q)$ involved in (4) cannot be obtained separately from an experimental curve $I(q)$ recorded within a limited q range. A model is therefore needed in order to deduce theoretical scattering curves and to compare them with the experimental data. It is important to have the scattering curves over a q range as large as possible and to change and monitor at least one of the parameters defining the sample. In the present experiments the water content was changed from 6 to 26 % (volume fraction).

3.2 THE MODEL. — From previous considerations [6, 10], our model can be detailed as follows.

3.2.1 *The structure factor* $|F(q)|^2$. — The micelles are described as homogeneous spheres of radius R , filled with water, embedded in the perfluorinated matrix. The structure factor for one sphere is then :

$$|F(q)|^2 = k \left(\frac{3(\sin x - x \cos x)}{x^3} \right)^2 \quad \text{with} \quad x = qR \quad (8)$$

k is a multiplicative constant depending upon the number of charges and the contrast.

For one micelle in the perfluorinated matrix, one has :

$$k = n^2(\nu + 1/2)^3 v_0(\rho_1 - \rho_2)^2 \quad (9)$$

where n is the number of acidic functions per micelle, ν is the number of water molecules per anion (the 1/2 factor takes into account the proton associated with each SO_3^- anion), v_0 is the volume of one water molecule ($v_0 = 30 \text{ \AA}^3$), ρ_1 and ρ_2 are respectively the coherent scattering length densities of water ($-0.00559 \times 10^{-12} \text{ cm \AA}^{-3}$) and of the ionomer ($0.04201 \times 10^{-12} \text{ cm \AA}^{-3}$) [11].

The form factor for $q = 0$ and N micelles is specially interesting. Its value is :

$$N \cdot |F(0)|^2 = N \cdot n^2 \cdot (\nu + 1/2)^2 \cdot (\rho_2 - \rho_1)^2 \cdot v_0^2. \quad (10)$$

As Nn , the total number of charges in the sample, is known and ν is calculated from the weight of absorbed water, the structure factor depends only on n . Furthermore it should not depend on deviations from a homogeneous sphere resulting from protuberances due to percolation or to a « hairy » interface with the polymer. However, for $q \neq 0$, $|F(q)|^2$ given in (8) should be modified when such deviations occur, and at least the « apparent » radius of the sphere could be different from that of a homogeneous sphere filled with the same amount of bulk water.

3.2.2 *The radial distribution function* $P(r)$. — This is the crucial point in the model. From physical considerations the micelles should be relatively well ordered, at least on a short range. A local structure similar to that of diamond has already been proposed [6, 10] ; around one micelle, there are $z = 4$ other micelles tetrahedrally located at a distance D . This *a priori* choice is justified by the strong interconnection of the micelles by the polymeric segments. To get the least extended segments, it is necessary to select the least compact crystallographic structure, which leads to the smallest D for a given density : in three dimensions, it is realized by the diamond structure.

The overall amorphicity of the polymeric matrix indeed prevents this crystallographic order to extend to infinity. A completely disordered distribution of micelles should be observed at distances larger than αD from the origin micelle with $\alpha > 1$. All these considerations are taken into account in the $P(r)$ function shown in figure 2. If v is the average volume offered to each micelle in the sample, the number z' of micelles in the volume $4\pi(\alpha D)^3/3$ corresponding to the « hole » between 0 and αD in the $P(r)$ function is given by :

$$z' = \frac{4}{3} \pi \frac{(\alpha D)^3}{v} \quad (11)$$

with $v = n \frac{V}{1 - \Phi}$ where V is the average volume offered to one charge in the dry polymer, Φ is the water volume fraction and n is the number of charges per micelle.

