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Ionic condensation theories and the liquidlike structures observed in colloidal dispersions

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Though the notion of effective charge has been widely used to fit experimental data, the possibility of predicting this adjustable parameter through a model remains unclear. A likely reason for this is the complexity involved in the theoretical approaches in the case of fluids with large asymmetries between their components. This paper deals with several condensation theories for spherical colloids, developed to provide effective charge values from simple models. Liquidlike structures are formed in colloidal dispersions for a set of latexes with different properties (charge, size, and polymeric composition). Effective charges are determined from experimental structure factors using a Derjaguin-Landau-Verwey-Overbeek potential and an Ornstein-Zernike scheme. The numerical coincidence between effective and post-condensation charges is fairly acceptable only for latexes with small size and charge. A simple approach based on the Manning condensation theory for linear polyelectrolytes is also discussed.

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I. INTRODUCTION

Colloidal dispersions of charged particles exhibit a wide variety of commercial, technological, and scientific applications. Glues, paints, or pharmaceuticals are all colloids. Nevertheless, the control of these complex systems depends strongly on a theoretical understanding of their constituents and the interaction between them. For instance, latex suspensions are useful in many cases if particles do not aggregate. Therefore, a theory of colloidal stability, in which electrostatic forces play an extremely important role, is essential. The electrostatic interactions between charged particles can cause a certain spatial ordering observed in many different ways.

For a long time, many workers have tried to determine an *effective charge* characterizing such phenomena from optical techniques [1–3] and others directly related to $u(r)$, (e.g., small angle neutron scattering, shear modulus titration, and torsional resonance digital video microscopy [4–7]). The Derjaguin-Landau-Verwey-Overbeek (DLVO) potential [8] has been widely used for this task. One of the most puzzling findings is that the obtained effective charges are considerably smaller than the total number of elementary charges (Z) on the particle surface. The strong accumulation of counterions in the vicinity of the macroion surface (due to *electrostatic* coupling between opposite charges) could be responsible for this noticeable reduction. To gain insight into this phenomenon, the concept of *ionic condensation* might be a useful tool. Accordingly, the colloid and the condensed counterions would be considered as a whole carrying a *post-condensation* charge Z^* that will be considerably reduced (as compared to Z), since the condensed counterions would neutralize (rather than screen) a great amount of surface sites on the particle.

This concept was initially developed by Oosawa and Manning for linear polyelectrolytes three decades ago [9,10]. According to the condensation theory, if the *dimensionless* charge density $\xi \equiv L_B \lambda$ (λ is the *linear* charge density, $L_B = e^2/4\pi\varepsilon_0\varepsilon_r k_B T$, ε_r the solvent dielectric constant, k_B the Boltzmann's constant, and T the temperature) exceeds a critical value $1/\nu$ (ν is the counterion valence) a condensed layer emerges (see a recent review by Manning [11]). The number of condensed counterions increases in such a way that the net density of the polymer and the counterions combined decreases up to the critical value. But can the Manning theory be extended to spherical colloidal particles? The answer to this question does not seem to be so clear. According to Belloni [12], simple laws for spherical colloids analogous to the laws for linear polyelectrolytes can be deduced from a Poisson-Boltzmann (PB) approach if a certain definition of which ions can be considered condensed is applied. It should be emphasized, however, that this one presents some different features when compared to the Manning condensation (see Sec. II for further details). Moreover, other models have been proposed recently in the attempt to predict effective charges. In the same spirit as the above-mentioned condensation model, the authors of Ref. [13] applied a PB cell model as well, but assuming a different criterion to say which counterions neutralize anionic sites on particles. The authors of Ref. [14] also developed a simple theory for charged spherical colloids. In this case, however, the number of counterions condensed on the macroions is calculated using a thermodynamic approach. However, these theories are so recent that experimental validation tests are quite scarce (practically nonexistent in the case of the models by Belloni and Levin), and a comparison between them in the view of data obtained from real systems has not been carried out yet.

At this point, the *renormalization* procedure proposed by Alexander *et al.* [15] must also be quoted. Although the strong accumulation of counterions close to the surface and the nonlinear screening is said to be responsible for this effect, there exist some differences between the renormalization and condensation approaches. The former consists of matching the nonlinear and linearized solutions of the PB equation at the edge of the spherical cell. Conversely, the

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latter focuses on the ion profile in the neighborhood of the particle surface. Consequently, some discrepancies between the Z_{eff} values predicted by both can appear (see, as an example, Fig. 7 in Ref. [11]). Apart from that, several experimental studies [5,16,17] suggested that the titrable charge is not a suitable input parameter for renormalization and the role of ions close to the particle surface could be essential. For instance, Gisler *et al.* tried to explain their results, allowing for the adsorption of protons on the surface (as well as the dissociation of carboxylate groups) [3]. This involves the knowledge of the so-called Stern capacitance. If condensation were able to predict effective charge in purely electrostatic terms, the use of specific *chemical* parameters could be avoided.

