Direct Measurement of Counterion Distribution around Cylindrical Micelles by Small-Angle X-Ray Scattering

C. F. Wu,[1],[a] S. H. Chen,[1] L. B. Shih,[2] and J. S. Lin[3]

[1]*Department of Nuclear Engineering and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

[2]*Polymer Research Department, S. C. Johnson & Son Inc., Racine, Wisconsin 53403*

[3]*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*

Small-angle x-ray scattering was used to measure the distribution of Cs^+ counterions around the surface of cylindrical micelles. The scattering intensity distribution was compared with that calculated by use of the analytical solutions of a nonlinear Poisson-Boltzmann (PB) equation in a cell model. Quantitative agreement was obtained for the cases without added salt. The addition of other monovalent salts did not modify the counterion distribution significantly in accordance with the prediction of the numerical solution of the PB equation.

The clustering of counterions around highly charged macromolecules in solution has long been theoretically predicted.[1] This phenomenon has been experimentally observed in many small-angle neutron scattering and small-angle x-ray scattering (SAXS) measurements involving polystyrene latex particles,[2] proteins,[3] and ionic micelles[4] in solutions at low ionic strength. We may call the clustering of counterions around the surface of a highly charged macroion a "charge condensation." The motivating idea is that the condensed counterions may effectively neutralize an equivalent amount of the surface charge of the macroion so that, as viewed from another macroion, the complex behaves as a macroion of lower effective surface charge. A practical consequence of such a phenomenon is that the thermodynamic and structural properties of the solution can be calculated with certain approximations by our assuming the lower effective charge on the macroions. In the literature the term "counterion condensation" is normally applied only to long cylindrical polyelectrolytes in solution. This idea probably originates from Manning,[5] who treated such a phenomenon theoretically with the Debye-Huckel approximation[6] for highly charged polyelectrolytes such as DNA molecules. Manning's counterion condensation theory (CC) was developed from a free-energy minimization scheme with a simple two-state model. In CC, a certain fraction of the counterions is "territorially bound" to the macroion while the rest remain "free" and form a Debye-Huckel cloud around the macroion.[7] This description has the advantage that a variety of thermodynamic and transport properties in polyelectrolyte solutions depend only on a few physical parameters, and can be obtained without complex calculations.[8] The CC theory, however, does not give a realistic counterion distribution around the macroion. Recently, Le Bret and Zimm[9] attempted to give a microscopic meaning to Manning's condensation theory using a known analytical

solution[10] of the Poisson-Boltzmann (PB) equation describing the electrostatic potential and charge distribution around a cylindrical macromolecule surrounded by an equal amount of neutralizing counterions in a cell model. Their main conclusion is that the condensed ions are to be interpreted as that fraction of the counterions remaining within a finite distance of the macroion when the volume of the system is expanded indefinitely. The PB equation solved in the cell model indeed predicts that there is such a fraction of ions around an infinitely long cylindrical polyion if the linear charge density of the polyion exceeds a certain critical value given by Manning's criterion.[7] More recently, Murthy, Bacquet, and Rossky[11] obtained numerical solutions to the hypernetted chain integral equation an the nonlinear PB equation for a model system representing an infinitely long rodlike polyelectrolyte in dilute 1-1 electrolyte solutions. The computed distribution functions for the counterion were compared with each other and also with the results of a Monte Carlo simulation. The remarkable conclusions are that the solutions of the PB equation are quantitatively accurate and are very close to the hypernetted chain results, especially away from the surface of the macroion; and the distribution of counterions near the surface is not affected appreciably by the addition of 1-1 electrolytes. However, the hypernetted chain and CC results are only in qualitative agreement as to the sharpness of the threshold condition given by Manning's criterion.[11] Belloni et al.[12] also applied the PB cell model to the cases where one or more other salt ions with different valences were added to the solution.

In this paper we present a series of SAXS intensity-distribution data of Cs^+ counterions around cylindrical micelles and an analysis in terms of the analytical solution of the PB equation in the cell model.[10] Since the dimension of the cylindrical micelle had been independently determined by previous small-angle neutron scattering

TABLE I. Parameters of 1% fully neutralized PODMA micellar solutions. Note: I_0 is deduced from from Eq. (2) and I_0^c is obtained by SAXS data fitting.

