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Does the Maximum in the Zeta Potential of Monodisperse Polystyrene Particles Really Exist? An Electrokinetic Study*

Ab J. van der Linde and Bert H. Bijsterbosch

Department of Physical and Colloid Chemistry, Wageningen Agricultural University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

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The zeta potential of monodisperse polystyrene latices as a function of ionic strength is usually reported to display a maximum. In this paper it is shown that this is either due to artefacts in measuring streaming currents and electrical conductances of plugs, or to the anomalous surface conductance inherent to these systems not being accounted for in the theories relating electrophoretic mobilities to zeta potentials.

INTRODUCTION

Ever since their discovery (as early as 1809[1]) electrokinetic phenomena have been used for the electrical characterization of interfaces in dispersed systems. Whereas originally only qualitative aspects, such as the sign of charge, were assessed, later on also quantitative information ensued. This was enabled by the introduction of quantitative relations between measured quantities and the zeta potential, the potential at the electrokinetic slipping plane. Gradually these theories became more involved, taking the intricate relation of particle size and shape to the thickness of the double layer into account.[2,3]

Electrophoresis is the experimental technique that has most abundantly been used, which is quite understandable considering its relative ease of operation.[2] Also theoretically has the emphasis for a long time been on this technique. Nevertheless, electrophoresis does have its limitations since it can not be employed in concentrated dispersions and is difficult (if at all) to perform in non-stable systems. Therefore electrokinetic techniques that are suitable for characterization of concentrated dispersions (and membranes, for that matter), such as electroosmosis and streaming potential have also gained a fair amount of attention. Although for these phenomena the theoretical foundation was laid by Smoluchowski as well[3], its further development was especially accomplished in the past two decades.[4,5] These advanced theories particularly account for overlap of double layers of individual particles.

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A definite advantage of studying concentrated systems is that the extent of (anomalous) surface conductance can very easily be assessed.[6] This enables verification of pertinent boundary conditions that are set out in formulating the various theories.

As most of the theories deal with spherically shaped particles of identical size, the introduction of monodisperse polystyrene latices[7] appeared to offer excellent chances for experimental verification of these theories and likewise of other quantitative relations developed in the area of colloid chemistry.[8] Unfortunately, doubt has arisen as to the presumed hard core character of these particles. Particularly the occurrence of a maximum in the zeta potential as a function of ionic strength has substantially contributed to this doubt.[9] However, the inferred existence of said maximum itself is open to criticism. In order to fully comprehend this accusation, it should be stressed that zeta potentials can never be measured directly, but are always quantities derived from experimental data by employing some theory. So, any dificiency in the data or the theory shows up in the inferred zeta potentials. The point at stake is that, beyond any doubt, electrophoretic mobility of polystyrene passes through a maximum when the ionic strenght is varied. However, the equations usually employed in the conversion of mobilities into zeta potentials[2,10] do not account for any contribution of the surface conductance beyond that of the diffuse double layer. It has been demonstrated that such an anomalous contribution can be rather substantial.[6,11,12] Very recently, Midmore and Hunter[12] have shown that if this additional surface conductance is properly accounted for, the maximum in the mobility does *not* imply a maximum in the zeta potential. The electrokinetic potential appears to be a smooth function of the ionic strength, as expected.

Considering this observation, it is worth elaborating what streaming potential, streaming current and conductance data obtained on concentrated systems (plugs) made up of the same latices of which electrophoretic mobilities are available, can contribute to this discussion. Most of the relevant data has been published before,[6,11,13,14] but can be assessed in combination with a number of new data obtained on plugs of monodisperse silica.

EXPERIMENTAL

Methods

Electrophoretic mobilities were measured with a Zetasizer II (Malvern Instruments, England).