As matters stand, the following fundamental question arises: Would the reduced charge predicted by any of the above-mentioned ion condensation models be a good estimation of the effective charge? It is not easy to give a answer to this question, which is intimately related to the validity of the DLVO potential. In order to do that from a *strict* theoretical viewpoint, one should consider ions and macroions on the same footing. In other words, primitive models ought to be used. But charged colloidal suspensions remain a severe challenge to any statistical-mechanics theory. Due to size and charge asymmetries between small ions and macroions, which can be as high as 1:10 000, to solve the integral equations of the liquid-state theory turns into a formidable task. Nowadays, several theoretical studies support the application of DLVO-like potentials [18–22], in which some parameters (like charge) are considered rather as *effective* than *bare* parameters. This is what eventually would enable the use of this potential to determine effective charges from experiments. Nevertheless, the relationship between this phenomenological parameter and the predictions of some simple models (namely, the above-raised question) is still a controversial issue as a consequence of the complexity involved in theoretical treatments.

This work attempts to throw light on this matter with the aid of experimental data obtained from a set of well-characterized polymeric latexes. Our main concern will be to find to what extent condensation models are able to predict effective charges successfully. As a result of the studied systems exhibiting different properties (size, charge, and chemical composition), a discussion on the likely influence of some factors (such as size and charge asymmetries) will also be feasible. The paper is organized as follows. First, the method for determining effective charges from light scattering measurements (taking polydispersity into account) and some models for predicting such quantities are reviewed. Second, experimental details on latex surface characterization and structure factor determination are given. Then results are presented and discussed focusing on a comparative study of the condensation theories. Furthermore, the effect of ionic impurities on both determination and prediction of effective charges will be examined. Some features of the original Manning theory will be also considered in order to account for certain unexpected results.

II. THEORETICAL BACKGROUND

A. Determination of effective charges from light scattering experiments

Although calculations become much more difficult, polydispersity in size and charge will be considered in determining effective charges. In order to do that, the continuous size distribution is replaced by an m-component discretization and number fractions x_i and diameters σ_i ($i=1,2,...,m$) [23]. The charge of species $i(Z_i)$ is assumed to scale linearly with the surface area. The microscopic structure of an uniform multicomponent colloidal fluid like this is described by the set of total correlation functions $h_{ij}(r)$ with $i\leqslant m$ and $j\leqslant i$. These can be obtained from the solutions of $m(m+1)/2$ coupled Ornstein-Zernike (OZ) equations

$$h_{ij}(r)=c_{ij}(r)+\rho\sum_{k=1}^{m} x_k\int h_{ik}(|\vec{r}-\vec{s}|)c_{kj}(s)d^3s \qquad (1)$$

plus $m(m+1)/2$ approximate closure relations connecting $h_{ij}(r)$, $c_{ij}(r)$, and the pair interaction potential $u_{ij}(r)$.

There exist many examples of closure relations [24]. A particularly simple one is the so-called mean-spherical approximation (MSA). As it leads to unphysical results for dispersions of highly charged particles, a rescaling procedure was proposed known as the RMSA. The Percus-Yevick (PY) and the hypernetted chain (HNC) approximations are more sophisticated schemes but numerical integration is needed. The HNC has been successfully applied to highly charged systems. The Rogers-Young closure [25] interpolates between PY and HNC schemes and provides even better results than the HNC for systems of strongly interacting particles. However, it is more time consuming (especially when polidispersity is allowed for). Because of this, the HNC will be used in this work.

Then the time-averaged light intensity (per unit of volume) scattered by the colloidal dispersion can be written in terms of suitably averaged structure and form factors as

$$\langle I(q)\rangle=\rho f^2\overline{P}(q)\overline{S}(q), \qquad (2)$$

where ρ is the number density of macroions, q is the modulus of the scattering vector, and

$$f^2=\sum_{i=1}^{m} x_i f_i^2, \qquad (3)$$

$$\overline{P}(q)=\frac{1}{f^2}\sum_{i=1}^{m} x_i f_i^2 B_i^2(q), \qquad (4)$$

$$\overline{S}(q)=\frac{1}{f^2\overline{P}(q)}\sum_{i,j=1}^{m} f_i f_j B_i(q)B_j(q)[1+h_{ij}(q)]. \qquad (5)$$

The expressions for f_i and $B_i(q)$ must be provided by a light scattering theory. In our case, the suitability of the Rayleigh-Gans-Debye theory was checked before calculations. Functions $h_{ij}(q)$ are obtained through a Fourier transformation from the correlation functions.

The advantage of using Eq. (2) is that the averaged structure factor can be extracted directly from experimental light intensities (as in the one component fluid) by means of

$$\overline{S}(q)=\frac{\rho_0}{\rho}\frac{\langle I(q)\rangle}{\langle I_0(q)\rangle}, \qquad (6)$$

where $\langle I_0(q)\rangle$ is the light intensity scattered by a sample of noninteracting particles with number density ρ_0.

