

Small-angle scattering from polyelectrolyte solutions. A novel method for studying counterion condensation

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A new method is proposed for the study of binding of a low-molar-mass compound to a polymer chain, based on the calculation of the excess scattering amplitude from small-angle scattering data. The procedure requires the measurement of the scattering curve on an absolute scale at two polymer concentrations. Both smeared and desmeared scattering data may be used. The method is applied to aqueous solutions of poly(methacrylic acid) neutralized with NaOH. The number of Na⁺ counterions bound to the polyion has been determined as a function of the degree of neutralization.

(Keywords: X-ray small-angle scattering; polyelectrolyte solutions; counterion condensation)

INTRODUCTION

In polyelectrolyte solutions the charge of polyions is compensated by simple counterions. The condensation theory developed by Manning^{1,2} is often used to describe the interaction of counterions with polyions. The charge density on the polyion plays an important role here; it is described by the parameter ξ defined as $\xi = e^2/DkTl$, where D is the dielectric constant of the solvent, l is the mean distance between charges along the chain, and the quantities e , k and T have their standard meaning. According to Manning's hypothesis, when ξ exceeds a certain critical value ξ_c (where $\xi_c = 1$ for monovalent counterions) the counterions condense to such an extent that the charge density is kept at $\xi = \xi_c$.

A study of counterion-polyion interaction is important not only as a problem of basic research but also because it can contribute to our understanding of the mechanisms underlying technological and natural processes that proceed in the presence of polyelectrolytes^{3,4}. Measurements of activity coefficients, diffusion, conductivity, refractive index and spectral characteristics can provide the required information. In this paper we intend to demonstrate that small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS) can also yield useful information in this respect.

Experiments have shown that scattering from solutions of polyelectrolytes sensitively reflects the interactions between individual components in the system. Thus, the interaction of solvent molecules with the charges on the polyion leads to the formation of a hydration shell which can substantially influence the scattered intensity^{5,6}. Counterions localized in the vicinity of the polyion also contribute significantly to the scattered intensity^{5,7}, while 'free' counterions are usually irrelevant for the intensity scattered at small angles. The contributions of the solvation shell and of counterions are particularly significant in the case of linear polyelectrolytes⁵.

Thus, by analysing SAXS curves one can obtain information on interactions that take place in poly-

electrolyte solutions. In an earlier paper⁵ we estimated the extent of condensation B (defined as the number of counterions bound to one monomeric unit) in solutions of poly(methacrylic acid) neutralized to different degrees with NaOH by comparing the intensity of X-rays and of neutrons scattered at small angles. Absolute calibration was required in the procedure employed for both types of radiation. In this paper we propose a novel method for the determination of the extent of counterion condensation, where data from only one type of radiation are necessary.

THEORETICAL

Consider a polyelectrolyte solution containing polyions, counterions and a solvent. An idealized model will be used to describe the state of counterions, where it is assumed that the counterions are either associated with the polyion or can move freely through the solution. Free counterions can then be included in the solvent and will influence the small-angle scattering only by changing the scattering density of the solvent, an effect that can usually be neglected for moderately concentrated solutions. On the other hand, bonded counterions must be considered as part of the scattering particle (polyion) and their contribution to the scattered intensity may be very important.

The excess scattering amplitude, defined as

$$\Delta b = b - \bar{V}\rho_0 \quad (1)$$

is a suitable parameter for the description of the variation in scattering power of the system due to counterion condensation; b in the last equation is the scattering amplitude, \bar{V} is the partial molar volume of the solute and ρ_0 is the scattering density of the solvent. Under the assumption that B counterions are condensed on one monomeric unit, we can write:

$$\Delta b = \Delta b^{\text{mono}} + B\Delta b^{\text{ion}} \quad (2)$$

where Δb^{mono} and Δb^{ion} are the respective amplitudes of the monomeric unit and of the counterion. These amplitudes can be calculated from the chemical composition and partial volumes of components, using formula (1). The number of condensed counterions B can then be estimated on the basis of the last formula from the experimentally determined excess amplitude of the system.

One of the present authors has already proposed a method for the determination of the excess amplitude Δb from the scattering data⁸. Although the procedure was claimed to be of a more general character, relationships were derived only for homogeneous particles. We now proceed to generalize the derivation to the case of inhomogeneous particles.

