A Direct Observation of Counterion Condensation Around Cylindrical Micelles

BY C. F. WU* AND S. H. CHEN

Nuclear Engineering Department, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

L. B. SHIH

Polymer Research Department, S. C. Johnson & Son, Inc., Racine, WI 53403, USA

AND J. S. LIN

NCSASR, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

(Received 26 October 1988; accepted 28 April 1988)

Abstract

Small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) techniques have been used to confirm and determine the size and shape of cylindrical micelles formed by a comb-shaped copolymer, poly(1-octadecene-co-maleic anhydride), abbreviated as PODMA, in aqueous solution. Upon full neutralization by the addition of alkaline hydroxide, PODMA becomes a polyelectrolyte carrying two negative charge per repeating unit. SANS measurement gives the dimension of the cylinder with a radius of 20 Å, and a length of 110 Å in D$_2$O solutions with Cs as counterion. SAXS measurements were made for a series of 1% PODMA solutions fully neutralized by CsOH. Linear charge density at the micellar surface was varied by adding an ionic surfactant, sodium dodecyl sulfate (SDS). The dimensionless linear charge density parameter, $\xi = l_b/b$, where $l_b$ is the Bjerrum length ($l_b = 7.15$ Å for water solvent at 295 K) and $b$ is the linear spacing between unit charges on the micellar surface, varies from 32.96 to 67.21. Since the electron densities of the micellar core and the aqueous solvent are nearly equal, the SAXS intensity distribution function is a Bessel transform of the Cs counterion distribution around the cylindrical micelles. Comparison is made between the results obtained from SAXS intensity distribution analyses and the prediction of Manning's condensation theory.

1. Introduction

The clustering of counterions around large highly charged macromolecules and ionic micelles has long been theoretically predicted (Oozawa, 1971). This phenomenon has been experimentally observed in many SANS experiments involving ionic micellar solutions at low ionic strength (Chen, 1986). We shall call generally the phenomenon of clustering of counterions around the surface of a highly charged macromion a 'charge condensation'. The basic idea is that the condensed counterions effectively neutralize an equivalent amount of the charge of the macromion so that, looking from another macromion, the complex acts as a macromion of lower surface charge density. In the literature the term 'counterion condensation' is normally applied only to long cylindrical polyelectrolytes such as DNA molecules. This idea probably originated from Manning (1969) who treated such a phenomenon theoretically for highly charged polyelectrolytes.

An interesting calculation based on the solution of the Poisson–Boltzmann equation involving a charged macromolecule surrounded by an equal amount of neutralizing counterions in a cell model has been made by Le Bret & Zimm (1984). Their main conclusion was that the condensed ions are to be interpreted as the fraction of the counterions remaining within a finite distance of the macromion when the volume of the system is expanded indefinitely (Zimm & Le Bret, 1983). The Poisson–Boltzmann equation solved in the cell model indeed predicts that there is such a fraction of ions around an infinitely long cylindrical polyelectrolyte if the linear charge density of the polyelectrolyon exceeds a certain critical value given by Manning (1978, 1979). More recently Bacquet & Rossky (1984) performed numerical solutions to the hypernetted chain (HNC) integral equation for a model system representing an infinitely long rod-like polyelectrolyte in a dilute aqueous 1–1 electrolyte solution. The distribution function of counterions was analyzed in terms of various structural parameters and compared with the prediction of the counterion condensation (C–C) theory and with available data obtained from the solutions of the Poisson–Boltzmann equation. The HNC and C–C results are only in qualitative agreement.
On the experimental side, the direct observation of the transition to counterion condensation was made recently by Klein & Ware (1984; Ware, 1986). They used dynamic light scattering to measure the electrophoretic mobility of 6,6-ionene, a polyelectrolyte with a linear charge spacing of 8.7 Å, under conditions of varying dielectric constant. In this way, the reduced charge density parameter $\xi$ can be varied between 0.81 and 1.85. At precisely $= 1$, Manning's criterion, they observed a drop in the electrophoretic mobility by a factor greater than two. However, the reduction of electrophoretic mobility, which is a result of the reduction of charge density due to counterion condensation, is substantially larger in magnitude than the current theory of C–C would predict. Clearly the most important test of the theory has to come from measurements of the actual counterion distribution function.