The interaction potential deserves a brief comment as well. This work deals with the microscopic structure exhibited by dispersions of negatively charged particles at a very *low* ionic strength. Under such conditions, the electrostatic interaction become so strong that other forces can be neglected. The potential used for the electrostatic contribution in this case (spherical particles with large double layers) is the widely known DLVO potential calculated by Overbeek some decades ago. In the case of moderate polydispersities, the following expression for the interaction potential between particles with radii a_i and a_j can be applied:

$$\frac{u_{ij}(r)}{k_BT}=L_BZ_iZ_j\frac{\exp(\kappa a_i)}{1+\kappa a_i}\frac{\exp(\kappa a_j)}{1+\kappa a_j}\frac{\exp(-\kappa r)}{r}, \qquad (7)$$

where κ is the reciprocal screening length. The DLVO interaction potential was derived under certain assumptions. *Some* of them are (i) low surface potentials, (ii) infinite dilution; and (iii) excess salt limit. Belloni gave a justification for low salt concentrations [26], but restrictions (i) and (ii) are still controversial issues. However, many theoretical studies point out the possibility of using the DLVO potential in a description of concentrated and/or highly interacting systems if the charge and κ are considered as *effective* parameters. Expression (7) will be applied in this context.

B. Condensation models predicting effective charges

As stated earlier, a condensation model for linear polyelectrolytes came out many years ago. According to this, when ξ is greater than a threshold value ν^{-1}, a condensation phenomenon occurs. Here we will only emphasize two facts (i) the charge fraction on the polymer is given by

$$\frac{Z^*}{Z}=\frac{1}{\nu\xi}, \qquad (8)$$

and (ii) the number of condensed counterions does *not* depend on their bulk ion concentration. More information on the Manning condensation for linear polyelectroytes and a survey of several experimental and theoretical aspects was given in Ref. [11] and the references cited therein.

Here the purpose is to test condensation theories for charged spherical particles. Belloni pointed out that *Manning-like* laws can be deduced for spheres from a PB approach if a specific definition of the cutoff distance r_0 separating condensed from uncondensed counterions is used. It consists of studying the number of counterions located between the particle surface and a sphere with radius $r, N(r)$. r_0 would be the distance at which an inflection point in the plot $N(r)$ vs $1/r$ is observed. Then Belloni clearly showed that condensation takes place if and only if $ZL_H/4a>1/\nu$ [12]. If ZL_B/a is identified with ξ, this expression is analogous to the Manning's criterion. Moreover, the post-condensation charge is given by

$$\frac{Z^*}{Z}=\frac{4y_0}{\nu\xi}, \qquad (9)$$

where $y_0\equiv r_0/a$. Equation (9) also resembles Eq. (8). Nevertheless, the theories for linear and spherical electrolytes do not present exactly the same features. As y_0 can depend on many factors (particle concentration, particle size, and bulk ion concentration), the ratio Z^*/Z also does. According to Eq. (7), this depends *exclusively* on ξ and ν for charged lines. In addition, it can be shown that the notion of ionic condensation for spheres has less meaning (and even disappears) in the limit of high ionic strength and/or very high concentrated systems.

Roberts, O'Dea, and Osteryoung also proposed a similar model (PB approach) [13]. In fact, the main difference is the definition of the cutoff distance, which in this case is based on the local counterion concentration $\rho(r)$. r_0 would be the distance at which this quantity equals its mean value $[\rho(r_0)=\langle\rho(r)\rangle]$.

Conversely, the authors of Ref. [14] put forward a theory for charged colloids surrounded by their counterions established on quite different ideas. The number of counterions condensed on a macroion is determined from a thermodynamic criterion (free energy minimization). Furthermore, the linear PB equation is used, which simplifies calculations. The omitted nonlinearity can be reintroduced into the theory allowing for ion association according to these authors.

III. EXPERIMENT

Five latexes were used in this work. Two of them, PS1 and PS2 (polystyrene) were prepared from styrene by conventional emulsion polymerization (with $K_2S_2O_8$ as initiator and $NaHCO_3$ as buffer). Latex polymethyl-methacrylate acid (PMMA) was also prepared by this procedure but from methyl-metacrylate [and $(NH_4)_2S_2O_8$ as initiator]. Latexes CS1 and CS2 are core-shell-type(s) polymer particles. In the first step of their synthesis, the core was prepared from styrene. In the second step, a shell of styrene and a small amount of metacrylic acid was put on the core. The use of surfactants (sodium dodecyl-benzene-sulfonate for PMMA and Aerosol MA80, Cyanamid (Sodium dihexyl sulfosuccinate) in the rest of the cases) is almost unavoidable if small latexes (diameter below 100 nm) are wanted. Polymerization reactions were carried out in a thermostat reactor fitted with reflux condenser and stainless steel stirrer. First, a distilled-deionized water, monomer, surfactant, and buffer (as well as the seed of latexes CS1 and CS2) were added to the reactor and purged with nitrogen. Then the initiator solution was added to the mixture.

Before being characterized, latexes were cleaned by serum replacement and ion exchange. The first step of cleaning took always more than ten days, in order to remove the emulsifier used in the synthesis (as much as possible) whereas the second step was carried out stirring the latexes with ion exchange resin Amberlite MB-3, suitably conditioned before use [27], for more than 4 h.

The size distribution of the studied latexes was determined by transmission electron microscopy (TEM). The average diameter (σ) is shown in Table I. A polydispersity index I_{PD} defined as $I_{PD}=\Sigma_i x_i\sigma_i^4/(\sigma\Sigma_i x_i\sigma_i^3)$ is also given in Table I. These sizes were confirmed through dynamic light scattering (DLS) for latexes PS1, PS2, CS1, and CS2. For latex PMMA, however, the size by TEM was found to be

TABLE I. Size, polidispersity, and charge of the latexes.