Streaming currents, streaming potentials and conductances were either obtained with a four-electrode or with a two-electrode cell.[6,11,18]

Materials

The preparation, cleaning and characterization of the positively and negatively charged polystyrene latices has been described before.[6,11,13,15]

The silica particles were prepared by hydrolysis of tetraethoxysilane in alcohol, according to Stöber *et al.*[16] The particle radius, as obtained by electronmicroscopy, amounts to 500±30 nm.

All chemicals were of A. R. quality, whereas water was always purified by the Millipore technique of reverse osmosis followed by percolation through charcoal and mixed bed ion exchange resins.

RESULTS AND DISCUSSION

To start with, we investigate what effect adsorbed polyelectrolytes exert on the maximum as it is observed in *electrophoresis*. Figure 1. illustrates the

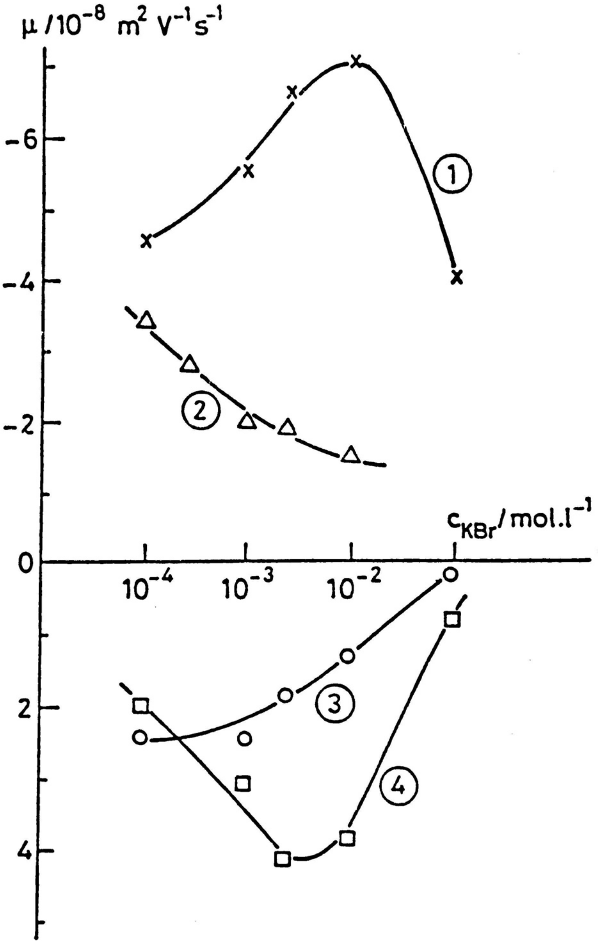

Figure 1. Electrophoretic mobilities (μ) of negatively charged polystyrene particles covered with different amounts of poly-L-lysine (of two different degrees of polymerization) as a function of the ionic strength. 1. bare latex; 2. 0.07 mg/m^2 PL_{260}; 3. 0.27 mg/m^2 PL_{19}; 4. 0.25 mg/m^2 PL_{260}.

effect of increasing amounts of adsorbed poly-L-lysine (PL) on the electrophoretic mobility of negatively charged polystyrene particles.[13] Line 1 refers to the bare particles (no PL adsorbed al all) and clearly demonstrates the maximum in the zeta potential as a function of ionic strength. When subsequently PL is adsorbed, but in a smaller quantity than necessary to fully compensate the surface charge of the particles (curve 2) not only does the mobility decrease, but, most strikingly, does the maximum disappear. Apparently, the decrease in charge density and the change in surface composition cause a different behaviour. The layer of grafted polyelectrolyte chains that is present on the bare surfaces and which is presumably rather loose (»hairy«), has been covered by a layer of adsorbed polyelectrolyte which according to polyelectrolyte adsorption theory[17] is more compact. Not only is thus the position of the slipping plane with regard to the particle surface less prone to variation in the electrolyte concentration, also has the amount (and thus the effect) of any surface conductance located between particle surface and slipping plane diminished. In this connection it is worth memorizing that surface conductance exerts its effect at low ionic strength and thus most likely causes the zeta potentials at the left side of curve 1 to be too low.[12,14]

When more PL is adsorbed than required to compensate the particle charge, but less than can be accommodated at full coverage (line 3), the electrokinetic charge changes sign. Due to the still compact structure of the adsorbed layer, curve 3 is more or less a mirror image of curve 2 with respect to the abscissa.

