Spherical Polyelectrolyte Microgels in Salt-Free Solution. 2. Combined Analysis of Static Structure and Viscosity and Quantitative Testing of the Mode−Mode Coupling Approximation

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ABSTRACT: The static structure of salt-free solutions of spherical polyelectrolytes, as determined by light scattering, is used as an input in the mode−mode coupling polyelectrolyte theory introduced by Hess and Klein and used to calculate the concentration-dependent solution viscosity of the same solutions. Quantitative agreement between measured and calculated values is obtained, underlining the appropriateness of the simplifications of the theory.

Introduction

In previous papers, we have analyzed both the concentration-dependent viscosity[1] and the static structure factor of salt-free aqueous solutions[2] of spherical polyelectrolyte microgels. In both cases, the typical polyelectrolyte behavior is observed, i.e., a steep increase of the reduced specific viscosity with decreasing concentration as well as formation of ordered solution structures. For a more detailed introduction into the discussion of polyelectrolyte effects, the interested reader is pointed at the review literature.[3,4]

The polyelectrolyte microgels with a spherical shape, narrow size distribution, and an adjustable size between 5 nm < R < 50 nm represent in our opinion a close-to-ideal model system since they cannot perform conformational changes, are free of hydrophobic interactions, and are—as small spherical objects—as close as possible to the theoretical premise of pointlike, charged objects.

This and similar work showed that the classical explanation of the polyelectrolyte effect, the so-called coil−rod transition, is unnecessary, and other theoretical descriptions describing the observed effects on the basis of the interparticle potentials and interactions had to be applied. Work on the viscometry of polyelectrolyte−surfactant complexes in different organic solvents showed that a rather general approach by Hess and Klein[5] based upon a mode−mode coupling approximation turned out to be very powerful to describe experimental data with a minimal set of experimental parameters.[6] The Hess−Klein theory, modified only with a term considering the spatial extension of a real macromolecule, was also applied to describe the behavior of linear, spherical, and branched macromolecules.[1,7] Although the found overlap of experiment and theory is not an unequivocal proof of validity, and the Hess−Klein theory was never made to consider the inherent structure and problems of "real systems", further work in this direction seemed to be very promising.

The aim of the present contribution therefore is a more critical benchmark testing of the modified Hess−Klein theory: Using the inherent formalism, it should be possible to directly relate structural data (as determined by light scattering) to viscometric data; i.e., it will be tried to relate two completely independent sets of experiments quantitatively without any additional parameter.

Theory

The *mode−mode coupling approximation* (MMCA) for electrostatically strongly coupling systems by Hess and Klein[5] (HK) relates the static structure of Brownian particles with their viscosity. Following the Green−Kubo relation, the viscosity of a medium is described by fluctuation of the mass flux, which is again controlled by intermolecular interaction potentials. The excess viscosity of an interacting system can be calculated by integration over time and momentum space of the static interactions and the diffusive processes. The HK theory considers multiparticle interaction without explicit assumption of a specific pair potential via the total density correlation function $h(r) = g(r) - 1$ or its Fourier transform $h(q)$. That way one can calculate for the excess specific viscosity

$$\eta_{\mathrm{sp}}^{\mathrm{HK}} = \frac{1}{80\pi^2} R_{\mathrm{H}} N^2 \int_0^{\infty} \mathrm{d}^3 q \left(\frac{\partial h(q)}{\partial q}\right)^2 \tag{1}$$

The total correlation function $h(q)$ can be connected to the structure factor $S(q)$ via $S(q) = 1 + Nh(q)$ where N is the particle number density. By introducing the "scattering property" $S(q)$, transformation into spherical coordinates, and integration over orientation space, one obtains

$$\eta_{\mathrm{sp}}^{\mathrm{HK}} = R_{\mathrm{H}} \frac{1}{20\pi} \int_0^{\infty} q^2 \left[\frac{\partial (S(q) - 1)}{\partial q}\right]^2 \mathrm{d}q \tag{2}$$

or the required connection between light scattering and viscometry due to intermolecular forces.

Until this point, the derivation is very general, and eq 2 can be used without any further assumptions to calculate the viscosity from the static structure by numerical differentiation and integration for each simple concentration where $S(q)$ was measured. This is one way how we will proceed in the Experimental Section.