Latex	Diameter[a] (nm)	Standard deviation[a] (nm)	I_{PD}[a]	$Z_{surface}$ (e^-/particle)
PS1	62.1	7.4	1.043	1270
PS2	99.0	4.4	1.006	5240
CS1	72.5	7.7	1.029	1030
CS2	81.4	8.2	1.031	2190
PMMA	74.8	7.8	1.028	3100

[a] Values obtained from TEM.

considerably smaller than the one determined by DLS (103 ± 2 nm). This could be attributed to the shrinkage that PMMA particles suffer as a consequence of the electron beam [28]. Thus the mean size obtained by DLS will be used for PMMA hereafter.

The number of ionizable groups on the surface of each system was determined by both conductimetric and potentiometric (forward and back) titrations. These experiments were performed with Crison instruments (pH-meter and conductimeter) at 25 °C in a stirred vessel flushed with nitrogen (using NaOH and HCl as titration agents). From the study of surface charge as function of pH, some worthwhile conclusions can be reported. For latex PS1, PS2, and PMMA, this quantity increases only slightly with increasing pH (from 4 to 9), which suggests a majority of strong acid groups (like sulfate provided by the initiator). A small amount of weak acid groups is also expected (presumably carboxylate as a result of the Kolthoff reaction [29]). Conversely, latexes CS1 and CS2 exhibit a strongly pH-dependent surface charge. The large number of weak acid groups (carboxylate) arising from the metacrylic acid used in their synthesis could be the cause for this behavior. There should also exist sulfate groups resulting from the initiator. To give the reader an idea of the surface charge ($Z_{surface}$) at usual experimental conditions, the number of charged groups at pH$\sim$5.5 is also shown in Table I (its uncertainty is not expected to exceed 5%). This quantity is nearly identical to the estimated sulfate group number. This is reasonable, since $pK_{carboxylate}$ must be about 5.

With regard to the scattered light measurements, the used set up was a 4700 °C System (Malvern) with an argon laser (75 mW) and $\lambda_0 = 488$ nm. These experiments were performed at 25 °C, from 20° to 140° in 2° steps. Average intensities were obtained from three individual measurements at each angle, with different cell positions to minimize the effect of scratches on the glass surface. Stock suspensions were filtered through 1.2-μm filters (millipore) prior to measurements.

Concerning structure formation, samples were prepared by dilution and kept for at least ten days over a bed of ion exchanger resin in cylindrical quartz glass cuvettes with two different outer diameters (10 and 25 mm). The function $I(q)$ (intensity vs the modulus of the scattering vector) was monitored until no significant changes were observed. Then the deionization process was supposed to be have been finished. In order to avoid gradients in particle density and artifacts like the ones reported by some authors [30], samples were homogenized quite repeatedly (even some minutes before intensity measurements). The light intensity scattered by dilute samples ($\rho_0 \sim 2.5\times10^{11}$ particle/ml), in which spatial ordering can be neglected, were used as references in order to determine both form and structure factors. The accessible range of particle concentrations is limited by several experimental factors. At low concentrations it is quite difficult to achieve well-ordered dispersions. Ionic impurities can have undesirable effects (as will be discussed later). At high concentrations, multiple scattering or absorption of the laser beam by the sample can occur.

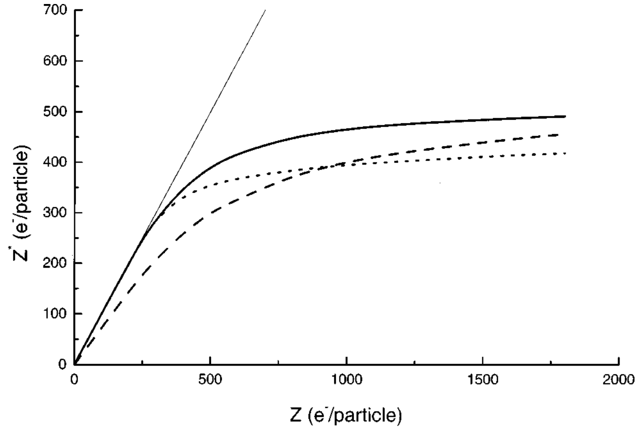

FIG. 1. Post-condensation charges (Z^*) predicted by theories I [12] (————), II [13] (-------), and III [14] (·········), for latex suspension ($\rho = 5.7\times10^{12}$ particle/ml) of particles with $\rho = 81.4$ nm. Straight line stands for $Z^* = Z$.

IV. RESULTS AND DISCUSSION

Before showing some experimental results, a comparison between the condensation theories reported in Refs. [12], [13], and [14] (hereafter noted as theories I, II, and III, respectively) may be helpful. The post-condensation charges Z^* (predicted by theories I, II, and III) as a function of Z are plotted for a representative system of those that will be analyzed later ($\sigma = 81.4$ nm and $\rho = 5.7\times10^{12}$particle/ml) in Fig. 1. As can be seen, there is a qualitative agreement between the three theories studied in this work. At low charge, Z^* increases linearly in all the cases, whereas it seems to reach a plateau with increasing Z considerably. Moreover, the numerical coincidence is moderately good. However, some discrepancies come into view as well. At low Z, the charges predicted by theories I and III are equal to Z. In this sense, both theories I and III could be considered as *threshold* theories, which means that condensation takes place if a critical value is exceeded (actually Belloni [12] showed this). Conversely, counterions condense even at vanishing Z according to theory II. Apart from this, small differences between saturation changes can be observed. More specifically, the values predicted by theory I are larger than the ones predicted by theory III. The resemblance between these curves and the ones derived from renormalization is just a consequence of the strong accumulation of ions close to the surface underlying these concepts (as mentioned earlier).

