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Electrokinetic Properties of Aqueous Suspensions of Rodlike fd Virus Particles in the Gas- and Liquidlike Phase

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Introduction. The structural and dynamic properties of suspensions of rodlike particles have been the subject of many experimental and theoretical investigations.[1-5] In nature, good representatives are found by different macromolecules, e.g., various viruses and micelles. Most of them possess acidic or basic groups at the surface. Therefore, when the particles are suspended in water, these groups dissociate partly, leading to an electric charge of the macromolecules. The accompanying electric interaction gives rise to different spatial order patterns of the rods and to new features in the diffusive properties.

Electrophoretic light scattering (ELS) monitors the mobility of the macroparticles in an external electric field. Taking the Gouy–Chapman theory as a basis, the mobility depends sensitively on the structure and charge of the Stern layer and the surrounding diffuse ion cloud. In particular, measurements as a function of ionic strength can give valuable insight into different charging mechanisms inside the Stern layer.

Recently we have investigated the electrokinetic properties of aqueous suspensions of tobacco mosaic viruses.[6] Again we were particularly interested in the conductivity and electrophoretic mobility μ at small ionic strength. Values down to 10^{-6} M could be achieved. It turned out that the electrophoretic mobility in the salt-free case decreases steadily with increasing particle concentration. When salt is added at a fixed particle concentration, the mobility changes smoothly without a relative maximum as has been observed for aqueous suspensions of latex spheres.[7]

In order to find out whether our recent observations are typical for rodlike systems, we have extended measurements to suspensions of fd virus particles. This virus has a length of 880 nm and a diameter of 9 nm; it is only slightly flexible.[8]

Experimental Section. Determination of the Debye–Hückel Parameter. For the interpretation of the data, the Debye–Hückel parameter κ, i.e., the small ion concentration, is required. It is determined by a measurement of the electric conductivity. If we assume that all small ions outside the plane of shear move independently from each other and from the viruses, the conductivity of the suspension can be written as

$$\sigma_{\text{tot}} = c_s e(\mu_{\text{Na}^+} + \mu_{\text{Cl}^-}) + c_p Z_{\text{eff}} e(\mu_{\text{H}^+} + \mu_p) + c_{\text{OH}^-} e\mu_{\text{OH}^-} \quad (1)$$

Here the mobilities of the small ions at infinite dilution μ_{Na^+}, μ_{Cl^-}, μ_{H^+}, and μ_{OH^-} can be taken from the literature,[9] while the mobility of the viruses is measured in the electrophoretic experiment. c_p and c_s are the particle and salt (NaCl) concentration, respectively, and Z_{eff} is defined as the effective charge number of a macroparticle transported in the electric field. Therefore, there are Z_{eff} H^+ ions per macroion.

To derive the Debye–Hückel parameter κ, the effective charge number Z_{eff} and the salt concentration are needed. For sufficiently large particle concentrations the OH^- concentration is small and can be neglected. In salt-free suspensions there are only the macroions with their H^+ counterions left, and Z_{eff} is given by

$$Z_{\text{eff}} = \frac{\sigma_{\text{salt free}}}{c_p e(\mu_{\text{H}^+} + \mu_p)} \quad (2)$$

In this equation, a mean value for μ_p is used. Since μ_{H^+} is considerably larger than μ_p its variation implies only small changes in Z_{eff}.

The salt (NaCl) concentration c_s is obtained by eq 1 neglecting the OH^- ions

$$c_s = \frac{\sigma_{\text{tot}} - \sigma_{\text{salt free}}}{e(\mu_{\text{Na}^+} + \mu_{\text{Cl}^-})} \quad (3)$$

Here $\sigma_{\text{salt free}}$ is the measured conductivity of the salt-free suspension. Only a very small amount of salt has to be added for studying suspensions of small and moderate ionic strength. Its exact concentration is difficult to determine by addition, but this can be sensitively achieved by measuring σ_{tot} and $\sigma_{\text{salt free}}$. Mostly the latter value can be neglected. The Debye–Hückel parameter can now be calculated by means of the well-known relation

$$\kappa = \left(\frac{e^2}{\epsilon\epsilon_0 k_B T}(Z_{\text{eff}} c_p + 2c_s)\right)^{1/2} \quad (4)$$

The model above is of course rather simple, because the small ions are considered as independent from each other. In reality, the mobilities are a function of their concentration and the particle concentration c_p. Retardation and relaxation effects of the small ions in the suspension and within the double layer of the macroions should be included. These effects may lead to a decrease of the mobilities of the small ions.[10] However, at the concentrations used in the investigations (<1 mmol/L), these changes are negligible. On the other side, one has to bear in mind that the mobilities of the H^+ ions inside the ion clouds are lowered. Therefore, the calculated charge number Z_{eff} is too small.

