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SHORT COMMUNICATION

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Examination of the atypical electrophoretic mobility behavior of charged colloids in the low salt region using the O'Brian–White theory

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Abstract Polystyrene microspheres having roughly the same size but different negative surface charge densities were prepared by emulsion polymerization. The amount of sulfate groups on the surface of the particles was controlled by variation of the amount and the decomposition rate of the initiator used, potassium, persulfate. After the cleaning process involving dialysis and extensive ultrafiltration the surface-charge density of the samples was determined and their electrokinetic behavior was studied.

A simple model based on the Gouy–Chapman theory and the O'Brian–White approach allows the calculation of the dependence of the electrophoretic mobility on salt concentration. Comparison of the theoretical and experimental curves showed that they were in good agreement in a number of qualitative features. Moreover, the model revealed that a monotonously increasing zeta potential with falling electrolyte concentration results in a mobility maximum, and that this so-called atypical behavior is in accordance with the standard electrokinetic theory. No ion adsorption mechanism or the existence of a charged hairy layer, current standard explanations for this anomality, had to be invoked.

Key words Polystyrene latices – electrophoretic mobility – zeta potential

Introduction

For some years, scientists have been puzzled about an atypical electrokinetic behavior of charged colloids in that the expected decrease of the electrophoretic mobility with increasing electrolyte concentration is only found at fairly high (>0.01 M) concentrations of the added electrolyte [1–3]. In the lower concentration regime the mobility however increases with concentration, so that the curve exhibits a maximum. In order to explain this apparent anomaly, a number of different models have been suggested. The hairy layer model involves an outward shift of the shear plane at lower electrolyte concentrations [4], and the co-ion adsorption model attributes the mobility maximum to the competing effects of preferential enrichment of the co-ions near the surface region, which compresses the electrical double layer [5]. A further route of explanation is given by the assumption of an anomalous conductivity within the shear plane [6–8]. All these models were compared and extensively discussed in a recent, advisable review [3].

A different attempt to explain this behavior is presented in this paper with the help of the O'Brian–White theory which explicitly predicts a maximum in the mobility vs zeta potential curve. By application of the appropriate equations for surface potential and zeta potential, this can be translated into a maximum of the electrophoretic mobility in dependence on the salt concentration.

Using this formalism, we calculate in this paper theoretical mobility vs electrolyte concentration curves. These data are subsequently compared with experimental results obtained from narrowly distributed model polystyrene latexes, synthesized by emulsion polymerization [9] with three different surface charge densities. Comparing both sets of curves, it should be possible to calculate a steadily increasing zeta potential with decreasing salt concentration from the experimentally measured mobilities.

Calculation of theoretical mobility-concentration curves

For the theoretical treatment, a spherical particle is considered whose electric surface structure can be approximated by a uniformly distributed charge density σ on the particle surface and the diffuse part of the double layer as described by the Poisson–Boltzmann equation, i.e. no Stern layer is assumed. If the charge density and the concentration of electrolyte (assumed to be a 1, 1-electrolyte at first) in the surrounding solution are known, the electric potential on the surface can be calculated by the Gouy–Chapman theory which has been modified for spherical particles by Loeb [10]:

$$\sigma = \varepsilon_0 D \frac{kT}{ze} \kappa \left\{ 2 \sinh(z\tilde{\Psi}/2) + \frac{4}{\kappa a} \tanh(z\tilde{\Psi}/4) \right\} . \qquad (1)$$

The plane of shear is assumed to be at a distance x from the particle surface. An approximate expression for the calculation of the zeta potential from the (diffuse layer) surface potential is Eq. (2), which is derived from the Gouy–Chapman theory for flat plates:

$$\tanh(z\tilde{\zeta}/4) = \tanh(z\tilde{\psi}/4) \exp(-\kappa x) . \qquad (2)$$

The values for the mobility μ are then obtained through a simplified, analytical form of the White–O'Brian theory [11] for electrophoretic mobilities. The corresponding expression Eq. (3) is accurate to the order of $1/\kappa a$ and valid for $\kappa a > 10$ [12]:

$$E = \frac{3\tilde{\zeta}}{2} - \frac{6[\tilde{\zeta}/2 - (\ln 2/z)(1 - \exp(-z\tilde{\zeta}))]}{2 + [\kappa a/(1 + 3m/z^2)] \exp(-z\tilde{\zeta}/2)} . \qquad (3)$$

The reduced, dimensionless values for mobility E, zeta potential $\tilde{\zeta}$, and surface potential $\tilde{\psi}$ are given as

$$E = \frac{3\eta e}{2\varepsilon kT} \mu, \quad \tilde{\zeta} = \frac{e\zeta}{kT}, \quad \tilde{\Psi} = \frac{e\Psi}{kT}, \qquad (4)$$

where m is the dimensionless ionic mobility

$$m_\pm = \frac{2\varepsilon RT}{3\eta} \frac{z_\pm^2}{\Lambda_\pm^0} . \qquad (5)$$

In this way μ vs c or ζ vs c curves are calculated for given values for σ, x, a, c.