The excess amplitude is a measure of the scattering power of the system. There exists another parameter characteristic of the scattering power, i.e. the mean-square fluctuation of scattering density, defined as

$$\overline{(\Delta\rho)^2} = (1/V) \int_V [\rho(\mathbf{r}) - \bar{\rho}]^2 d^3r \quad (3)$$

where $\bar{\rho}$ and $\rho(\mathbf{r})$ are the mean and the local scattering density, respectively. It is a well known fact^{9,10} that this parameter is related to the scattering cross-section $d\Sigma(q)/d\Omega$ through the expression

$$\overline{(\Delta\rho)^2} = (1/2\pi^2) \int_0^\infty q^2 [d\Sigma(q)/d\Omega] dq \quad (4)$$

where $q = (4\pi/\lambda) \sin \theta$ is the magnitude of the scattering vector, λ is the wavelength of the radiation and 2θ is the scattering angle.

Let us now derive a relationship between the parameters describing the scattering power (Δb , $(\Delta\rho)^2$) for the case of inhomogeneous particles.

In the following we shall limit our considerations to scattering vectors q smaller than some fixed (but arbitrary) value q_0 . Let us divide the inhomogeneous particle into regions characterized by linear dimension L such that the inequality $q_0 L \ll 1$ is satisfied. Waves scattered from points in space which belong to one of these regions will have practically the same phase. Consequently, the contribution of each region to the overall scattered intensity is given only by the total scattering amplitude and is independent of the distribution of mass inside the region. It then follows that—from the point of view of scattering at $q < q_0$ —one may replace any inhomogeneous particle by a particle consisting of a finite number of regions, each having a constant scattering density. The system will then be described by volume fractions v_i and scattering densities ρ_i ($i = 1, \dots, N$), where N is the number of components (regions) in the particle; quantities with index $i=0$ refer to the solvent. Definition (3) can be rewritten in the form:

$$\overline{(\Delta\rho)^2} = \overline{\rho^2} - \bar{\rho}^2 = \overline{(\rho - \rho_0)^2} - \overline{(\rho - \rho_0)}^2 \quad (5)$$

where the bar designates averaging over the sample volume. The expression for $(\Delta\rho)^2$ in terms of volume fractions and scattering densities of individual phases is:

$$\overline{(\Delta\rho)^2} = \sum_{i=1}^N v_i (\rho_i - \rho_0)^2 - \left(\sum_{i=1}^N v_i (\rho_i - \rho_0) \right)^2 \quad (6)$$

If we express the volume fractions by means of mass concentrations c_i and partial specific volumes V_i as

$v_i = c_i V_i$ and insert $\rho_i = b_i/V_i$ (where the scattering amplitude b_i refers to 1 g of the i th phase), we obtain after a trivial rearrangement the formula:

$$\overline{(\Delta\rho)^2} = c \frac{\sum_{i=1}^N (c_i/V_i) (\Delta b_i)^2}{\sum_{i=1}^N c_i} - c^2 \left(\frac{\sum_{i=1}^N c_i (\Delta b_i)}{\sum_{i=1}^N c_i} \right)^2 \quad (7)$$

where $\Delta b_i = b_i - V_i \rho_0$ represents the excess amplitude of the i th phase and

$$c = \sum_{i=1}^N c_i \quad (8)$$

is the overall solute concentration. The fraction in parentheses on the right-hand side of (7) denotes the excess amplitude of 1 g of solute. Similarly as in the case of homogeneous particles⁸ we obtain from formula (7) for inhomogeneous particles the result in the form:

$$\frac{d}{dc} \left(\frac{\overline{(\Delta\rho)^2}}{c} \right) = -(\Delta b)^2 \quad (9)$$

This formula is also valid for particles surrounded by a solvation shell which can be identified—within the framework of our model—with one or several phases. Naturally, in the calculation of the particle concentration one must then omit the corresponding terms from equation (8).

Formulae (4) and (9) enable one to determine the excess amplitude from the small-angle scattering data. It is necessary however to point out several circumstances that might simplify the situation to a certain extent.