In this paper we present a series of SAXS data of Cs counterion distribution around a cylindrical micelle and their preliminary analyses. The micelle is formed by a comb-shaped copolymer, poly(1-octadecene-co-maleic anhydride), abbreviated as PODMA, in aqueous solution (Shih, Luccas, Chen & Lin, 1987). The cylindrical micelle has a dimension of length $L = 110$ Å and a cross-sectional radius $R = 20$ Å. We were able to vary the linear spacing $b$, and correspondingly the linear charge density parameter $\xi$, by the addition of an ionic surfactant SDS which is adsorbed on the surface of the micelle. We can thus measure the counterion distribution as a function of $\xi$. If we approximate the counterion distribution around the cylindrical surface by a shell of thickness $t$ and inner radius $R$, we can successfully fit all the SAXS data. The effective thickness of the shell is found to increase from 7.40 to 19.06 Å when $\xi$ is varied from 67.21 to 32.96. At the same time the scattering intensity at zero angle, $I_0$, decreases by a factor of 3. We shall interpret this observation in terms of the condensation model (Manning, 1979).

### 2. Experiment

Alternating copolymer PODMA has weight-average and the number-average molecular weights of 6660 and 3960, respectively, as determined by gel permeation chromatography using polystyrene as a standard. The procedures for sample preparation are described in detail elsewhere (Shih, Sheu & Chen, 1988). A series of 1% PODMA solutions in D2O was used. The polymer solutions were fully neutralized by adding equivalent amounts of CsOH. Different amounts of SDS were then added to each solution. The stoichiometry of neutralization was experimentally determined by monitoring the disappearance of the –COOH band with FTIR (Fourier transform infrared spectroscopy). In this experiment we used 1% polymer solutions with [SDS] = 0.00 M, 0.01 M, 0.015 M, 0.04 M, 0.10 M and 0.20 M.

SAXS measurements were made at the small-angle X-ray scattering facilities of the National Center for Small-Angle Scattering Research (NCSASR) in Oak Ridge National Laboratories. X-rays from the Cu Kα line with $\lambda = 1.54$ Å were used for the measurement. The power supply for the X-ray generator was maintained at 3.2 kW throughout the experiment. The sample-to-detector distance was chosen at 1.126 m resulting in a $Q$ range coverage of 0.02 to 0.50 Å$^{-1}$. The magnitude of the scattering vector is defined as $Q = (4\pi/\lambda) \sin(\theta/2)$, with $\theta$ the scattering angle and $\lambda$ the X-ray wavelength. A $20 \times 20$ cm position-sensitive proportional counter with 64 × 64 effective channels was used. Scattering signals from each sample were collected over a time interval of about 2 h. The raw data were corrected for cosmic radiation background, electronic noise in the detection circuits, and the scattering from the empty sample container. The detector uniformity calibration was made by a detector sensitivity run using a $^{55}$Fe standard source. The scattering intensity was then normalized by the primary X-ray fluence.

The sample holder was made of aluminium with 0.09 mm Kapton films (trade mark of polyimide films, DuPont product) as windows. The sample thickness was 1 mm. During the measurement the sample was kept in a vacuum chamber and thermally controlled.

### 3. Results and discussion

Normalized SAXS intensities as a function of $Q$ are shown in Fig. 1 for four typical cases. Two characteristic features are readily seen. The scattering intensity at low $Q$ decreases as a function of the added surfactant concentration. This is because the interaction between the micelles becomes more pronounced as the surface charge density increases. The interaction would depress the forward scattering intensity owing to the decrease in osmotic compressibility as a result of the interaction. The SAXS intensity distribution has