Additive	Conc. (mol)	ξ	R (Å)	R_m (Å)	β	I_0 (cm^{-1})	I_0^c (cm^{-1})
SDS	0.0000	32.96	24.80	100.43	1.0985	3.45	3.47
	0.0100	35.27	24.80	100.52	1.0995	3.65	3.63
	0.0150	36.57	24.80	100.57	1.1000	3.76	3.77
	0.0400	41.97	24.80	101.74	1.1015	4.29	4.04
LiF	0.0226	32.96	25.23	101.19	1.1060	3.45	2.66
	0.0321	32.96	25.65	101.93	1.1133	3.45	2.46
	0.0448	32.96	26.38	103.19	1.1258	3.45	2.31
	0.0505	32.96	26.95	104.16	1.1356	3.45	2.20
CsF	0.0223	32.96	24.96	100.71	1.1013	3.45	2.98
	0.0327	32.96	25.25	101.23	1.1063	3.45	3.05
	0.0437	32.96	25.49	101.64	1.1105	3.45	3.12
	0.0557	32.96	26.02	102.57	1.1196	3.45	3.17

measurements,[13] the computation of SAXS intensity distribution could be made without using any adjustable parameters. We can thus quantitatively test the accuracy of the analytical solutions of the PB equation against the experimental data.

The cylindrical micelles are formed by a comb-shaped copolymer, poly-(1-octadecene-co-maleic anhydride) (PODMA) in aqueous solution. 1 wt.% PODMA solutions were used throughout this experiment. In aqueous solutions, upon full neutralization by CsOH, the hydrophilic head groups of the polymers become negatively charged (carboxylic groups, COO$^-$). The polymer molecule has 22 repeating units. The length of its backbone is $L = 110$ Å. The hydrophobic side chain length is 20.5 Å which, when the head-group size of 4.3 Å is added, gives $R = 24.8$ Å. Ten of these polymer molecules form a cylindrical micelle of dimensions 110 Å (axial length)×24.8 Å (radius). The surface of the cylinder contains 502 units of negative charge.[14] This gives a linear charge spacing $b = 110/502 = 0.219$ Å. The Bjerrum length[6] of water at 25 °C is $l_B \equiv e^2/\epsilon k_B T = 7.15$ Å, where ϵ is the dielectric constant of water. Consequently, the linear charge-density parameter, defined as $\xi \equiv l_B/b$, is 32.96 for the micelles in water. We varied this parameter systematically by the addition of sodium dodecyl sulfate (SDS), an anionic surfactant. These SDS molecules probably insert themselves in between the carboxylic groups on the surface of the micelle and thus increase the value of ξ (see Table I). In order to test the effects of the added salts, two more series of 1% PODMA solutions were also studied. Each of them consisted of four samples with LiF and CsF at different concentrations (Table I).

Experiments were performed at the SAXS facilities of the National Center for Small-Angle Scattering Research at the Oak Ridge National Laboratory. X rays from the Cu $K\alpha$ line with a wavelength $\lambda = 1.54$ Å were used. The sample-to-detector distance was 1.126 m. A 20×20-cm^2 position-sensitive detector, with 64×64 effective channels, was used. This configuration resulted in a Q range[3] of 0.02 to 0.50 Å^{-1}. The scattering data were corrected for the instrumental noise, radiation background, sample container scattering, and detector uniformity. The absolute normalization of the scattering intensity was made with a protein solution of known scattering cross section.[3]

In a cell-model representation of a micellar solution, each micelle is enclosed in a cylindrical cell of dimensions L and R_0 such that $\pi R_0^2 L N_p = 1$, where N_p is the number density of micelles in the solution. The molar concentration of monomers in 1% PODMA solutions is $C_m = 0.027\,32M$, which gives $N_p = 7.48 \times 10^{16}$ cm^{-3} and hence $R_0 = 196.7$ Å. This value is 7.93 times the radius of the cylindrical micelle. For an assembly of N_p noninteracting micelles per unit volume, the scattering intensity per unit volume can be expressed as $I(Q) = I_0 \bar{P}(Q)$. The intensity at $Q = 0$ is given by $I_0 = N_p r_0^2 \bar{z}_c^2 Z^2 X^2$, where r_0 is the classical radius of the electron, Z is the total charge on the micelle, and $\bar{z}_c$ is the effective counterion atomic number.[14] The factor X, arising from consideration of the fraction of solute excluded solvent molecules, is defined as

$$X = 1 - \left[\frac{z_{D_2O}}{v_{D_2O}} \right] \left[\frac{\bar{v}_c}{\bar{z}_c} \right], \tag{1}$$

where z_{D_2O} is the number of electrons in a water molecule, v_{D_2O} is the volume of a water molecule, and $\bar{v}_c$ is the average counterion volume.[14]