Some tests on the reproducibility of structure factors measured in dilute deionized suspensions were carried out. Structures of latex PS1 were formed (in presence of ion exchange resins) at two different concentrations ($\rho = 1.77\times10^{12}$ and

TABLE II. Some specific parameters of the samples looked into in this work. Particle concentrations (ρ_{fit}) and effective charges (Z_{eff}) and obtained by fitting experimental structure factors (assuming $c_s=0$ and $10^{-6}M$). Particle concentrations calculated from the dilution procedure (ρ) as well as the number of elementary charges on the particle surface (Z) are also shown. Z was estimated from Z_{surface} and assuming charge regulation (see text for further explanations).

Sample	Latex	$10^{12}\rho$ (particle/ml)	$10^{12}\rho_{\mathrm{fit}}$ (particle/ml)	Z_{eff} (e^-/particle) $c_s=0$	Z_{eff} (e^-/particle) $c_s=10^{-6}M$	Z (e^-/particle)
1	PS1	1.77	2.0	260	300	654
2	PS1	2.94	3.6	270	300	650
3	PS1	4.79	5.7	280	300	646
4	PS1	6.76	7.8	290	300	644
5	CS1	1.73	1.8	240	280	690
6	CS1	2.88	3.1	270	300	685
7	CS1	4.79	5.2	290	300	681
8	PS2	0.85	0.85	180	220	1822
9	CS2	1.77	2.0	300	330	1058
10	CS2	2.94	3.3	320	330	1055
11	CS2	4.79	5.7	330	330	1051
12	PMMA	1.54	1.8	340	400	1545
13	PMMA	2.99	3.2	360	400	1543

6.76×10^{12} particle/ml) in different cells. It was observed that at the highest concentration, structure factors were quite reproducible. However, one must be more careful about the functions measured at low particle concentrations. In most of the cells the same structure factor was encountered but, in some of the them, the main peak of $S(q)$ was found to be lower. This could be attributed to a certain ionic contamination, which would have a more pronounced effect if ρ is too low (as will be discussed later).

The samples looked into in this work are summarized in Table II, and the corresponding experimental structure factors are plotted in Fig. 2. With increasing ρ, the height of the first peak increases, whereas its position shifts toward higher q values [1–3]. The first effect is a result of a higher degree of interference in scattered light, since both interaction and correlations become more intense when particles are closer. The change in the mean interparticle distance produces the shift in the peak position.

In order to fit these experimental data, the particle concentration and the *mean* effective charge (Z_{eff}) were used as fitting parameters. The Debye screening parameter is usually calculated from them assuming complete deionization, which leads to $\kappa=\sqrt{4\pi L_B\rho Z_{\mathrm{eff}}}$. Nevertheless, there could exist a *residual* stray ion concentration, and it would be desirable to know its effect on the effective charge determination. Unfortunately, the precise concentration of these ionic impurities is extremely difficult to monitor, but a certain value may be assumed if just an *estimation* of its influence is wanted. Then, the Debye screening length is given by $\kappa=\sqrt{4\pi L_B(\rho Z_{\mathrm{eff}}+N_A c_s)}$, where c_s would be the contribution to ionic strength (in mM) due to these unidentified small ion concentrations. Evers *et al.* often studied suspensions of charged colloidal spheres at very low ionic strength. They estimated that c_s is below $10^{-6}M$ in deionized samples [31]. In this work, calculations with $c_s=0$ and $10^{-6}M$ will be done.

Polydispersity was modeled by a m discretization of the size distribution obtained by TEM. In order to avoid extremely long computational times, $m=3$ was chosen. For each latex, the diameters and number fractions were calculated requiring the equality of the first moments of the 3-component discretization and the original size distribution. For the numerical solution of the resulting set of 12 coupled equations (six OZ integral relations plus six HNC closures) the iterative algorithm described in Ref. [22] was applied.

The theoretical structure factors fitting the experimental ones are also plotted in Fig. 2. As can be seen, the agreement is quite good for all the systems except in the region of low q. As polydispersity is said to be responsible for this discrepancy, it was taken into account in this case. However, differences at low q are still observed. Large aggregates scattering preferentially in the forward direction could be the main contribution to this effect. In Table II, the effective charges and particle concentrations determined by fitting are also shown (charges are expressed in absolute value). The particle number densities are close to those calculated from the dilution procedure, although systematically larger. However, these deviations could be fairly reasonable if certain experimental errors, such as those derived from size measurements, are taken into account.