![Fig. 1. Experimental SAXS intensity vs $Q$ for 1% PODMA cylindrical micelles.](image-url)
a second peak at $Q \approx 0.15 \text{ Å}^{-1}$, which shifts to a larger $Q$ and increases in height as the surface charge density increases. The second peak is a result of the shell-like structure of the counterions around the micelle. Both these features may be explained in terms of the expression

$$I(Q) = I_0 P(Q) S(Q),$$

(1)

where $P(Q)$ is the normalized intraparticle structure factor and $S(Q)$ is the orientationally averaged interparticle structure factor (Chen, 1986). For a cylindrical shell of length $L$, inner radius $R$ and shell thickness $t$, the normalized intraparticle structure factor can be expressed as (Wu, 1988)

$$P(Q) = \int_0^1 d\mu \left[ \sin\left(\frac{\mu Q L}{2}\right) \right]^2 \times \left( J_0 [Q(R + t/2)(1 - \mu^2)^{1/2}] \right)^2,$$

(2)

after a lengthy derivation based on its original definition (Chen, 1986). $J_0(x)$ in (2) is the zeroth-order Bessel function. The integration over $\mu$ is an angular average over randomly oriented cylindrical micelles in solution. The scattering intensity at zero angle, $I_0$, is given by

$$I_0 = AN_p[(\Delta \rho) r_0 V_p]^2,$$

(3)

where $A$ is a calibration factor, and $N_p$ and $V_p$ are the number density and the volume of the cylindrical micelle. $\Delta \rho$ is the electron density difference between the counterion shell and the water solvent, and $r_0 = 2.82 \times 10^{-13} \text{ cm}$, the classical radius of an electron. According to Manning's charge condensation theory, the fraction of the condensed counterions is $1/\xi$. Thus the fractional charge can be equated to $(1 - 1/\xi)$. By substituting $(\Delta \rho) r_0 V_p = Z (1 - 1/\xi) b_c$ into (3), we get

$$I_0 = AN_p[Z(1 - 1/\xi) b_c]^2,$$

(4)

where the number density is calculated according to

$$N_p = C_m N_A/(P N \times 10^3),$$

(5)

with $C_m$ the concentration of the monomers, $N_A$ Avogadro's number, $P$ the degree of polymerization, and $N$ the micelle aggregation number. The total surface charge $Z$ is obtained by

$$Z = \frac{[\text{CsOH}] + [\text{SDS}]}{N_p} N_A,$$

(6)

where $[\text{CsOH}]$ and $[\text{SDS}]$ are the molar concentrations of CsOH and SDS respectively. The averaged X-ray scattering length of the counterions $b_c$ is calculated from

$$b_c = b_{\text{Cs}^+} \frac{[\text{CsOH}] + 15/4 [\text{SDS}]}{[\text{CsOH}]+[\text{SDS}]} = b_{\text{Cs}^+} y,$$

(7)

with $b_{\text{Cs}^+} = 1.5228 \times 10^{-11}$ cm, the scattering length of the Cs$^+$ ion, and $y = ([\text{CsOH}] + (10/54)[\text{SDS}])/([\text{CsOH}]+[\text{SDS}])$ is introduced to simplify the expression. Note here that the surfactant SDS contributes an Na$^+$ ion, and its scattering length is 10/54 that of the Cs$^+$ ion. Combining (6) and (7) with (4) we have

$$I_0 = A(N_A^2/N_p) b_{\text{Cs}^+}(1 - 1/\xi)^2 y^2 = A(1.1242 \times 10^3) (1 - 1/\xi)^2 y^2.$$

(8)

This expression means that the value of $I_0$ is proportional to $(1 - 1/\xi)^2 y^2$, since the other parameters are constant for all the samples.

For 1% PODMA solutions the double layer interaction between micelles is not strong, and the averaged interparticle structure factor $S(Q)$ becomes unity for $Q \geq 0.1 \text{ Å}^{-1}$. It is thus plausible to fit the SAXS data at higher $Q$ values by $I_0 P(Q)$ to get parameters related to the counterion distribution. The geometrical parameters of the micelles were obtained from a separate SANS measurement (Shih, Lucas, Chen & Lin, 1987). Theoretical curves were obtained by fitting two parameters, $I_0$ and $t$, according to (1) and (2). Two sets of representative results are shown in Fig. 2. We