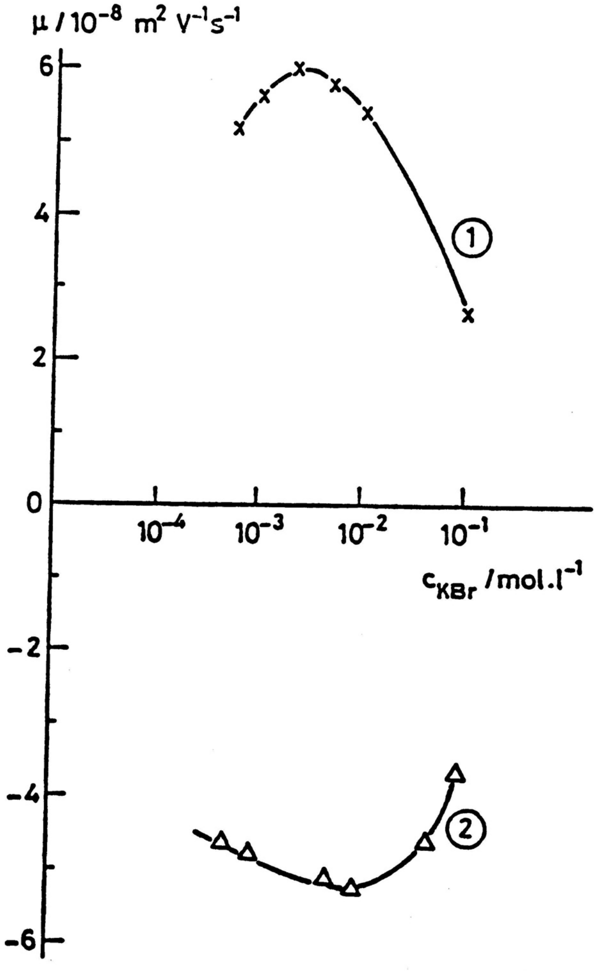

Figure 2. As Figure 1, for positively charged PS latex covered with poly-L-glutamate. 1. bare latex; 2. 0.72 mg/m^2 PGA$_{210}$.

If, however, the surface is completely covered with PL, loops and tails contribute to the conformation of the surface layer. Consequently, another hairy-like particle is created implying sensitivity of conformation towards ionic strength and increased surface conductance. Not surprisingly, curve 4 thus has the same shape as curve 1, including a maximum. Remember, however, that a maximum in the mobility not necessarily implies a maximum in the zeta potential.

Figure 2 demonstrates that the occurrence of a maximum is not limited to negatively charged latices, since positively charged samples behave analogously (curve 1).[13] Here too, it appears that complete coverage with an oppositely charged polyelectrolyte (poly-L-glutamate) causes the maximum to reappear, though with reversed sign (curve 2).