Sample Preparation and Electrophoretic Light Scattering Apparatus. The fd stock suspension was prepared with the help of Prof. Rasched and L. Cobianchi (Fakultät Biologie). To obtain small ionic strengths, the suspension is moved with a tube pump[11] from a reservoir through an ion-exchange resin directly into the electrophoretic cell and back. A filter keeps the resin and dust particles back. The conductivity of the suspension can be

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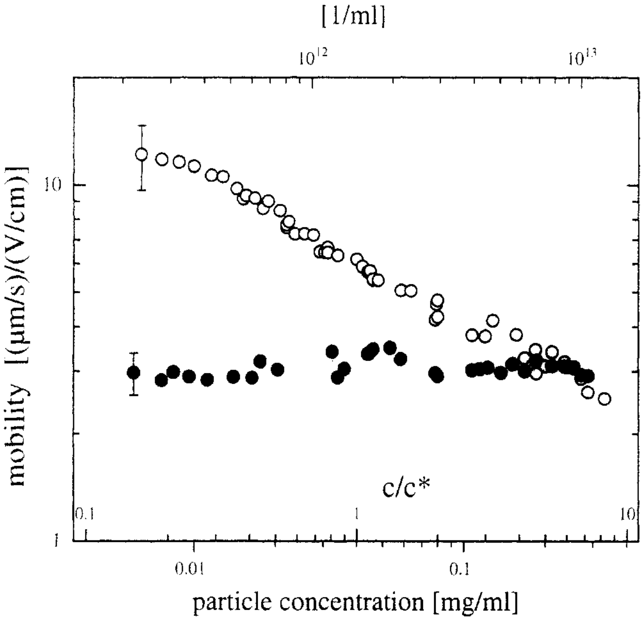

Figure 1. Electrophoretic mobility versus particle concentration for salt-free suspensions (○) and for suspensions at c_s = 0.8 mmol/L (●).

measured immediately behind the electrophoretic cell. To determine the mobility as a function of salt concentration, the ion exchanger was bypassed and an appropriate quantity of carefully neutralized NaCl was added to the sample.

The electrophoretic mobility measurements were carried out with a conventional ELS apparatus (Zetasizer II, Malvern Instruments, England). Merely, its HeNe laser (5 mW) was exchanged by a more powerful one (35 mW). A detailed description of the apparatus is given elsewhere.[12] The electrophoretic mobility of the viruses is independent of the applied electric field. Therefore, we can assume that neither the electric field nor the velocity gradient in the electrophoretic cell alters the orientation of the rods. The orientation distribution is isotropic.

According to eq 1 the conductivity of salt-free suspensions neglecting the OH^- ions is proportional to the charge number Z_{eff}. From the corresponding measurements a mean charge number of Z_{eff} = 400 is obtained.

Results and Discussion. Figure 1 shows measurements of the fd virus mobilities as a function of particle concentration. The mobilities were measured on salt-free suspensions as well as on suspensions at a salt (NaCl) concentration of about 0.8 mmol/L. The smallest macroparticle concentration providing a detectable scattered signal was 0.15c*. Nevertheless, at small ionic strength particle–particle interaction is still present. This can be concluded from static light scattering measurements which give still a well-defined static structure factor. First let us have a look at the mobilities of the completely deionized suspensions. With increasing particle concentration the mobility decreases continuously. A linear fit in the log–log plot yields a proportionality of $\mu \propto c_p^{-0.41}$. It seems reasonable to correlate the decrease in mobility at small ionic strength to macroparticle interaction. The only theory in this direction (for spherical particles only) is due to Levine and Neale,[13,14] who discuss friction effects occurring with increasing double layer overlap, which lead to a decrease in the mobility. This effect can lower the mobilites in our measurements, since in salt-free suspensions the double layers are expanded widely. With increasing particle concentration, the overlapping of the double layers increases and therefore the mobility decreases. Another fact we have to consider is that the higher the particle concentration, the lower is the resulting pH value of the suspension, due to the dissociation of H^+ ions from the virus surface. But the lower the pH value, the smaller the dissociation degree of the acidic virus surface groups, leading to a smaller virus charge. So this effect also reduces the mobility with increasing particle concentration.