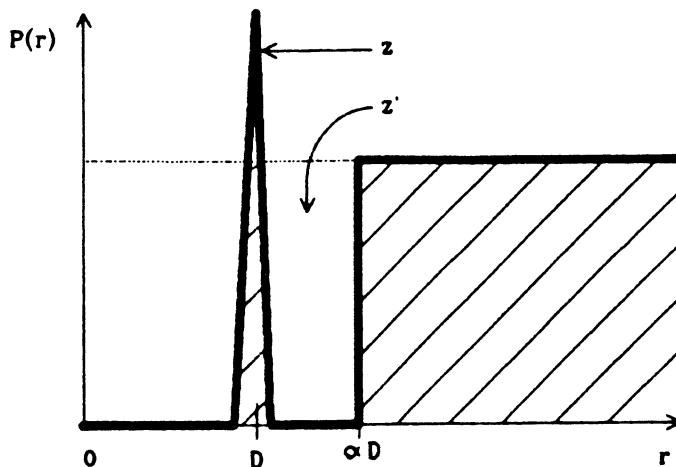


Fig. 2. — Radial distribution function proposed in the model.

With the above $P(r)$, one gets

$$S(q) = 1 + z \frac{\sin qD}{qD} - z' \frac{3(\sin y - y \cos y)}{y^3} \quad \text{with } y = \alpha qD \quad (12)$$

and therefore :

$$I(q) = \frac{I(0)}{S(0)} \left(\frac{3(\sin qR - qR \cos R)}{(qR)^3} \right)^2 \left(1 + z \frac{\sin qD}{qD} - z' \frac{3(\sin \alpha qD - \alpha qD \cos \alpha qD)}{(\alpha qD)^3} \right) \quad (13)$$

with $S(0) = 1 + z - z'$.

It must be emphasized that the values which will be further adopted for α , z and z' will be kept unchanged in the mathematical function (13) for all the samples, and the only adjustable parameters for each of them will be D and R describing the different water contents.

3.3 ADJUSTMENT OF THE PARAMETERS. — We summarize the successive steps for the adjustment of the parameters :

As the curves $I(q)$ versus q^2 are nearly linear for all the samples when $q^2 < 4 \times 10^{-3}$ (Fig. 3), we obtain an accurate determination by extrapolation of $I(0)$ that will be introduced in the theoretical $I(q)$ function (13).

The *a priori* choice of a diamond-like structure led us to take $z = z' = 4$ and $\alpha = 1.137$ from simple crystallographic considerations (volume of a sphere containing 4 atoms). This choice is *a posteriori* justified by further final refinements giving very close values.

For each set of parameters (z, z', α) , the « minuit program » [11] for function minimization has been used to get refined values for R and D for each water content. The experimentally determined maximum of the ionomer peak has been overweighted in order to constrain the fitting curve to preserve the position and the intensity of the peak. Variations of D and R values induce changes in the fits, the ionomer peak position being mainly sensitive to D and its intensity to R .