The obtained effective charges (assuming $c_s=0$ and $10^{-6}M$) are also shown in Table II. As many factors are involved in its determination, it is not easy to calculate the uncertainty in this adjustable parameter. Nevertheless, it might be approximately 10–20 %. As expected, the effective charges are found to be much smaller than the number of ionizable groups onto the particle surface. This remarkable reduction in charge will be discussed later with the aid of condensation. Previously, we will focus on the effect of ionic impurities. Despite of the fact that $10^{-6}M$ is rather an upper bound of c_s, the differences between the Z_{eff} values calculated using $c_s=0$ and $10^{-6}M$ are not very significant. What

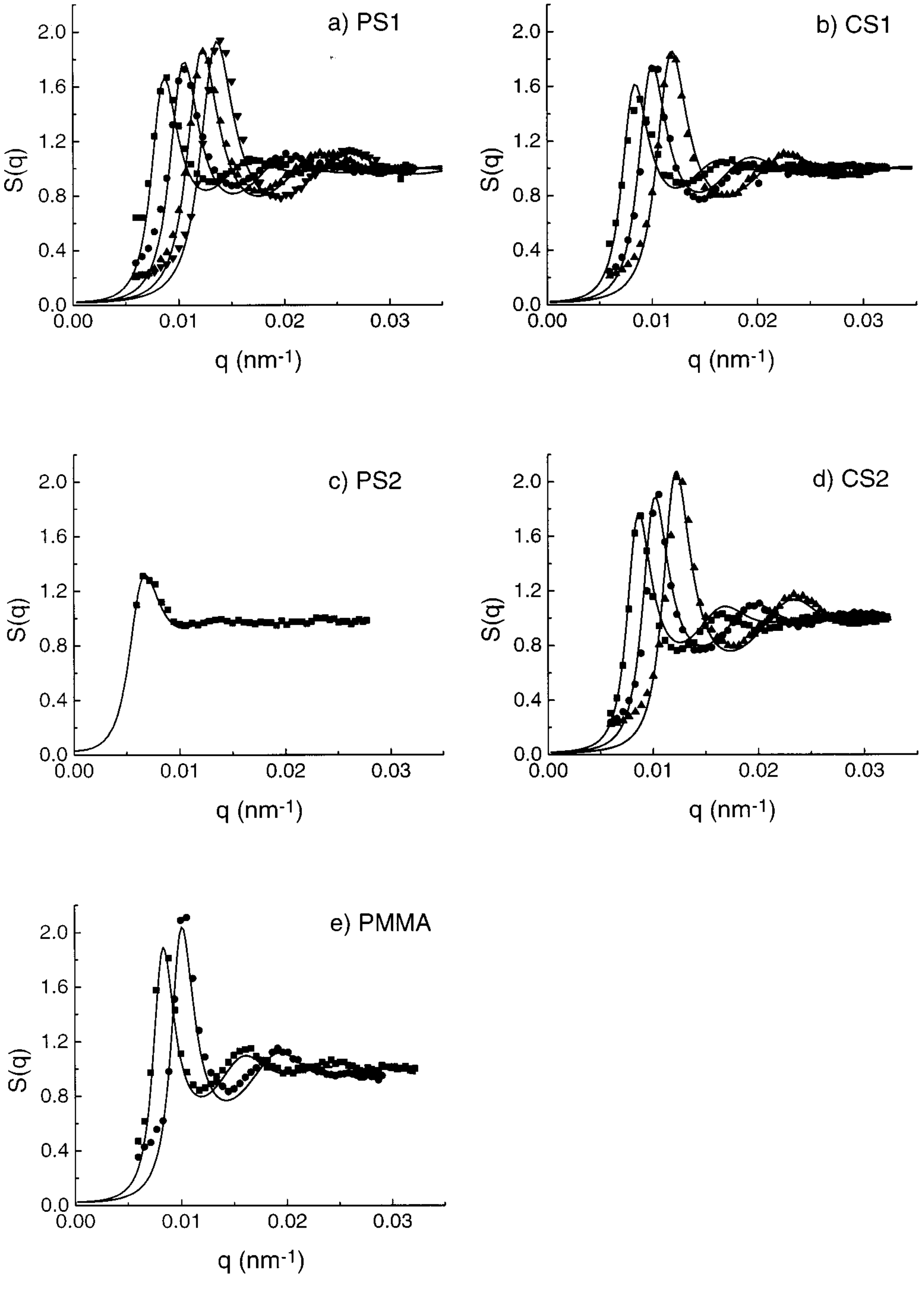

FIG. 2. Structure factors measured for (a) latex PS1, sample 1 (■), sample 2 (●), sample 3 (▲), and sample 4 (▼); (b) latex CS1, sample 5 (■), sample 6 (●), and sample 7 (▼), (c) latex PS2, sample 8 (■); (d) latex CS2, sample 9 (■), sample 10 (●), and sample 11 (▲), and (e) latex PMMA sample 12 (■), sample 13 (●). Solid lines denote the fits obtained using the HNC closure along with the OZ relation (and allowing for polydispersity).

is more, these discrepancies lower (and even vanish) if particle concentration is high enough. This is logical since the share of stray ions corresponding to one macroion decreases. Moreover, it should be stressed that assuming $c_s = 10^{-6} M$, the experimental structure factors at different particle concentrations can be fitted using the same effective charge.