![Fig. 2](image-url)
Table 1. Parameters of CsOH-neutralized PODMA micelles

<table>
<thead>
<tr>
<th>[SDS]</th>
<th>t (Å)</th>
<th>y</th>
<th>f</th>
<th>I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00M</td>
<td>32.96</td>
<td>19.06</td>
<td>0.06300</td>
<td>3.73</td>
</tr>
<tr>
<td>0.01M</td>
<td>35.27</td>
<td>15.94</td>
<td>0.06485</td>
<td>3.97</td>
</tr>
<tr>
<td>0.015M</td>
<td>36.57</td>
<td>14.88</td>
<td>0.06578</td>
<td>4.09</td>
</tr>
<tr>
<td>0.04M</td>
<td>41.97</td>
<td>12.06</td>
<td>0.07041</td>
<td>4.72</td>
</tr>
<tr>
<td>0.10M</td>
<td>52.79</td>
<td>9.60</td>
<td>0.08152</td>
<td>6.40</td>
</tr>
<tr>
<td>0.20M</td>
<td>67.21</td>
<td>7.40</td>
<td>0.10004</td>
<td>9.70</td>
</tr>
</tbody>
</table>

Note: \( f = (1 - 1/\xi)^2 y^2 \times 10^3 \).

noticed that the agreement in the position and the height of the second peak between the theory and the experiment is fairly good. The discrepancy between the fitted curve and the experimental data at low \( Q \) becomes more noticeable when the added SDS concentration is higher. This is because the interaction between the double layers of the micelles becomes important when the surface charge density is increased. Under this condition the structure factor \( S(Q) \) at low \( Q \) would be depressed significantly to below unity. The fitted parameters \( I₀ \) and \( t \) are tabulated in Table 1, together with the calculated parameters \( b \) and \( \xi \).

This shell model predicts that \( I₀ \) is proportional to \((1 - 1/\xi)^2 y^2\), as shown in (8). To compare this theoretical prediction and the experimental results, a plot of the experimental values of \( I₀ \) vs \((1 - 1/\xi)^2 y^2\) is given in Fig. 3. The slope of the line can be used to estimate the calibration factor \( A \). The value thus obtained is 0.65.

Previous SANS data (Shih, Luccas, Chen & Lin, 1987) of LiOH-neutralized PODMA micelle systems show that the cross-sectional radius of the cylindrical micelles is higher than the value obtained from SAXS data for CsOH-neutralized PODMA micelles. A SANS measurement of the same sample as used in the SAXS experiment was therefore made to check the validity of the parameter \( R \) obtained by fitting SAXS data. We obtained \( R = 20 \) Å for micelles with Cs⁺ counterions. The corresponding intraparticle structure factors of these two systems are shown in Fig. 4.

4. Concluding remarks

Owing to the high contrast between Cs⁺ ions and both the solvent and the polymers for the X-ray radiation used, the SAXS intensity distribution is dominated by the spatial distribution of the condensed counterions around a micelle. The cylindrical shell approximation used in this paper describes moderately well the measured \( Q \) dependence of the intensity through (2). In the \( Q \) region where the \( S(Q) \) factor is expected to be unity, one can accurately fit (2) to the data to obtain the parameter \( t \). The basic cylinder dimensions \( L \) and \( R \) were independently determined by a SANS measurement. The intensity at zero angle, \( I₀ \), in this simple model is given by (8) with an effective fractional charge parameter \( 1/\xi \), the parameters \( N_p \) and \( b_{Cs⁺} \), being known quantities.

Two major conclusions are: (1) the shell thickness decreases rapidly as a function of \( \xi \), showing an increased clustering of the counterions near the surface, and (2) the fractional charge is approximately given by \( 1/\xi \), agreeing with the charge condensation theory. This latter approximation holds only in this simple shell model of counterion distribution. With more extensive measurements as a function of added salt and more thorough analyses, we hope to obtain the detailed counterion distribution which will serve to test the Poisson–Boltzmann equation prediction.

This research is supported in parts by a fund from S. C. Johnson & Son, Inc., by NSF grants administered through the Center for Materials Science and Engineering and the Biotechnology Process En-
gineering Center of MIT, by the NSF grant DMR-8616912 with the Division of Materials Science and ORNL, and by USDOE under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems. Use of the X-ray spectrometer at the National Center for Small Angle Scattering Research in ORNL is gratefully acknowledged.

References