In most cases of scattering from solutions at sufficiently large angles the interparticle interference is negligible and the scattered intensity represents a sum of contributions from the individual particles. In this region the intensity related to unit concentration, $(1/c) d\Sigma(q)/d\Omega$, is independent of particle concentration. Consequently, to calculate Δb it suffices to replace the infinite upper integration limit in the integral in (4) by some finite value q_m . Combining (4) and (9) we then have:

$$(\Delta b)^2 = -dZ/dc \quad (10)$$

where

$$Z = \frac{1}{2\pi^2} \int_0^{q_m} \frac{1}{c} \frac{d\Sigma}{d\Omega}(q) q^2 dq \quad (11)$$

The integration limit q_m in (11) is selected so as to ensure that at $q > q_m$ the normalized scattering curve $(1/c) d\Sigma(q)/d\Omega$ is independent of concentration.

It is apparent from (7) that $\overline{(\Delta\rho)^2}/c$ is a linear function of concentration. Accordingly, to determine Δb it suffices to measure the scattering curves at two particle concentrations.

Scattering curves are usually measured using a camera with a slit collimation system and converted to the absolute scale by using the experimentally determined energy of the primary beam per unit length in the registration plane¹¹. Instead of the cross-section $d\Sigma/d\Omega$ we then obtain the smeared scattering curve $d\tilde{\Sigma}/d\Omega$, which includes the collimation error and can be expressed as¹²:

$$\frac{d\tilde{\Sigma}}{d\Omega}(q) = -\frac{2}{K} \int_0^\infty P(t) \frac{d\Sigma}{d\Omega}([q^2 + t^2]^{1/2}) dt \quad (12)$$

where

$$K = 2\pi/a\lambda \quad (13)$$

a is the sample-detector distance and $P(t)$ describes the distribution of intensity along the primary beam, normalized so as to have $P(0)=1$. For an infinitely long primary beam ($P(t)=\text{const.}$) we obtain the following simple relationship between the integrated intensities¹³:

$$\int_0^\infty q \frac{d\tilde{\Sigma}}{d\Omega}(q) dq = \frac{2}{K} \int_0^\infty q^2 \frac{d\Sigma}{d\Omega}(q) dq \quad (14)$$

It follows from formula (12) that only values of $d\Sigma(q)/d\Omega$ corresponding to $q \geq q'$ can contribute to the smeared intensity $d\tilde{\Sigma}/d\Omega$ at the point q' . Hence, from the fact that $(1/c) d\Sigma(q)/d\Omega$ is independent of concentration at $q > q_m$ it follows that the function $(1/c) d\tilde{\Sigma}(q)/d\Omega$ will also be independent of concentration in the same region. This circumstance enables us to express $(\Delta b)^2$ by means of (14) in terms of smeared intensities as:

$$(\Delta b)^2 = d\tilde{Z}/dc \quad (15)$$

where

$$\tilde{Z} = \frac{K}{4\pi^2} \int_0^{q_m} \frac{1}{c} \frac{d\tilde{\Sigma}}{d\Omega}(q) q dq \quad (16)$$

K is defined by formula (13) and q_m is again the value that delimits the region where $(1/c) d\tilde{\Sigma}(q)/d\Omega$ ceases to depend on c .

It is important to note that the infinite integration limit may be replaced by q_m only in (15) and (16) (differentiation with respect to concentration), but not in (14).

The assumption that the primary beam is of infinite length usually conforms reasonably well with reality, and will be certainly justified in the proposed method for the determination of $(\Delta b)^2$, where only the inner parts of the scattering curves are used.

EXPERIMENTAL

Samples

Poly(methacrylic acid) (PMA) with molecular weight $M_w = 43\,000$ was prepared by J. Labský from this Institute by a method described previously¹⁴. Solutions of PMA ($0.005 \leq c \leq 0.05 \text{ g cm}^{-3}$) were prepared by dissolving the dry polymer in boiled distilled water; the degree of neutralization was adjusted by carbonate-free NaOH.

Small-angle X-ray scattering (SAXS)

Scattering curves were registered on a Kratky camera and converted to absolute scale by mean of a Lupolen standard, using the formula¹¹:

$$\frac{d\tilde{\Sigma}}{d\Omega}(q) = \frac{a}{\tilde{I}_L K_L T d} \tilde{I}(q) \quad (17)$$

where $\tilde{I}(q)$ is the measured scattered intensity, a is the sample-detector distance, T is sample transmittance, d is the sample thickness, K_L is a calibration constant and \tilde{I}_L is the intensity of radiation scattered by the standard at $q = (2\pi/150 \text{ \AA})$. The differential scattering cross-section (cm^{-1}) was then obtained by means of Glatter's desmearing program¹⁵ based on the transformation (12) applied to the curve $d\tilde{\Sigma}(q)/d\Omega$.