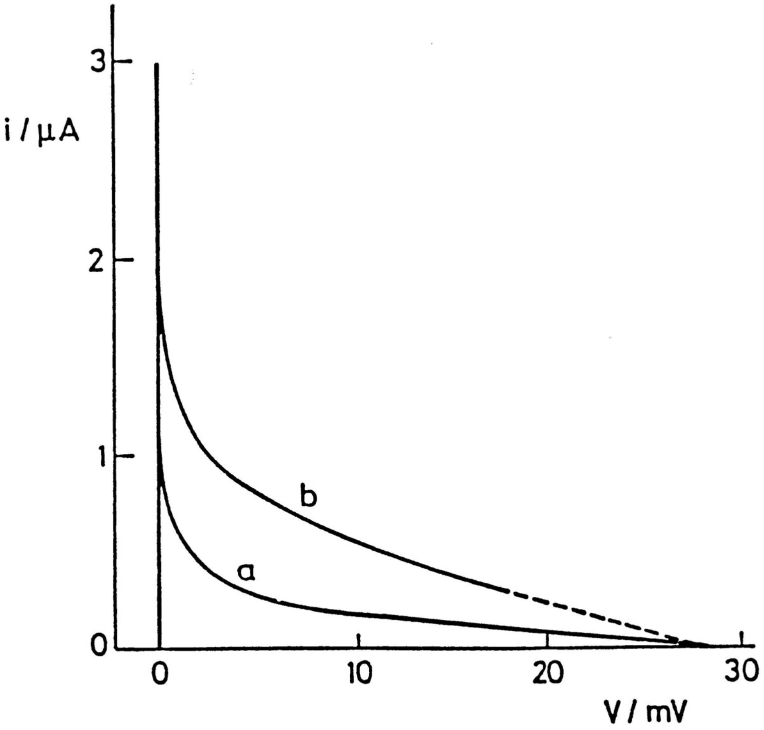

Figure 3. I-V plots of a plug consisting of PS latex for two different types of electrodes: a) blank platinum; b) platinizad platinum. (From ref. 18 with permission from Elsevier Science Publishers B. v.)

Before discussing the data obtained on plugs, we have to digress to some extent on the way the experimental data for these systems have been obtained. The four-electrode arrangement[11] enables to simultaneously measure the current, I, between two electrodes making direct contact with the plug and the potential, V, between two electrodes in the reservoirs containing the equilibrium solution. I and V, as they arise when a hydrostatic pressure is applied across the plug and the equilibrium solution is forced through it, can be introduced as ordinate and abscissa values in a so-called I—V plot, of which

Figure 3 is an example. This example clearly shows that the result is very much dependent on the type of electrodes that is being used, curve a referring to blank platinum and curve b to platinized platinum electrodes. Extrapolation of both curves to $I = 0$ provides a value for the potential that has been demonstrated be unequivocally identical to the streaming potential V_s.[11] Since the slopes of the two curves are different, one would have to infer, however, that the conductance of the plug depends on the electrode material used in its assessment, which is an obvious impossibility. Equally impossible would be the inference that the streaming current I_s, obtained by extrapolating the straight parts of the curves to $V = 0$, would be electrode-dependent. By analyzing this electrode dependency in some more detail and especially by analysing the independently obtained frequency dependence of the plug conductance, we were able to show that electrode polarization phenomena are responsible for the distinctions in the two I—V plots.[18] Consequently, is it impossible to correctly measure streaming currents. Moreover, it is experimentally much easier to directly measure V_s and the a. c. conductance (at frequencies ranging around 10^3 Hz), which together provide essentially the same information as I_s.