The normalized micellar structure factor is given by $\bar{P}(Q) \equiv \int_0^1 |F(Q,\mu)|^2 d\mu$, where the angular-dependent form factor $F(Q,\mu)$ is[14]

$$F(Q,\mu) = \left[\frac{\sin(Q\mu L/2)}{Q\mu L/2} \right] \int_R^{R_0} 2\pi r L \frac{n(r)}{Z} J_0[Qr(1-\mu^2)^{1/2}] dr. \tag{2}$$
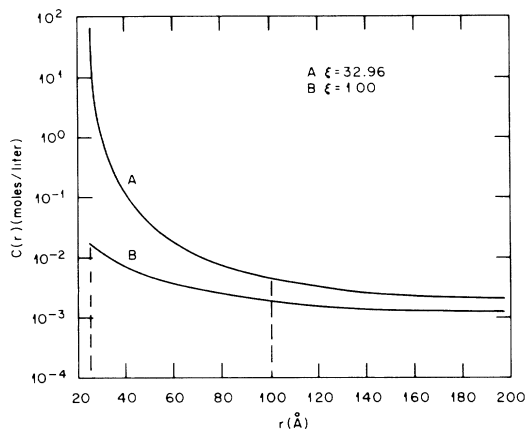
FIG. 1. Counterion distribution functions from $\xi = 32.96$ and $\xi = 1.0$. Input parameters are $R = 24.8$ Å and $R_0 = 196.7$ Å. The first case is the salt- and SDS-free sample for which $R_m = 100.4$ Å. The second is a hypothetical case which shows no counterion condensation and gives $R_m = R$.

$J_0(x)$ is the zeroth-order Bessel function, and μ is the cosine of the angle between the cylindrical axis and the $\mathbf{Q}$ vector.

The counterion distribution function around the micelle is given by the solution of the PB equation as[9]

$$\frac{n(r)}{n(R_0)} = \left\{ \frac{2|\beta|}{\kappa r \cos[\beta \ln(r/R_m)]} \right\}^2. \tag{3}$$

From the known values of the three parameters ξ, R, and R_0, the first integration constant β can be obtained by

$$\tan^{-1}\left[\frac{\xi - 1}{\beta}\right] + \tan^{-1}\left[\frac{1}{\beta}\right] - \beta \ln(R_0/R) = 0, \tag{4}$$

and the second integration constant R_m is given by

$$R_m = R \exp\left[\frac{1}{\beta} \tan^{-1}\left(\frac{\xi - 1}{\beta}\right)\right]. \tag{5}$$

The screening constant κ and the counterion number density at the cell boundary, $n(R_0)$, are given by the following equation: $\kappa^2 = 8\pi l_B n(R_0) = 4(1 + \beta^2)/R_0^2$. Note here that the counterions are assumed to be point charges in the theory.[5,12] R_m has a physical meaning of the radial distance within which the counterions are considered to be condensed.

Figure 1 gives the counterion distribution function calculated for two cases, $\xi = 32.96$ (curve A) and $\xi = 1.00$ (curve B), respectively, for $R_0/R = 7.93$. We see from curve A that the counterion concentration drops by 2 orders of magnitude within about 5 Å from the surface of the micelle. This clearly illustrates the counterion condensation phenomenon. It should be noted, however, that, according to Manning's prediction, the counterions within a radius $R_m = 100.43$ Å are considered to be condensed in this case; and furthermore, the effective fractional surface charge in this case will be $\alpha = 1/\xi = 0.03$.
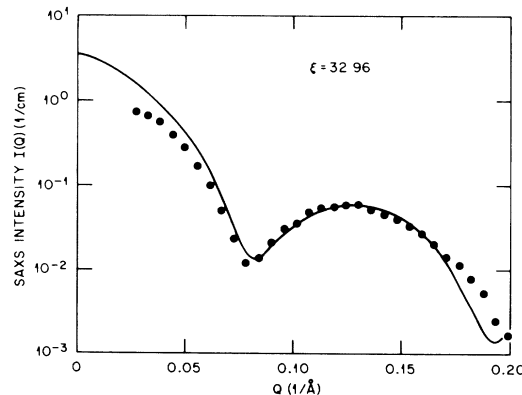

FIG. 2. A comparison of the calculated scattering intensity (solid curve) and the experimental SAXS data (circles) for $\xi = 32.96$.

Both statements appear to be rather unphysical. Curve A in Fig. 1 shows that the counterion concentration $C(r)$ at the micelle surface exceeds the limiting value of 55 mol/l. This is due to the point-charge assumption in this model. Figure 2 is a comparison of the calculated scattering intensity and the experimental SAXS data for the salt-free case with $\xi = 32.96$. It can be seen that the characteristic oscillation of the intensity distribution as a
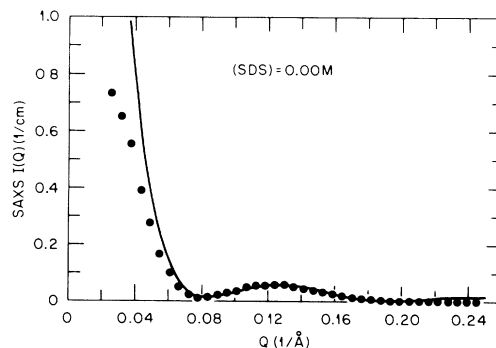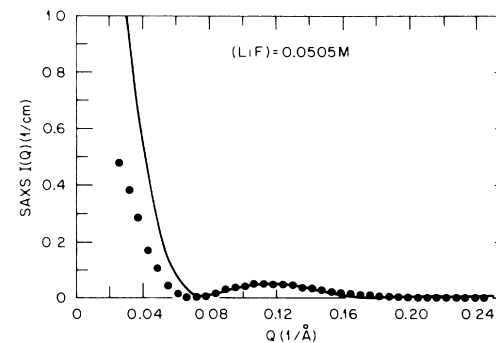
FIG. 3. Theoretical curves (solid lines) and experimental data (circles) for solutions (a) without salt and (b) with [LiF] $= 0.0505M$.