RESULTS AND DISCUSSION

The method proposed for studying counterion condensation was tested on aqueous solutions of poly(methacrylic acid) neutralized by NaOH at several values of the degree of neutralization α . Small-angle scattering curves were measured for each α at three to six concentrations of the polyelectrolyte. After normalization to unit concentration the curves exhibited the expected course in all instances. As an example we present the results for $\alpha=1$.

Both the smeared (Figure 1a) and desmeared (Figure 1b) scattering curves coincide when the value of the scattering vector q is sufficiently large ($q \geq 0.13 \text{ \AA}^{-1}$). This allowed us to select the limit of integration $q_m = 0.13 \text{ \AA}^{-1}$ in the calculation of integrated intensities Z and \tilde{Z} from

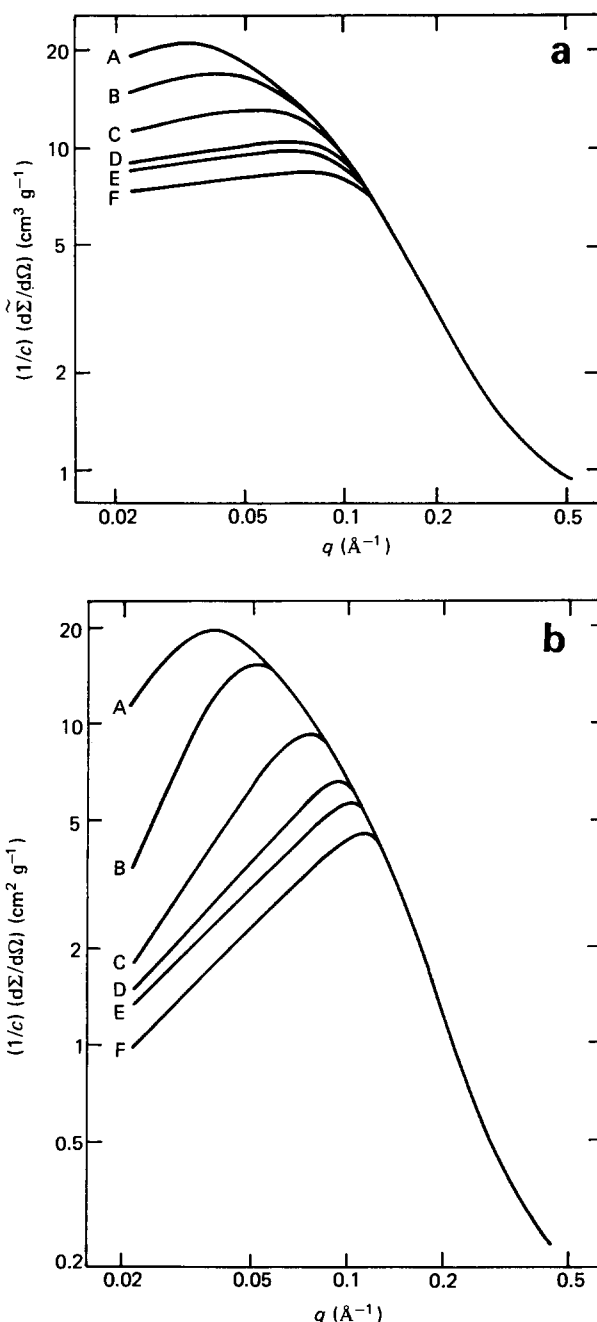


Figure 1 Smeared (a) and desmeared (b) SAXS curves for aqueous solutions of PMA neutralized with NaOH ($\alpha=1$) at different PMA concentrations: $c=0.005$ (A), 0.01 (B), 0.02 (C), 0.03 (D), 0.035 (E) and 0.045 g cm^{-3} (F)