To obtain a closed expression for the specific viscosity, one has to assume a distinct interaction potential. Taking the standard screened Coulomb potential

$$V(r) = \frac{Z^2 e^2}{4\pi \epsilon_{\mathrm{r}} \epsilon_0} \frac{\exp(-\kappa r)}{r} \quad \text{or} \quad V(q) = \frac{Z^2 e^2}{\epsilon_{\mathrm{r}} \epsilon_0} \frac{1}{\kappa^2 + q^2} \tag{3}$$

considering two particle interactions only, and elaborat-

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ing the whole formalism in the weak coupling approximation (WCA, $V(r) < kT$), Hess and Klein obtained

$$\eta_{\mathrm{red}}^{\mathrm{HK}} = \frac{1}{160}\left(\frac{4\pi e^2 N_{\mathrm{A}}}{\epsilon_{\mathrm{r}}\epsilon_0 kT}\right)^{1/2} \frac{R_{\mathrm{eff}}}{M_{\mathrm{w}}^{1/2}} \frac{Z_{\mathrm{eff}}^{4} c_{\mathrm{P}}}{\left(2\frac{M_{\mathrm{w}}}{M_{\mathrm{s}}}c_{\mathrm{S}} + Z_{\mathrm{eff}}c_{\mathrm{P}}\right)^{3/2}} \tag{4}$$

where M_{w}, M_{s} and c_{P}, c_{s} are the molecular mass and mass concentration of the polyelectrolyte and the added salt, respectively. R_{eff} and Z_{eff} represent effective values for radius and charge, as will be discussed below. In this step of an algebraic solution of eq 2, a number of assumptions can be questioned, and already the starting assumption of a screened Coulomb potential turned out to be experimentally wrong for most highly charged, coupled polyelectrolyte systems. This is especially true for the present polyelectrolyte microgels where static light scattering proved the existence of electrostatic attraction[2] but also found for dozens of other experiments which were listed in ref 2. For that reason, we also refrained from using more elaborated Hess–Klein-type descriptions as those of Nägele, who nicely incorporated multibody interactions and hydrodynamics, but on the basis of experimentally irrelevant potentials.[8,9] To our opinion, a more realistic picture of interparticle potentials in such systems was elaborated by Belloni et al.,[10–12] who recalculated the fields under consideration of nonlinear counterion condensation which results in non-mean-field ion–ion correlations; this approach results in very realistic interparticle potentials.

However, it is not the purpose of the present paper to enter this complicated discussion of complex coupled electrostatic effect, and it is not needed. It was experimentally also shown that the static structure factor and therefore the viscosity can be described within experimental uncertainty with a variety of different potentials[2] (and references therein) while the numerical parameters counterbalance the mistakes of the shape of the potential (i.e., a "wrong" potential leads to a rather good description, but with physically meaningless parameters). This is why we will use the "potential assumption" just for parametrization, and here, the tradional Hess–Klein approach is most simple and ends up with a single parameter, Z_{eff}.

From an experimental point of view, it also turned out that the measured viscosity not only is due to contributions from electrostatic interactions but also contains effects due to the space filling by the molecules as well as hydrodynamic interactions, which however can be treated in a classical way (with respect to hydrodynamics, polyelectrolyte solutions are dilute). For simplicity, the single-particle space-filling contribution $[\eta]_{\mathrm{e}}$ (to be understood analogous to the intrinsic viscosity of polymers as the volume occupied per gram of polymer), a Huggins contribution $k_{\mathrm{H}}[\eta]_{\mathrm{e}}^2$ (binary, dilute hydrodynamic interactions) and the electrostatic interaction term $\eta_{\mathrm{red}}^{\mathrm{HK}}$ are simply added

$$\eta_{\mathrm{red}} = [\eta]_{\mathrm{e}} + k_{\mathrm{H}}[\eta]_{\mathrm{e}}^{2} c_{\mathrm{P}} + \eta_{\mathrm{red}}^{\mathrm{HK}} \tag{5}$$

Cross-terms between hydrodynamic and electrostatic contributions coming from the Green Kubo relation are neglected here. By the standard relations of polymer solution theory,[13] the single particle term $[\eta]_{\mathrm{e}}$ can be translated into an effective viscometric radius R_{eff}:

$$[\eta]_{\mathrm{e}} = \frac{10\pi N_{\mathrm{A}}}{3M_{\mathrm{w}}} R_{\mathrm{eff}}^{3} = [\eta]_0\left(1 + \frac{r_{\mathrm{B}}}{R}\right)^3 \tag{6}$$

This effective viscometric radius is larger than the hard core microgel radius R, as found in viscometry and dynamic light scattering experiments.[1,2,6] In addition, dynamic light scattering measurements confirm the larger effective radius for our polyelectrolyte microgel system. It is possible to express the effective radius R_{eff} following Barker and Henderson[14] within a perturbation correction by adding a "Bjerrum radius r_{B}" to the hard-core radius, as it is done in the second part of eq 6.