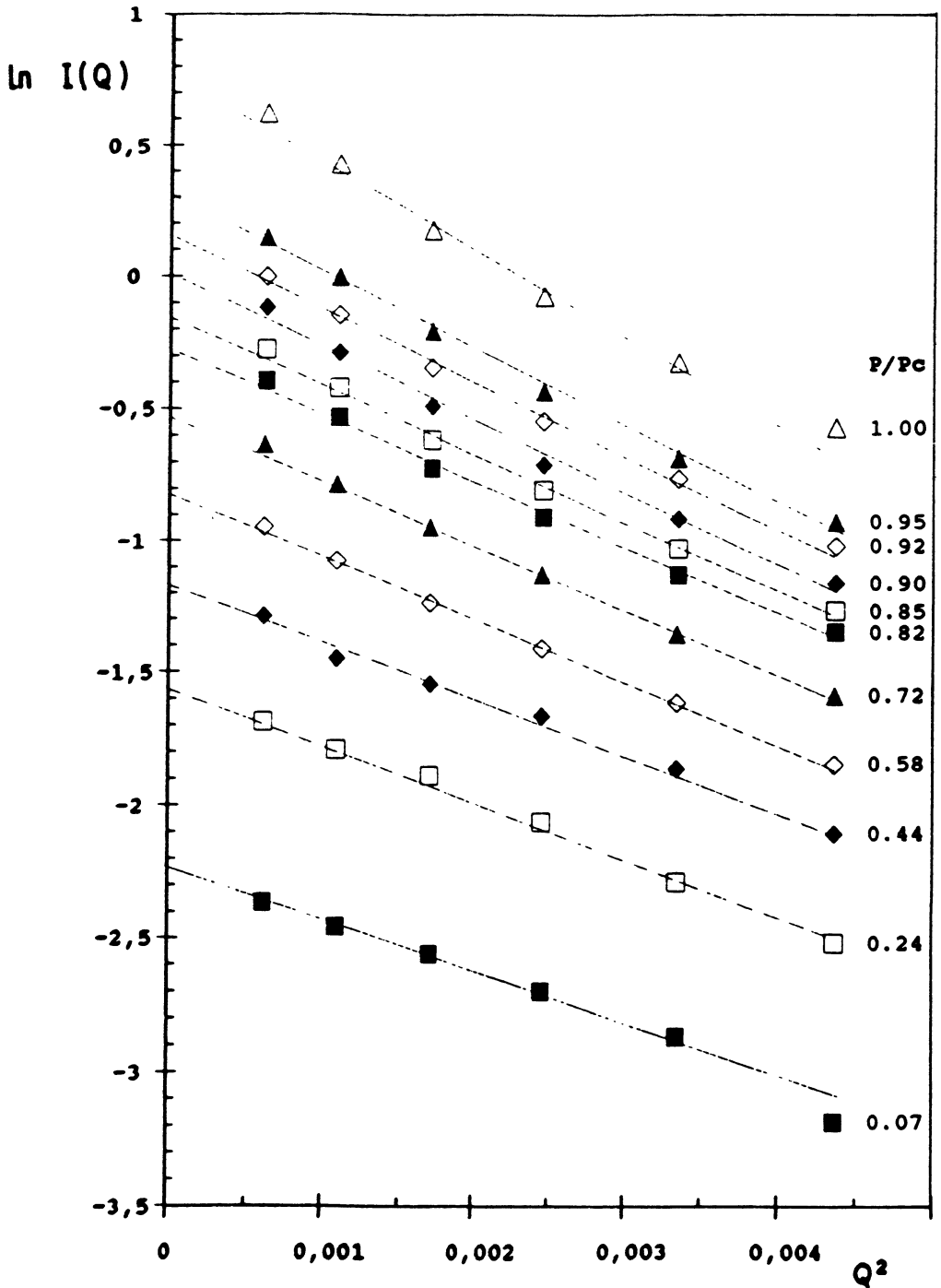


Fig. 3. — Determination of $I(0)$ by extrapolation of $I(q)$ at $q = 0$ from the $\ln I(q)$ versus q^2 plot.

In fact the minimum observed between the central and the ionomer peak strongly depends on α (Fig. 4). The best overall agreement reproducing the width of the peak allows an

accurate determination of α for each water content (Tab. II). α is rather constant with P/P_C and a mean value has been chosen, thus reducing the number of adjustable parameters.

No change in the fitted curve is observed with variations of z' , so that a different method is used to determine z' , as we shall see further. The α value which has been determined will not be affected by this final refinement.

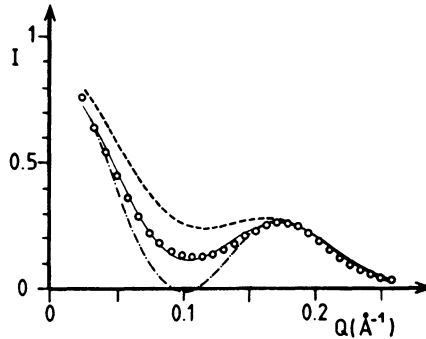


Fig. 4. — Best fits obtained for $P/P_C = 0.85$, $z = 4$, $z' = 4.45$ with $\alpha = 1.122$ (—), $\alpha = 1.160$ (---) and $\alpha = 1.085$ (-.-).

Table II. — Values of α giving the best fits.

P/P_C	0.07	0.24	0.44	0.58	0.72	0.82	0.85	0.90	0.92	0.95	1.00
α	1.095	1.110	1.115	1.118	1.122	1.122	1.122	1.122	1.122	1.125	1.128

3.4 DETERMINATION OF THE NUMBER OF CHARGES PER MICELLE. — Absolute scattered intensities besides the shape of the curves allow the determination of the number of charges per micelle by three different and independent methods.