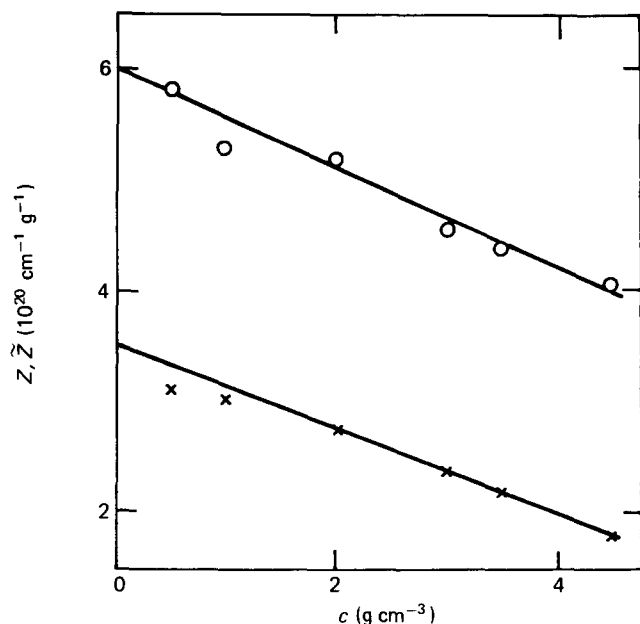


Figure 2 Concentration dependence of integrated intensities calculated from desmeared (\times) and smeared (\circ) SAXS curves according to equations (11) or (16) for aqueous solutions of PMA neutralized with NaOH ($\alpha=1$). The straight lines were determined by the weighted least-squares method

(11) and (16). As shown by *Figure 2*, the dependence of these quantities on concentration is linear, in accord with formulae (4) and (7). The slopes of these lines yield the negative squared excess scattering amplitudes.

The excess scattering amplitudes are plotted in *Figure 3* against the degree of neutralization. The values determined from the desmeared curves agree very well with those determined directly from the measured curves. A somewhat larger deviation (10%) is seen only at $\alpha=1$, apparently because of an imprecise collimation correction. At the smallest angles the scattering curves of polyelectrolytes increase with increasing q (*Figure 1b*); it is known that such curves are difficult to correct¹⁶.

The experimentally determined values of Δb are compared in *Figure 3* with those calculated from formula (1) for the polyions themselves (i.e. with counterion condensation neglected); this quantity is denoted as Δb^{mono} in equation (2). The scattering density of water, $\rho_0 = 9.38 \times 10^{10} \text{ cm}^{-2}$, and the scattering amplitude of PMA, $b = 9.07 \times 10^{10} \text{ cm g}^{-1}$, were used in the calculation. These values were determined from the scattering amplitude of electrons, equal to $b_e = 0.282 \times 10^{-12} \text{ cm}$ according to the Thomson formula. Ionization of PMA (proton dissociation) does not affect b but strongly influences the value of partial volume; at $\alpha=0$ we inserted $\bar{V} = 59.3 \text{ cm}^3 \text{ mol}^{-1}$ (ref. 17), which corresponds to a partial specific volume of $0.693 \text{ cm}^3 \text{ g}^{-1}$. For non-zero values of α we calculated this quantity from the volume changes reported by Ikemagi¹⁸ for the dissociation of PMA.

The experimental and calculated values of Δb are similar in the region of low degrees of neutralization ($\alpha \leq 0.3$), in agreement with the concept that counterions at low α move 'freely' in the solution and do not contribute to the scattering by polyions. On the other hand, when α is large the experimentally determined excess scattering amplitudes exceed the values calculated for polyions themselves; the difference must be attributed

to the condensed counterions, which are localized in the vicinity of polyions and contribute to their scattering amplitude.

The number of bound counterions associated with one monomeric unit was calculated from equation (2). Since both the experimental and calculated values of excess scattering amplitude ($\Delta b, \Delta b^{\text{mono}}$) are in centimetres per gram of PMA, the excess scattering amplitude of the counterion (Δb^{ion}) must also be expressed in these units. For Na^+ we obtain (using the scattering amplitude of the ion, $b = 2.82 \times 10^{-12} \text{ cm}$, and the partial molar volume¹⁹, $\bar{V} = -7 \text{ cm}^3 \text{ mol}^{-1}$) the excess amplitude $\Delta b^{\text{ion}} = 235.5 \times 10^{10} \text{ cm mol}^{-1} = 2.74 \times 10^{10} \text{ cm/g PMA}$.