The electrostatic effective intrinsic viscosity $[\eta]_{\mathrm{e}}$, a single particle property, is therefore composed of a "standard", molecular volume based intrinsic viscosity $[\eta]_0$, which in principle is accessible under high salt conditions, and a Bjerrum shell, which is occupied by a coupled counterion cloud and considers the hydrodynamic influence of the coupled counterion cloud. The Bjerrum radius is defined by the distance where electrostatic and kinetic energy balance:[1]

$$r_{\mathrm{B}} = \frac{1}{2}\frac{Z_{\mathrm{eff}}^{2}}{4\pi\epsilon_{\mathrm{r}}\epsilon_0 kT} \tag{7}$$

Results and Discussion

The analysis of the data is exemplarily delineated with the data set of sample K7**.** The size of this sample is $r_{\mathrm{H}}(\mathrm{NaCl}) = 44$ nm, as determined by dynamic light scattering in salt-containing solutions; the polydispersity is below 10%, as expressed as a Gaussian width.

The angular dependent light intensity is measured, normalized, and corrected for the form factor, as described in ref 2. The correction is rather uncritical and easy to perform, since the particles are small enough to possess a weak angular dependence of the form factor. The resulting structure factors are shown in Figure 1 (full symbols).

It is seen that we found no less than four oscillations of the structure factor within the q-window of shifted light scattering data. The accuracy of the following numerical integration procedures relies on the careful extrapolation to extend the q range (the integration base). For the low q part, this is done by the well-known Guinier extrapolation. For the more integration-relevant high q part, we take advantage of the fact that all scattering curves superimpose to a master curve after normalization in q and (slightly) in the ordinates.[2] Therefore, the structure factors measured for higher concentration samples can be numerically extrapolated by using a lower concentration structure factor (with more oscillations in the q range covered by the measurement). Figure 1 shows these extrapolations as full lines, together with the shifted data points of the low-concentration sample on which this extrapolation is based (open symbols).

Figure 2a,b graphically illustrates the calculation of the interparticle interaction contribution to the intrinsic viscosity: The data in Figure 2b are weighted with q^2, numerically integrated, multiplied with the effective radius (as determined by dynamic light scattering), and divided by the concentration as given in eq 2. This procedure is carried out for all concentrations, as shown in Figure 3. Due to the weighting with q^2, the data in the high q region significantly contribute to the integration result; the extrapolation to high q is of importance.

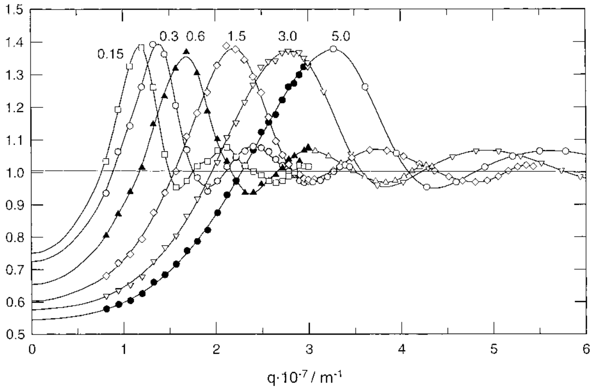

Figure 1. Extrapolated structure factors of sample K7 with r_H(NaCl) = 44 nm for different concentrations (in g/L). Since all structure factors do have the same shape (master curve behavior), extrapolation toward large *q* can be performed with the structure factors of the lower concentrations. The extrapolation toward small *q* is done with the Guinier approximation.