3.4.1 From the coherent and incoherent intensities of the peak at $q = 0$. The incoherent scattering is isotropic and independent of q . The total incoherent cross section per charge of hydrated material is given by :

$$\sigma = 79.9(2\nu + 1) + 32.2 \quad (14)$$

where the incoherent cross section of H is 79.9 barns and the calculated incoherent cross section of polymer associated with one charge is 32.2 barns.

The water contents are always sufficiently high to neglect the incoherent scattering due to the unprotonated matrix and one can write :

$$I_{\text{inc}} = Nn \frac{\sigma}{4\pi} \approx Nn(6.358(2\nu + 1)). \quad (15)$$

The incoherent scattering of a 1 mm thick water film has been measured and used to determine the incoherent scattering I_{inc} of the water layer equivalent to the overall water content. I_{inc} values are given in table I.

The coherent scattering intensity at $q = 0$ obtained from (4) and (9) is :

$$I(0) = Nn^2(\nu + 1/2)^2 v_0^2(\rho_2 - \rho_1)^2 S(0) \quad (16)$$

with $S(0) = 1 + z - z'$.

Numerical values for $I(0)$ have been obtained from extrapolation of linear $\log I(q)$ versus q^2 (Fig. 2) and are given in table I.

Values for n are then obtained from the ratio of $I(0)$ to I_{inc} :

$$n_0 = 6.616 \frac{I(0)}{I_{\text{inc}}(\nu + 1/2)(1 + z - z')} \quad (17)$$

3.4.2 *From the intermicellar distance D.* — From equation (11) the average volume associated with one micelle in the hydrated polymer is given by :

$$v = \frac{4}{3} \pi \frac{\alpha^3 D^3}{z'} \simeq 5.917 \frac{D^3}{z'} \quad (18)$$

and

$$v = \frac{nV}{1 - \Phi}$$

where V is the volume associated with one charge in the dry polymer and Φ the water volume fraction. Hence we obtain

$$n_D = \frac{5.917}{Vz'} D^3(1 - \Phi) \simeq 6.480 \times 10^{-3}(1 - \Phi) \frac{1}{z'} D^3 \quad (19)$$

3.4.3. *From the micellar radius R.* — The micelles whose volume is $4\pi/3 R^3$ contain $n\nu$ water molecules ($v_0 = 30 \text{ \AA}^3$) which allows us to get n :

$$n_R = \frac{4}{3} \pi \frac{R^3}{\nu v_0} \simeq 0.1396 \frac{R^3}{\nu} \quad (20)$$

This is a crude determination since the volume of the anions has been neglected. νv_0 has to be replaced in (20) by $\nu v_0 + v_1$, where v_1 is the volume of the anion and probably of a part of the perfluorinated side chain. Furthermore if the micelle is not a perfect homogeneous sphere, for example if it has some protuberances towards the neighbours or if its interface is not ideally abrupt, there is a discrepancy between the parameter R determined in the model and the R which could correspond to the volume of water.

For all the above mentioned reasons, it is difficult to reliably extract n from R and we conclude that n_0 and n_D are the most significant.

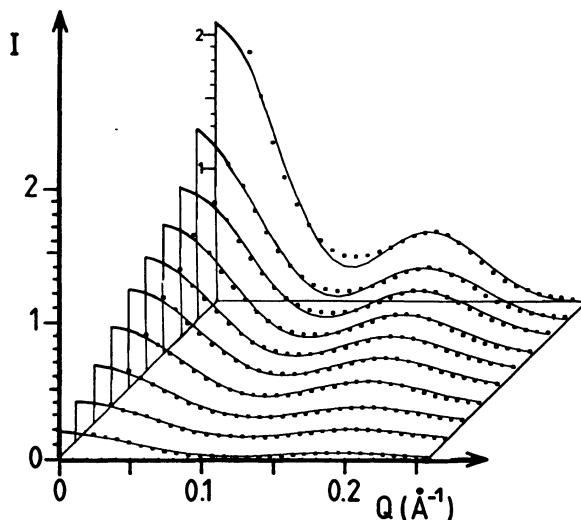
With the trial set of parameters $z = z' = 4$, $\alpha = 1.122$, a series of values for n_0 , n_D and n_R as a function of the degree of hydration is determined (Tab. III). Due to the quite different origins of their determination, such an agreement is a support for the model.