The number B of condensed counterions per one monomeric unit is plotted in *Figure 4*, where data from smeared and desmeared scattering curves are included. The results can be compared with values based on the Manning hypothesis, which predicts that no counterions are bound when the degree of neutralization is lower than

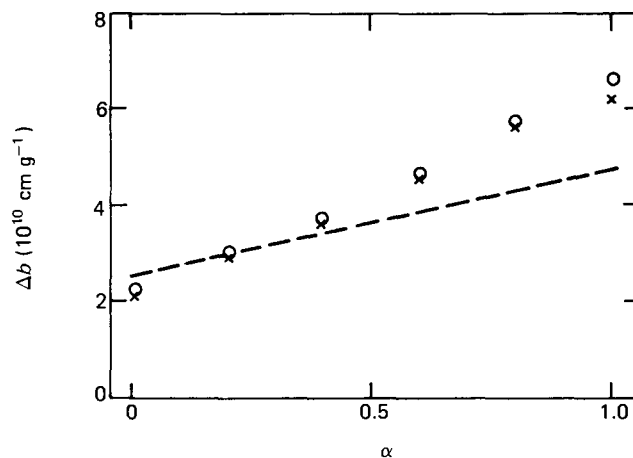


Figure 3 The excess scattering amplitude Δb of an aqueous solution of PMA neutralized with NaOH, determined from desmeared (\times) and smeared (\circ) SAXS data at various degrees of neutralization. The broken line is Δb calculated from the partial volume and composition of PMA with counterion condensation neglected

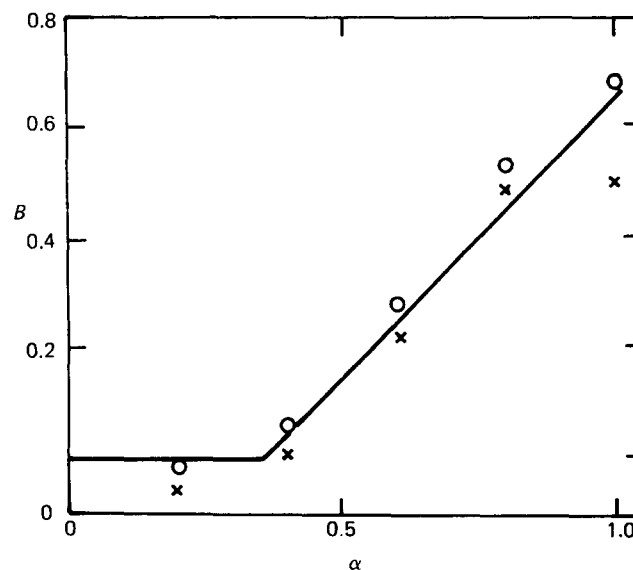


Figure 4 The number of Na^+ counterions bound to one monomeric unit of PMA, determined from SAXS data at various degrees of neutralization. The full line represents the Manning hypothesis

that corresponding to the critical charge density $\xi_c = 1$ (for PMA, $\alpha_c = 0.35$), while at $\alpha > \alpha_c$ the number of counterions bound to one monomeric unit is $\alpha - \alpha_c$. The data in Figure 4 are seen to be in reasonable agreement with the hypothesis.

The new method proposed for the study of counterion condensation makes use of the changes in scattering power, induced by the association of counterions with the polyion, and requires knowledge of the excess scattering amplitudes of the monomeric unit and of the counterion (Δb^{mono} , Δb^{ion}). The sensitivity of the method increases with increasing ratio $\Delta b^{\text{ion}}/\Delta b^{\text{mono}}$.

It is assumed in the method used for the determination of B that this quantity is independent of concentration within the interval studied. If this assumption is not valid, one may employ the previous procedure based on the combination of X-ray and neutron scattering data⁵ and determine B separately at each concentration level.

The proposed method is naturally not limited to polyelectrolytes. Interaction of neutral low-molar-mass compounds with macromolecules can be studied in the same manner.

We have shown that the excess scattering amplitude can be determined directly from the scattering curves measured under conditions of an infinitely long primary beam or from the curve corrected for the collimation effect. It is more advantageous to use equations (15) and

(16) derived for the smeared curves since in this case the necessity to employ a correction procedure and the associated error will be avoided.

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