function of Q comes from the convolution of the shell-like structure of the counterions accumulation and $J_0(x)$ due to the cylindrical geometry. Agreement between experiment and theory is good if one considers that there is no adjustable parameter in the calculation. In Fig. 3 we show a comparison of the calculations and the SAXS measurements for 1% PODMA solutions without added salt (a) and with $0.0505M$ LiF (b). The parameters used in the calculation are summarized in Table I. Several comments are due at this point. (i) The assumption of noninteraction micelles in the cell model is, strictly speaking, not valid in the small-Q region due to the depression of the interparticle structure factor $S(Q)$. This effect can be seen in Figs. 2 and 3 for the region of $Q < 0.08$ Å^{-1}. Our future task should be to include this factor in the calculation.[15] (ii) For the cases with added salt, the expression given in Eq. (3) is not valid and the numerical solution of the PB equation needs to be used. It has been shown,[9,11] however, that the addition of salt does not significantly modify the original counterion distribution. In our analyses of these cases, Eq. (3) was still used but with R an adjustable parameter. It can be seen from Table I that, to fit the data, R has to be varied slightly. (iii) The calculated values of I_0 are in good agreement with measurements in the cases of no added salt, but they deviate from the measured values in the cases with added salts. In the cases of LiF, the deviation is mainly due to the competition between different counterion species in the condensation process.

In conclusion, we have directly tested the counterion distribution function predicted by the solution of the PB equation. For monovalent counterions and 1-1 electrolytes the PB equation seems to correctly describe the counterion condensation phenomenon. This result has already been anticipated by the theoretical work of Rossky and co-workers.[11] For the case of large ξ, Manning's CC theory predicts the effective charge fraction of micelles to approach zero as $1/\xi$, leading to vanishing macroion interactions. This prediction contradicts our observation that the structure factor $S(Q)$ at $Q = 0$

is appreciably less than unity. It indicates that finite-charge interaction occurs even in the dilute macroion solutions such as those used in this study.

This research is supported partially by a grant from the National Science Foundation administered through the Center for Materials Science and Engineering of the Massachusetts Institute of Technology, by a grant from S. C. Johnson & Son Inc., and by the U.S. Department of Energy Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems.

[a]Present address: Environmental and Health Protection Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

[1]F. Oozawa, *Polyelectrolytes* (Dekker, New York, 1971).

[2]D. W. Schaefer and B. J. Ackerson, Phys. Rev. Lett. **35**, 1448 (1975).

[3]C. F. Wu and S. H. Chen, J. Chem. Phys. **87**, 6199 (1987), and to be published.

[4]S. H. Chen, Annu. Rev. Phys. Chem. **37**, 351 (1986).

[5]G. S. Manning, J. Chem. Phys. **51**, 924 (1969), and **52**, 3249 (1969).

[6]H. L. Friedman, *A Course in Statistical Mechanics* (Prentice-Hall, Englewood Cliffs, 1985).

[7]G. S. Manning, Acc. Chem. Res. **12**, 443 (1979).

[8]G. S. Manning, Q. Rev. Biophys. **11**, 179 (1978).

[9]M. Le Bret and B. H. Zimm, Biopolymers **23**, 287 (1984).

[10]T. Alfrey, P. W. Berg, and H. Morawetz, J. Polym. Sci. **7**, 543 (1951).

[11]R. J. Bacquet and P. J. Rossky, J. Phys. Chem. **88**, 2660 (1984); C. S. Murthy, R. J. Bacquet, and P. J. Rossky, J. Phys. Chem. **89**, 701 (1985).

[12]L. Belloni, M. Drifford, and P. Turq, Chem. Phys. **83**, 147 (1984).

[13]L. B. Shih, E. Y. Sheu, and S. H. Chen, Macromolecules **21**, 1387 (1988).

[14]C. F. Wu, Ph.D. thesis, Massachusetts Institute of Technology, 1988 (unpublished).

[15]J. Schneider, D. Karrer, J. K. G. Dhout, and R. Klein, J. Chem. Phys. **87**, 3008 (1987).