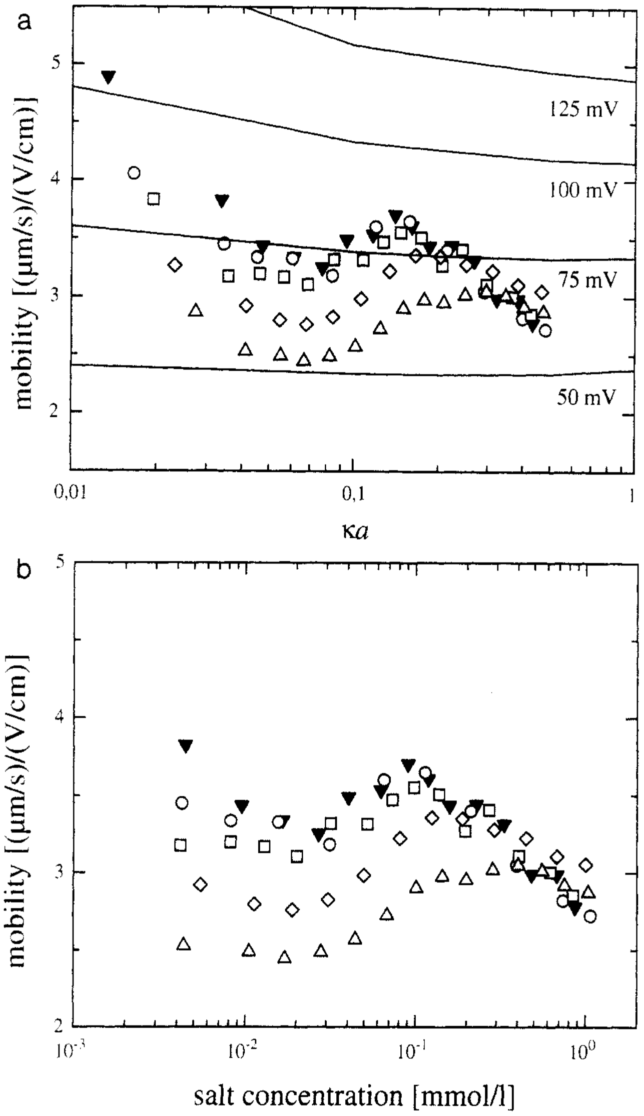

Figure 2. (a) Electrophoretic mobility versus κa: (▼) 1.7 c*; (○) 2.6c*; (□) 3.6c*; (◇) 5.1c*; (△) 7.2c*. The full drawn lines are from theory[10] corresponding to noninteracting particles. (b) The same electrophoretic mobilities as in Figure 2a, plotted as functions of added salt concentration.

In the salt case the virus charges are completely screened and there exists no double layer overlap respectively interparticle interaction. Therefore, we should expect higher mobilities as in salt-free suspensions. Nevertheless, the measured mobilities lie beyond these and have a constant value of about 3 (μm/s)/(V/cm) over the whole investigated particle concentration range. So there has to be another effect which lowers the particle mobility. Zukoski and Saville,[15] for example, show that we have to be aware of counterion adsorption (and also with smaller extent co-ion adsorption) which lowers the net charge of the particles. This could explain the smaller particle mobilities of salt-containing suspensions compared to those of salt-free ones. The fact that the mobilities do not depend on particle concentration in salt-containing suspensions shows that either the pH-value dependence of the mobility is only weak or it is compensated by ion adsorption.

In Figure 2a the mobility of various particle concentrations is plotted versus κa. At low ionic strength the mobility decreases with increasing κa. But at κa values of about 0.07 the mobility passes through a minimum and increases to a maximum value at κa values between 0.1 and 0.3 depending on particle concentration. To higher salt concentrations, the mobilities of all particle concentrations decrease continuously. The lines in Figure 2a show the mobilities of noninteracting rodlike particles versus κa for various ζ-potentials predicted by the standard theory.[10,16] There is no correlation between the theoretical and experimental curves. Various qualitative explanations for this maximum observed already in latex suspensions have been proposed. Two of these models are the preferential adsorption of counterions and co-ions at the surface mentioned above and the hairy layer model.[15,17]

In Figure 2b the same results as in Figure 2a are now plotted as a function of the added salt concentration (whereby we had to omit the data point measured at minimum ionic strength, i.e., at zero NaCl concentration). These curves have qualitatively the shape as predicted by Zukoski and Saville[15] for suspensions of spherical particles; in their theory adsorption and desorption processes in the Stern layer are taken into account.

Following the line of Zukoski and Saville, we explain qualitatively the strong decrease at small salt concentrations with the adsorption of counterions (here mainly Na^+) in the Stern layer, reducing the surface charge density of the virus. The minimum in the mobility appears since the counterion adsorption sites are saturated and the co-ion adsorption predominates, resulting in an increasing particle surface charge. Finally, to higher salt concentrations, the mobility decreases due to the compression of the double layer.

It is useful to compare the results on fd suspensions with those on TMV.[6] Data on the latter at small ionic strength are very similar to the results reported here. Measurements of the salt dependence of the mobility of TMV suspensions were originally performed under slightly different conditions than described here. We have repeated these measurements in exactly the same way as for fd particle suspensions. No maximum was observed in the mobility. If Zukoski and Saville's theory is applicable, we may conclude that adsorption of co-ions is less important for TMV suspensions.

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