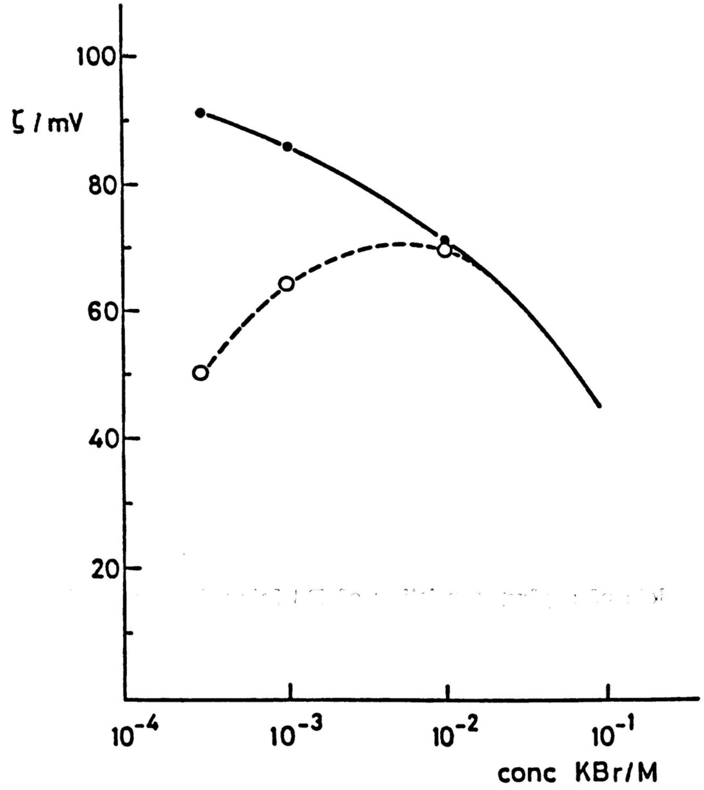

Figure 4. Zeta potentials for a plug of PS latex, as calculated according to Levine. Dashed line, as calculated with the d.c. conductance; full line, as calculated with the a.c. conductance. (From ref. 18 with permission from Elsevier Science Publishers B. v.)

The interesting observation ensues that zeta potentials for polystyrene plugs as obtained from I—V plots obtained with non-reversible electrodes, or by applying the d. c. rather than the a. c. conductance do show a maximum in dependence on the ionic strength. This is illustrated by the dashed line in Figure 4.[18] So we are actually facing an example of an experimental artefact. By properly employing the a. c. conductance in the conversion of V_s into zeta the maximum disappears, as shown by the full line.

It has to be explicited that in the V_s-ζ conversion involved in Figure 4. the Levine theory for capillary geometry[19] has been used. Obviously, modelling plugs of small particles as a bundle of straight capillaries is a poor representation of the actual structure. Reality will be much better represented by cell theories as the one O'Brien[5] has developed for electroosmosis (or for streaming potentials, for that matter). O'Brien's theory does not provide an analytical expression relating the measured streaming potential and conductance signals to the zeta potential. For various ionic strengths, sets of streaming potentials[5] and conductances[20] are provided that go along with a set of selected ζ-potentials. In practice this means that for a given plug at given conditions the experimental data for streaming potential and conductance should correspond. Quite clearly, however, for polystyrene they do not, the experimental con-

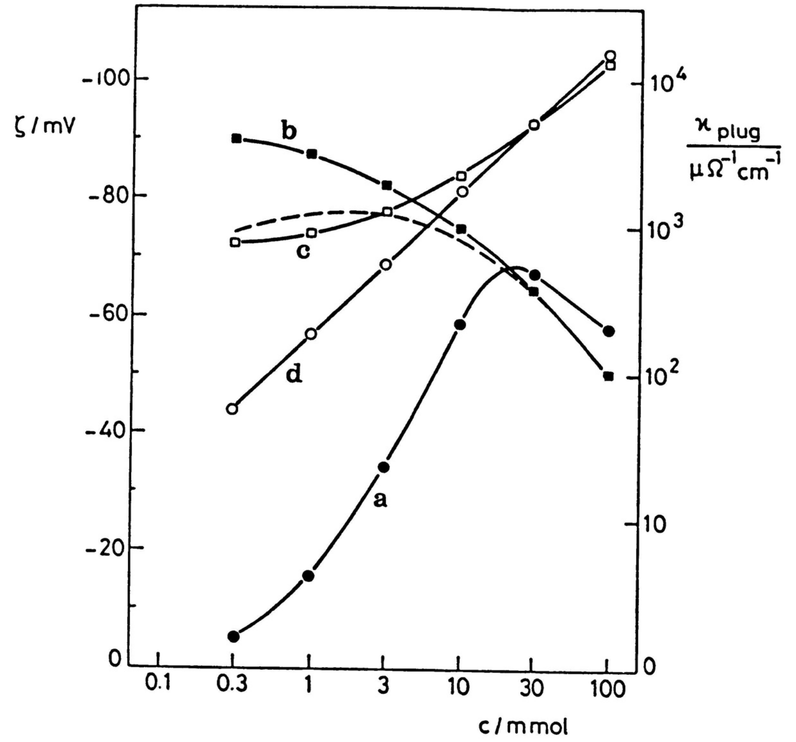

Figure 5. Data for PS latex a,b: ζ potentials according to O'Brien and Levine, respectively: c, d: conductivities, experimental and according to O'Brien, respectively; dashed line: see text