Apart from the numerical disagreement between Z_{surface} and Z_{eff} what additional preliminary qualitative conclusions does a comparison between them yield? Being more precise, could one say that the greater the former the larger the latter? Latex PS1 and CS1 present the same effective charge and comparable surface charges. The Z_{eff} values for latexes CS2 and PMMA are a bit larger. Likewise, the numbers of ionizable groups on their surface are larger. Therefore, one could be tempted to think that a qualitative relation linking both quantities seems to exist. But this is not the case. Latex PS2 has the highest surface charge but, surprisingly, the lowest effective charge. This result has been confirmed using turbidimetry [32].

Can ionic condensation account for these effective charges? With the aim of giving an answer to this question, the post-condensation charges predicted by theories I and III were calculated. For sake of simplicity only these two theories were applied. Theories I and III were chosen because they are based on quite different ideas. It should be noted, however, that in deionized suspensions the proton concentration close to the particle surface could be so extremely high that the local pH would even be comparable to pK_{sulfate}. Consequently, the *actual* number of dissociated surface groups (Z) could be smaller than Z_{surface} (mainly sulfate groups). In our calculations, Z was estimated from Z_{surface}, allowing for charge regulation in the applied PB approach using a mass equation. According to this, the dissociation constant of the sulfate surface groups would be

$$K_{\text{sulfate}}=[H^{+}]_0\alpha/(1-\alpha) \tag{10}$$

in which $[H^{+}]_0$ is the proton concentration close to the particle surface, and $\alpha=Z/Z_{\text{surface}}$ is the degree of dissociation. From some studies [5,33,34], a $pK_{\text{sulfate}}\approx 2$ was assumed. Take, as an example, the case of sample 1 (assuming $c_s=0$). The PB equation together with Eq. (10) yields $-\ln[H^{+}]_0\approx 2.03$ and $Z=654$. The rest of Z values calculated in this way are also presented in Table II.

The predictions for the latex samples studied in this work and calculated from theories I and III are given graphically in Figs. 3(a) and 3(b), in which predictions can be compared to the effective charges obtained from light scattering data (charges are plotted as a function of the volume fraction of the corresponding samples). Some interesting conclusions can be inferred from this figure. As a general rule, condensation theories I and III overestimate Z_{eff}, though the values derived from theory III are always closer to this phenomenological parameter. However, a more detailed analysis is beneficial. There exist a extremely good agreement between Z_{eff} and the post-condensation charge predicted by theory III for latex PS1, whose surface charge and size are the smallest. The numerical agreement is moderately pleasant for latex CS1, whose size is a bit larger. Its charge is more or less the same than CS1 (it depends on which value, Z_{surface} or Z, is picked as the illustrative parameter). When size and/or charge are increased a bit more, the disagreement between Z_{eff} and Z^{*} become considerable (see latexes CS2 and PMMA). Eventually, if the latex with the highest charge and size (PS2) is examined, drastic discrepancies are observed. Size and charge asymmetries between small and large ions are found to play an important role, which suggests that theoretical models should be revised in some way.

Recently, some papers [35,36] have stated that ion-ion correlations (neglected in PB approaches) could have marked effects on the effective charge. This quantity would even pass through a maximum with increasing Z. Nevertheless, these results are reported for systems with sizes comparable to L_B (see Fig. 6 in Ref. [35]). In the limit of vanishing L_B/a, the PB theory is recovered. Our systems would be in this latter case, thus predictions would not be improved noticeably.

One might also wonder whether ionic contamination contributes to explain these results. Particularly, what would its effect be on post-condensation charge predictions?. Unfortunately, further information on impurities (nature, valency) is needed to clarify this matter. In any case, an estimation (as an illustration) for sample 1 assuming monovalent ions (with $c_s=10^{-6}M$) was performed by means of theory I. It yielded $Z^{*}=385\ e^{-}$/particle instead of $Z^{*}=395\ e^{-}$/particle if $c_s=0$. Lower differences between both values are found at higher particle concentrations. Though this improvement is not enough one should bear in mind that (i) multivalent counterions (which have been ignored in this estimation) would have a much higher local concentration in the neighborhood of the surface than monovalent ions; and (ii) specific interactions between this stray ions and the particle surface have not been considered (because of chemical parameters being necessary, as noted in Sec. I). Nevertheless, this kind of ion binding would presumably increase with the charge and size (surface area) of particles.