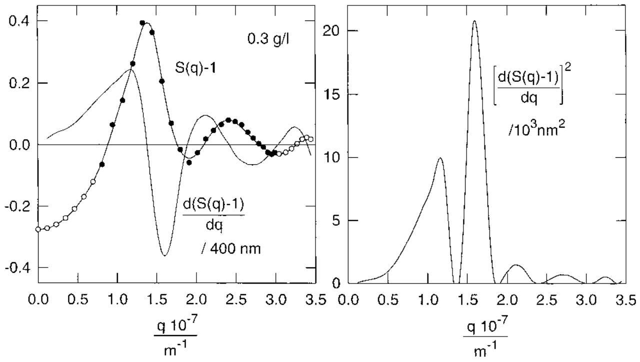

Figure 2. Graphical illustration of the numerical calculation of the intrinsic viscosity with the Hess–Klein MMCA for *c* = 0.3 g/L: (a) [*S*(*q*) − 1] and first derivative of the extrapolated structure factor; (b) squared first derivative of the structure factor.

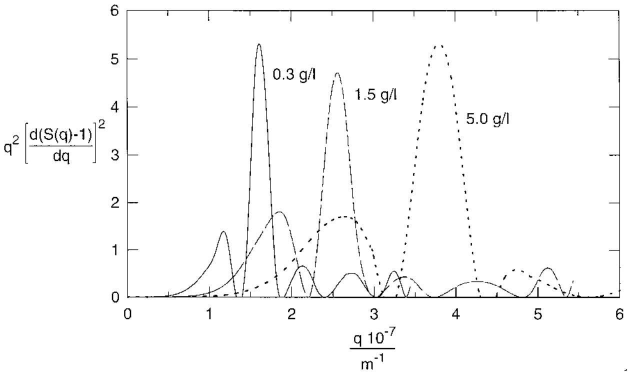

Figure 3. Graphical illustration of the numerical calculation of the intrinsic viscosity with the Hess–Klein MMCA (2): The squared first derivative is multiplied with q^2 for three different concentrations. The area below the curves multiplied with the effective hydrodynamic radius corresponds to the (dimensionless) interaction contribution to the intrinsic viscosity. (Note that for the 5 g/L sample data are calculated and further used up to a *q* value larger than plotted here.)

However, since the master curve is measured up to a *q* range where structure influence is low, the exact cutoff at high *q* after extrapolation is not critical, as can also be judged by the relative contribution of the areas under the curves at high *q* in Figure 3.

The final comparison of the intrinsic viscosity calculated solely from static and dynamic light scattering (the values contain the single particle contributions according to eq 5) and the experimental data as determined by Ubbelohde viscometry is shown in Figure 4.

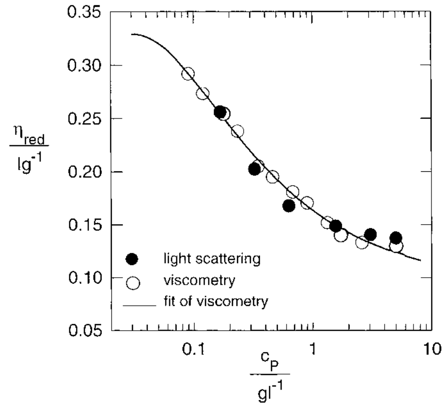

Figure 4. Comparison of the viscosity data calculated from scattering and experimental data from viscometry. Filled symbols: calculated values containing both single particle contributions and a concentration-dependent Hess–Klein MMCA interaction contribution. Empty symbols: viscosity data measured in an Ubbelohde viscometer. Full line: fit of the Ubbelohde data according to eqs 4–8. Here, a screened Coulomb potential and validity of the weak coupling approximation are assumed for parametrization, and the single particle contributions are added.

It is noteworthy that both magnitude and functional dependence of the two sets of data agree surprisingly well. This agreement reflects the fact that the polyelectrolyte effect in viscosity is mainly intermolecular in nature: The increase of the intrinsic viscosity with decreasing concentration is quantitatively related to the increase of intermolecular interactions. It is again underlined that, using the way of numerical integration, no specific interaction potential had to be assumed; the applied formalism is that universal that any experimental structure factor is converted into an interaction potential based viscosity.