ductance always surpassing the value that should go along with the observed value of the streaming potential (curves c and d in Figure 5.). This is another indication that under most circumstances not only the diffuse double layer contributes to the surface conductance (a contribution that is properly accounted for in O'Brien's theory) but that a process of additional conductance between slipping plane and particle surface is operative. These high conductances cause ζ-potentials calculated from the observed streaming potentials to be too low, particularly at low electrolyte concentrations. This effect quite likely explains the maximum in the ζ-log c curve (line a in Figure 5.) that is inferred from these measurements as well. It is rather striking that this maximum disappears when the data is multiplied by the ratio of the actually measured conductance and the value that according to O'Brien should go along with the measured value of the streaming potential. The resulting (dashed) curve not only illustrates the disappearance of the maximum, but also the results to almost coincide with those obtained when applying Levine's capillary theory (curve b). In passing it is worth mentioning that the actual conductances being so high cause the ζ-potentials directly inferred from that date to be higher than those inferred from the corresponding streaming potentials. This effect has been discussed by O'Brien[5] and Zukoski and Saville.[21]

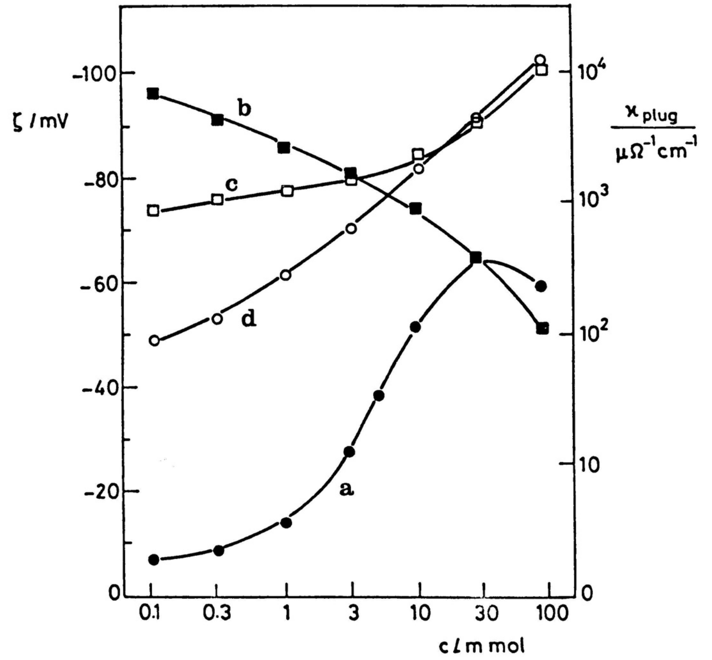

Figure 6. As Figure 5, for silica at PH = 8.5

Having established that the maximum for polystyrene latex in all likelihood is caused by the anomalously high conductance,it is of some interest to establish if this effect is typical for latices or that it also occurs for other compounds. To that purpose, we have investigated plugs of monodisperse silica particles. Since the surface charge density of oxides is dependent on the pH, this parameter constitutes an additional variable.

Figure 6 refers to a silica plug of pH 8.5, corresponding to complete dissociation of all surface silanol groups. Curve a representing ζ-potentials being calculated from streaming potential data by means of O'Brien's tables and curve b corresponding to those obtained by Levine's theory, the similarity with the results for polystyrene in Figure 5 is striking. Curve c shows the actual conductance of the plugs to be (much) higher again than what according to O'Brien (curve d) would have to go along with the measured streaming potentials (note the logarithmic scale of the ordinate). So, for silica at pH 8.5 equally well as for polystyrene a mechanism of anomalous surface conductance appears to be operative.