A closer agreement between n_0 and n_D can be reached by adjustment of z' but to the prejudice of the agreement with n_R . It is clear from (17) and (19) that an increase of z' leads to an increase of n_0 and a decrease of n_D . Now a mean value $z' = 4.39$ can be determined ; however n_R becomes too high compared to n_0 and n_D , especially for small ν values (Tab. I).

The best fits with this final set of parameters ($z = 4$, $\alpha = 1.122$, $z' = 4.39$) are given in figure 5. The quality of the adjustment is excellent for almost all the water contents. The

Table III. — Values of n_0 , n_D and n_R determined with $z = z' = 4$, $\alpha = 1.122$.

ν	3.02	4.04	4.82	5.72	6.46	6.53	7.36	7.61	8.11	10.46
n_0	21.6	18.6	19.0	19.2	19.8	21.7	20.8	22.9	24.0	22.9
n_D	39.5	41.7	45.2	51.6	49.8	55.0	57.0	52.3	63.5	64.9
n_R	101.3	62.3	56.7	53.8	54.2	55.2	50.7	51.3	55.1	55.7

Fig. 5. — Best fits between theoretical (—) and experimental (\square) curves with $z = 4$, $z' = 4.39$ and $\alpha = 1.122$.

small discrepancies for the higher water contents are due to the fact that the value of α is kept constant in the model.

Now the weakest point lies in the n_R values which are too large in comparison with the n_D and n_0 values. Even a dry micelle (the cluster) should have a finite R , since the ionic species have a finite volume and contrast. Tentatively, we attribute a finite volume v_1 to the ionic element and with $v_1 = 175 \text{ \AA}^3$, we get corrected values for n_R also listed in table I. Although such a value for v_1 seems to be rather large, it is not incompatible with the existence of the complex side chains which, in the case of nafion, carry the ionic charges. n_0 , n_D and the corrected n_R are represented in figure 6.

4. Discussion.

First it should be stressed that the distribution function $P(r)$ is shaped by z , α and z' which are kept constant for all the series of water contents. So during the hydration process the distribution of micelles is scaled by only two adjustable parameters, D and R .

We emphasize that, for the first time, both the central and the ionomer peak have been reproduced with correct widths and intensities. It has not been necessary to involve voids, cracks or fluctuations of a range much longer than D or αD . In fact the central peak is immediately a consequence of a $S(0)$ larger than what is assumed in hard-core repulsion models. The perturbation relative to a uniform average density, due to the micelle at the