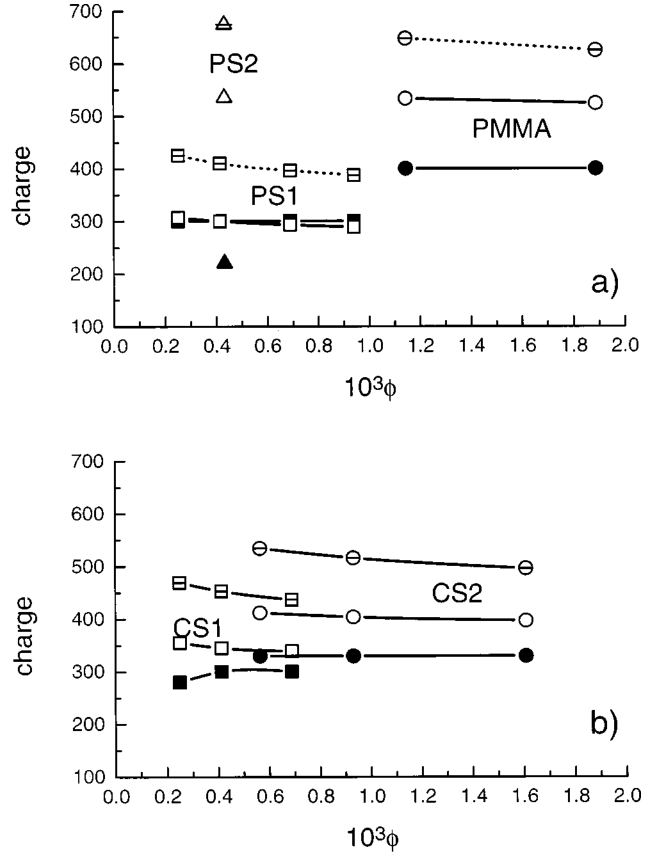

FIG. 3. (a) Effective charges as a function of the volume fraction (calculated from the fitted particle concentration) for latexes PS1 (■), PMMA (●), and PS2 (▲); post-condensation charges predicted by theory I for latexes PS 1 (the dashed square), PMMA (⊖), and PS 2 (the dashed triangle); and post-condensation charges predicted by theory III for latexes PS1 (□), PMMA (○), and PS2 (△). (b) Effective charges as a function of the volume fraction (calculated from the fitted particle concentration) for latexes CS1 (■) and CS2 (●); post-condensation charges predicted by theory I for latexes CS1 (the dashed square) and CS2 (the dashed circle); post-condensation charges predicted by theory III for latexes CS1 (□) and CS2 (○).

Although condensation models for spherical particles have not completely validated by our experiments, some clues will be looked for in speculating on specific features of the original Manning theory. Particularly, the fact that the ratio Z^{*}/Z is proportional to ξ^{1} regardless of other factors (like particle concentration) will be given attention. *None* of the theories for charged spheres looked into in this study

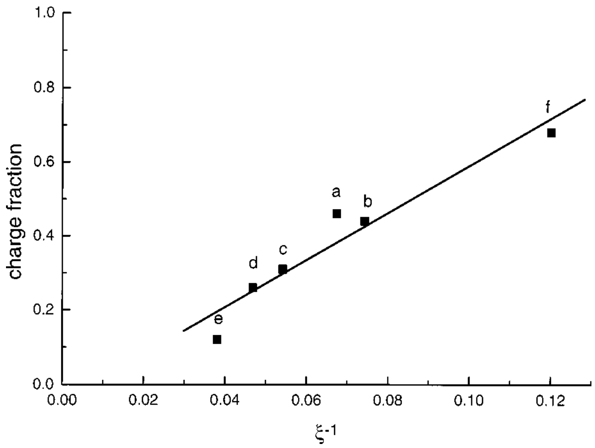

FIG. 4. Charge fraction (Z^*/Z) as a function of ξ^{-1} for several samples (see labels): latex PS1 sample 3 (a), latex CS1 sample 6 (b), latex CS2 sample 10 (c), latex PMMA sample 13 (d), latex PS2 sample 8 (e), and latex (Ref. [5]) (f). Straight line: best linear fit.

theories I, II, or III exhibits this peculiarity. As an example, a ρ dependence is reported in all the cases [see Fig. 3 or Eq. (8)]. If one assumes $\xi = Z/a$ for spherical charged polyelectrolytes, and Z_{eff} is identified with Z^*, some of the results obtained in this study could be summarized in Fig. 4. Data from Ref. [5] have been also included for comparison. Since, given a latex, the effective charges are practically the same at different particle concentrations, only one sample was chosen for each system. As can be seen, these points present a monotonic trend. What is more, if a linear fit is tried, it yields $Z^*/Z = (6.37 \pm 0.89)\xi^{-1} + (-0.04 \pm 0.06)$ (see the straight line in Fig. 4). The correlation coefficient r is found to be 0.963, which confirms this linear law. Moreover, the independent term is practically zero (within the error). Though the error in the slope seems to be considerable, it becomes reasonable if one does not forget that these points (whose coordinates are ξ^1 and Z^*/Z) have been obtained from an extensive numerical treatment (which includes the use of differential and integral equations). Due to the same reason, this *Manning-like* dependence, which would be justified somehow if the constancy of y_0 in Eq. (9) were postulated, is highlight. It should also be emphasized that this behavior does account for the unexpected effective charge found for latex PS2.

V. CONCLUSIONS

Several condensation models (for spherical particles) have been tested using effective charges [in the sense of Eq. (7)] determined from light scattering experiments. Size and/or charge asymmetries between small ions and colloidal particles have found to be important factors for the success of these theories in accounting for the observed liquidlike structures. For latexes with small sizes and charges, the agreement between effective and post-condensation charges is fairly acceptable. It should be emphasized, however, that deviations between both charges become larger with increasing size and/or charge. Nevertheless, a simple approach based on particular features of the Manning condensation theory for linear polyelectrolytes seems to explain these results reasonably well (at least qualitatively). But a well-established justification for this semiempirical behavior is still missing. These conclusions suggest a revision of some theoretical aspects of the condensation notions reported by several authors.

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