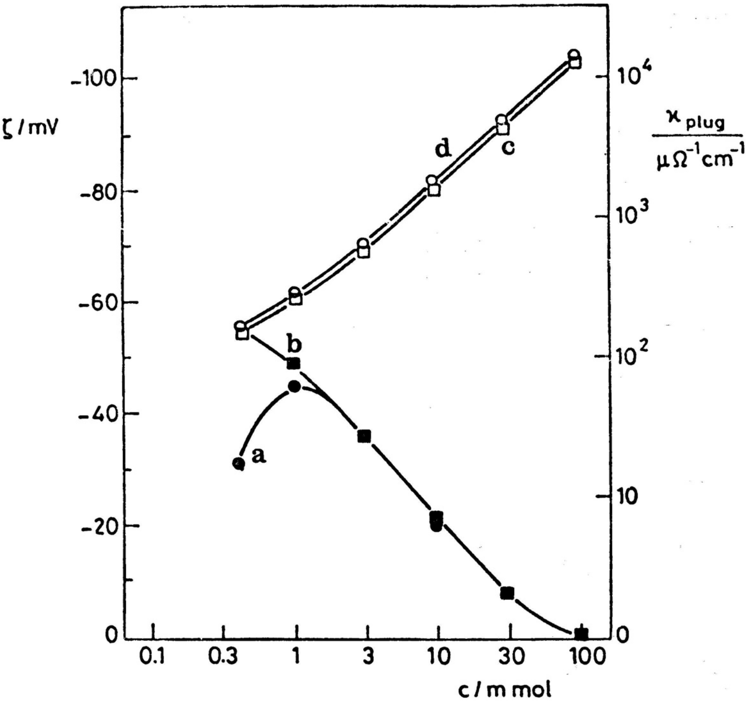

Figure 7. As Figure 5, for silica at PH = 4.

The surface charge density of silica being so strongly pH-dependent raises the question if this mechanism is also around at much lower values of surface charge density and thus of pH. The answer is given in Figure 7, the data of which was obtained at pH 4. The experimental conductance, curve d, appears to be only slightly higher than the theoretically predicted curve c. In line with this close correspondence the ζ-potentials calculated according to O'Brien (curve a) and Levine (curve b) also match, except below 10^{-3} M. Obviously, the extent and effect of extra conductance is related to the magnitude of the surface charge density, a conclusion that was also reached in a study on the effect of adsorbed tetraalkylammonium ions on the electrokinetic behaviour of negatively charged polystyrene.[11]

All evidence leads to the conclusion that a maximum in the zeta potential of polystyrene latices as a function of ionic strength in all likelihood does not exist. Either its occurrence is based on experimental artefacts, like in their calculation from presumed streaming currents, or is due to the actual surface conductance not properly being accounted for in the relevant theories.

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SAŽETAK

Da li maksimum u zeta-potencijalu monodisperznih polistirenskih čestica zaista postoji? Elektrokinetička istraživanja

Ab J. van der Linde i Bert H. Bijsterbosch

U radu se ukazuje na podatke u literaturi o maksimumu zeta-potencijala u ovisnosti o ionskoj jakosti medija. Mjerenjima elektroforetske gibljivosti, potencijala i struje strujanja, te površinske vodljivosti za monodisperzni polistirenski lateks, za negativno nabijeni lateks s adsorbiranim poli-L-lizinom, za pozitivno nabijeni lateks pokriven poli-L-glutamatom, i uspoređujući te podatke s onima za siliku, zaključuje se da su maksimumi eksperimentalne pogreške. Uzrok se tome nalazi u površinskoj vodljivosti koja proističe ne samo iz difuznog dijela dvosloja, već i iz doprinosa vodljivosti između ravnine smicanja i površine čestica.