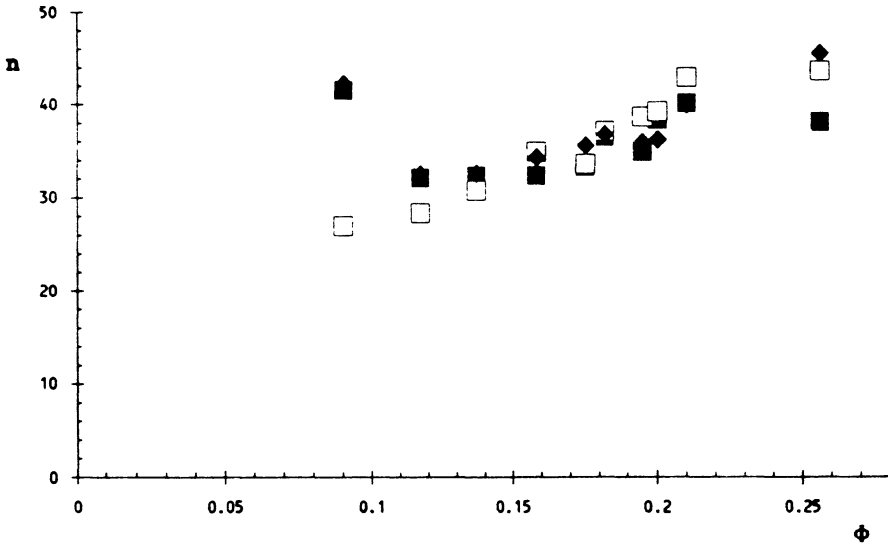


Fig. 6. — Numbers of charges per micelle: n_D (□), n_0 (■) and n_R ($v_1 = 175 \text{ \AA}$) (◆) versus the water volume fraction.

origin, is limited to a sphere of radius αD . In its immediate vicinity the micelle *attracts* neighbouring micelles, and this attraction is not completely cancelled by the hard-core repulsion described by the hole of radius αD . This overall attraction $1 + z - z'$ of about 0.61 micelle is sufficient to produce the central peak. According to the preceding considerations this overall attraction can be physically understood in terms of the linking segments of polymer between adjacent micelles.

An image of the *local ordering* for the micelles within the sample can be deduced from our model, however the values of the parameters must not be too literally accepted. First, the choice of $z = 4$ is what is expected, having in mind a diamond structure. However to check the validity of this hypothesis, we tried different z values ranging from 2 to 8, following the same method as for $z = 4$. An example of best fits is given in figure 7 for $P/P_C = 0.85$ with z equal to 2, 4, 6 and 8. It is clear that fitting is not possible with $z = 2$ and $z = 8$ and that, if z values from 3 to 6 leads to acceptable curves, the best fit is obtained with $z = 4$. So the conclusion of a loose structure for the packing cannot be avoided since the value $z = 4$ resulting from physical considerations appears to be confirmed by the mathematical analysis. We have also tried modified $P(R)$ profiles, with a less abrupt step at αD , a width for the peak at D and with a small secondary peak at a distance D' . None of these attempts gave any significant improvement justifying an increase in the number of parameters.

Furthermore the numerical relation between the average volume V occupied by one micelle in the sample as a function of D ,

$$V = \frac{4}{3} \pi \frac{\alpha^3 D^3}{z'} = \beta D^3 \quad (21)$$

gives $\beta = 1.3480$ which is closer to the diamond structure than to any other one (Tab. IV).

A comment about α is necessary. If the distance αD where the disorder starts is smaller than the distance of the second neighbours in the diamond structure, the volume occupied by

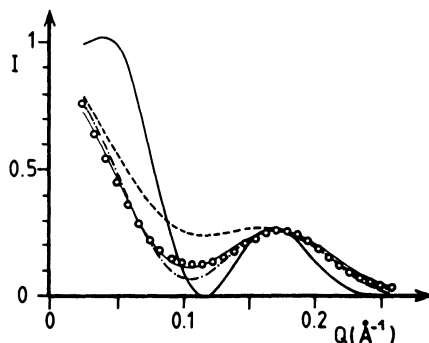


Fig. 7. — Best fits obtained for $P/P_C = 0.85$, $z' = z + 0.45$ with $z = 2$ $\alpha = 1.005$ (---), $z = 4$ $\alpha = 1.122$ (—), $z = 6$ $\alpha = 1.195$ (-.-), $z = 8$ (—).

Table IV. — Values of β for the most common crystallographic structures.

Structure	Diamond	Simple cubic	Body centred cubic	Face centred cubic
β	1.5396	1	0.7698	0.7011

four atoms in this structure is a sphere of radius $1.137 D$ with a numerical coefficient very close to α .