It was nevertheless interesting to simplify the definitely more complicated pair potential[2] with a screened Coulomb potential, which then allows algebraic integration. In the weak coupling approximation, i.e., $V(r) < kT$ (which is justified per definition at larger distances outside the Bjerrum shell), eq 4 was obtained.[5] After addition of the single particle contribution as indicated by eq 5, the whole expression is fitted to the experimental data. This fit is shown in Figure 4 as a full line and describes the data rather well with the effective charge of the polyion Z_{eff} being the only fit parameter. k_H and R_{eff} were taken from hydrodynamic measurements. The effective radius used for calculations has been measured in the salt-free solution itself by dynamic light scattering via the apparent diffusion coefficient extrapolated to diminishing concentration, i.e., in the "allowed concentration regime" where single particle properties can be measured and no slow mode is observed. For this sample, the result is 72 nm. Alternatively, it can be estimated from viscosity measurements itself, resulting in a value of 70 nm. Additionally, the increased effective radius has been further confirmed by ultracentrifugation experiments. k_H is obtained as fit parameter from the viscosity data; for a discussion see also ref 1. The value of k_H for the results presented here is 0.08; i.e., the contribution of this term is not of numerical importance for salt-free polyelectrolyte solutions where the Hess–Klein multiparticle interaction dominates. We have however included this parameter in our additive approach, since it becomes of larger relative importance for salt-containing solutions, as has been discussed in ref 1. The magnitude of Z_{eff} was already discussed in ref 1; it is important to state that it has nothing to do with the real charge but is something like an equivalent effective charge seen outside the Bjerrum radius under an equivalent screened Coulomb field.

It is necessary to mention that the structure factors of the samples were determined shortly after stirring of the solution in the light scattering cells. All samples undergo slow colloidal crystallization where the structure factor develops sharper and more intense peaks. Following the procedure delineated above, much higher viscosities (at least 1−2 orders of magnitude larger) would be calculated; i.e., the sample is really in a transition from a complex fluid to a colloidal crystal. However, a similar increase of the calculated intrinsic viscosity of such samples with decreasing concentration is obtained. It is open by which technique such viscosities of colloidal crystals can be measured. The Ubbelohde setup is intuitively expected to characterize a situation closer to the freshly stirred complex fluids, and effects such as shear thinning or shear ordering which might contribute are obviously not relevant for the described data set.

Conclusion

Spherical polyelectrolyte microgels with high charge density and with just weak van der Waals interactions exhibit in salt-free aqueous solutions phenomenologically similar effects as linear polyelectrolytes: both a steep increase of the reduced specific viscosity with decreasing concentration and formation of ordered solution structures were found.

Since these colloidal polyelectrolyte models realize a situation that is as close as possible to the prerequisites of polyelectrolyte theory, i.e., pointlike charges without additional Hamaker or excluded-volume interactions, it was possible to perform a benchmark testing of the mode−mode coupling approximation, as at first introduced by Hess and Klein. Here, the viscosity effects due to interactions are related to the intermolecular structure; in other words, static light scattering can be used to predict the concentration-dependent viscosity from the scattering curves. For the samples examined here, the curves were both qualitatively and semiquantitatively reproduced, while there was no free parameter in the calculation. This clearly underlines previous statements that there is no pronounced intramolecular structural rearrangement required to explain the physicochemical behavior of polyelectrolytes.

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References and Notes

(1) Antonietti, M.; Briel, A.; Förster, S. *Chem. Phys.* **1996**, *105*, 7795.
(2) Gröhn, F.; Antonietti, M. *Macromolecules* **2000**, *33*, 5938.
(3) Schmitz, K. S. *Macroions in Solution*; VCH: Weinheim, 1993.
(4) Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 53.
(5) Hess, W.; Klein, R. *Adv. Phys.* **1983**, *32*, 173.
(6) Antonietti, M.; Conrad, J.; Förster, S.; Zisenis, M. *Macromolecules* **1995**, *28*, 2270.
(7) Antonietti, M.; Briel, A.; Förster, S. *Macromolecules* **1997**, *30*, 2700.
(8) Banchio, A. J.; Nagele, G.; Bergenholtz, J. *J. Chem. Phys.* **1999**, *111*, 8721.
(9) Nagele, G.; Bergenholtz, J. *J. Chem. Phys.* **1998**, *108*, 9893.
(10) Belloni, L.; Spalla, O. *J. Chem. Phys.* **1997**, *107*, 465.
(11) Belloni, L.; Spalla, O. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 905.
(12) Belloni, L. *Colloids Surf. A* **1998**, *140*, 227.
(13) Flory, P. J. *Principles of Polymer Chemistry*; Cormell University Press: Ithaca, NY, 1953.
(14) Barker, J. A.; Henderson, D. *Annu. Rev. Phys. Chem.* **1972**, *23*, 439.

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