Another interesting comment lies in the ratio $2R/D$. For the smallest ν it equals 0.87 and it increases regularly with ν , becoming slightly greater than 1 for the most hydrated sample. This result, namely that $2R$ is close to D , is in fact now rather well accepted and means that the micelles have a strong tendency for *percolation* at a rather small value of ν . In a previous paper [10] the percolation effect, which is imposed by the minimization of the polymer-micelle interface, was studied by one of us for micelles filled with bulk water. It is interesting to obtain an idea of the specific surface σ occupied by each charge on the surface of the micelle. For the case of spherical micelles, if one considers that the *external* radius is R and the number of charges is n_D , which is a reliable determination, one gets :

$$\sigma = \frac{4 \pi R^2}{n_D}. \quad (22)$$

The values of σ are reported in table I. They are remarkably gathered around 73 \AA^2 in a rather good agreement with what has been proposed previously (58 \AA^2). The discrepancy for the less hydrated samples is probably not significant since there are less than 4 molecules of water per charge and the concept itself of a micelle may be unrealistic. The too large value of σ for $P/P_C = 1$ ($\Phi = 0.25$) can be interpreted as a sign for percolation. The true σ for « connected spheres » can be calculated from figure 2 of reference [10] and is about 0.86 times that deduced for an isolated sphere. This reduction gives $\sigma = 73.7 \text{ \AA}^2$ instead of $\sigma = 85.7 \text{ \AA}^2$, in good agreement with the rest of the series.

Furthermore, a constant σ during the hydration process seems to be accompanied by an increase of $n(n_D)$. This conclusion is in agreement with previous studies [10].

5. Conclusion.

The neutron scattering intensity curves have been obtained for a large range of q values and for an extended set of hydrated samples. The results have been interpreted with a model for the distribution function of the micelles in space. An *invariant* form has been attributed to this function characterized by the same *structural* coefficients for the entire set. It describes a situation with a rather strong local order, where a small overall attraction prevails. The number of first neighbours is found to be four which is in agreement with general physical considerations. The distribution function explains the existence of a central peak at $q = 0$, without having to postulate long-range fluctuations.

The adjustable parameters, the radius of the micelles and the distance to the first neighbours have been obtained for each sample and allow us to determine the number of charges per micelle by 3 independent ways. This number is found to increase slightly with the hydration process from 20 to 45 in order to keep constant the specific surface occupied by each charge over the interface with the polymer ($\approx 73 \text{ \AA}^2$).

Acknowledgements.

We appreciate very much the help of Drs J. P. Cotton and J. Teixeira in using the PACE spectrometer (L.L.B., Saclay). The help of J. P. Casquilho with computing is gratefully acknowledged. We also wish to thank M. Brotte for the construction of the cell. One of us (G. Gebel) is indebted to ATOCHEM Company for support.

References

- [1] Eds. M. Pineri, A. Eisenberg, Structure and Properties of Ionomers, NATO ASI Ser. 198 (D. Reidel, Dordrecht) 1987.
- [2] Eds. H. L. Yeager, A. Eisenberg, Perfluorinated Ionomer membranes, ACS Symp. Ser. 187 (American Chemical Society, Washington) 1982.
- [3] EISENBERG A., *Macromolecules* **3** (1970) 147.
- [4] WILLIAMS C. E., p. 163 in reference [1].
- [5] a) EARNEST T. R., HIGGINS J. S., MACKNIGHT W. J., *Macromolecules* **15** (1982) 1390 ;
b) YARUSSO D. J., COOPER S. L., *Macromolecules* **16** (1983) 1871 ;
c) KUMAR S., PINERI M., *J. Polym. Sci. Polym. Phys.* **24** (1986) 1767.
- [6] DREYFUS B., *Macromolecules* **18** (1985) 284.
- [7] a) DING Y. S., HUBBARD S. R., HODGSON K. O., REGISTER R. A., COOPER S. L., *Macromolecules* **21** (1988) 1698 ;
b) REGISTER R. A., COOPER S. L., *Macromolecules* **23** (1990) 310.
- [8] THOMAS M., ESCOUBES M., ESNAULT P., PINERI M., *J. Membrane Sci.* **46** (1989) 57.
- [9] GUINIER A., FOURNET G., Small Angle Scattering of X-rays (John Wiley Ed., New York) 1955.
- [10] DREYFUS B., p. 27 in reference [1].
- [11] LOVESEY S. W., Theory of Neutron Scattering from Condensed Matter (Clarendon press) 1984.
- [12] JAMES F., ROOS M., Minit Program, CERN, Genève (1975).