Experimental section

Styrene monomer was obtained from Aldrich and distilled under reduced pressure. The purified monomer was stored at −5 °C until required. All other reagents were of analytical grade and used as received. Dialysis tubes were purchased from Serva (Servapor, pore size 29 nm) and ultrafiltration membranes provided by Millipore (pore size 0.05 μm). Deionized water was used throughout. Emulsion polymerizations were carried out in a 400 ml glass reactor. Before polymerization, nitrogen was bubbled through the water phase for 10 min, and a slow nitrogen purge was maintained during the reaction.

For the adjustment of the surface-charge density, the following recipes were applied:

Latex PS1: Potassium peroxodisulfate 0.06 g; sodium dodecyl sulfate 0.06 g; sodium tetraborate 0.01 g; styrene 9 g; temperature 65 °C, rotation rate 400 min^{-1}; reaction time 18 h.

Latex PS2: recipe analogous to PS1, temperature 85 °C; reaction time 6 h.

Latex PS3: recipe analogous to PS2; Potassium peroxodisulfate 0.24 g; sodium tetraborate 0.03 g.

Table 1 summarizes the values of surface-charge density σ and diameter for the three latices. The polydispersity was checked by dynamic light scattering and was found to be below the instrumental resolution. The three latices have approximately the same size but exhibit different charge densities.

The charge density was adjusted by means of the higher reaction temperature for PS2 compared to PS1 which causes a faster decomposition of the charge-generating initiator and hence a higher charge density. The charge density can be further increased by using a larger amount of initiator, as shown in the case of PS3, while the particle size is still controlled by the constant amount of surfactant.

All latexes were purified after polymerization by dialysis against deionized water (3 l each, changed every day for three days) and then washed in a 0.4 l ultrafiltration cell until the conductivity of the eluent remained constant, and the surface tension of the latex was above 70 mN/m (as measured by the Wilhelmy-plate method). Dynamic light

Table 1 Latex samples

Sample	Diameter [z-average, nm]	Negative charge density [μC/cm²]
PS1	283.7	1.72
PS2	256.9	3.09
PS3	253.7	7.51

scattering (Zetamaster S, Malvern instruments, England) was used to determine the particle size and the polydispersity. Surface-charge densities were measured by titrating the diluted, purified latices (0.1–10 g/l) with a polyelectrolyte standard (0.1 mmol polydiallyldimethylammoniumchloride) in a particle-charge detector (PCD 02, Mütek), indicating the streaming potential. This set-up was used to determine the point of zero charge on the surface of the particles, only.

Electrophoretic mobilities were obtained with a Zetamaster S to which a titrater was connected (Mettler DL 21). Adjustment of salt concentration through successive addition of concentrated salt solution to the original latex suspension (200 ml, 2 g/l), circulation of the sample and the measurement itself were conducted fully automatically and computer controlled. In this fashion one titration run yields a sequence of mobility values for increasing electrolyte concentrations. The sample was sonicated (1 min) before each series of measurements to remove any potential agglomeration of particles. The vessel containing the sample and the block supporting the measurement cell were kept at 25 °C during the titration.

For each latex sample at least four titration runs were performed, and the arithmetic mean of the values for each given electrolyte concentration were taken for the presentation and comparison.

Results and discussion

In Fig. 1 theoretical mobility vs electrolyte concentration and zeta potential vs electrolyte concentration curves calculated for the sample PS2 are shown.

These curves were calculated for KCl ($\Lambda^0_\pm = 70\,\mathrm{cm^2/ohm\,mol}$). It is evident that all the qualitative features of the anomalous electrophoretic mobility behavior are reproduced: the electrophoretic mobility passes through a maximum although the zeta potential steadily increases with falling electrolyte concentration. The lowest concentration value of 0.0005 mol/l corresponds to a κa of 9.2, thus, ensuring the validity of Eq. (3). At the lower end of the electrolyte concentration range under examination, the relaxation force becomes more and more important. This force is created by an electric field induced in the opposite direction to the applied field as a result of the induced polarization within the diffuse layer of ions surrounding the particle. The relaxation effect causes a deviation from the direct proportionality of zeta potential and mobility as described by the Smoluchowski equation, i.e. the second term on the right-hand side of Eq. (3) becomes increasingly dominant.

Figures 2 and 3 show the theoretically calculated and experimental curves for the comparison of the three latexes

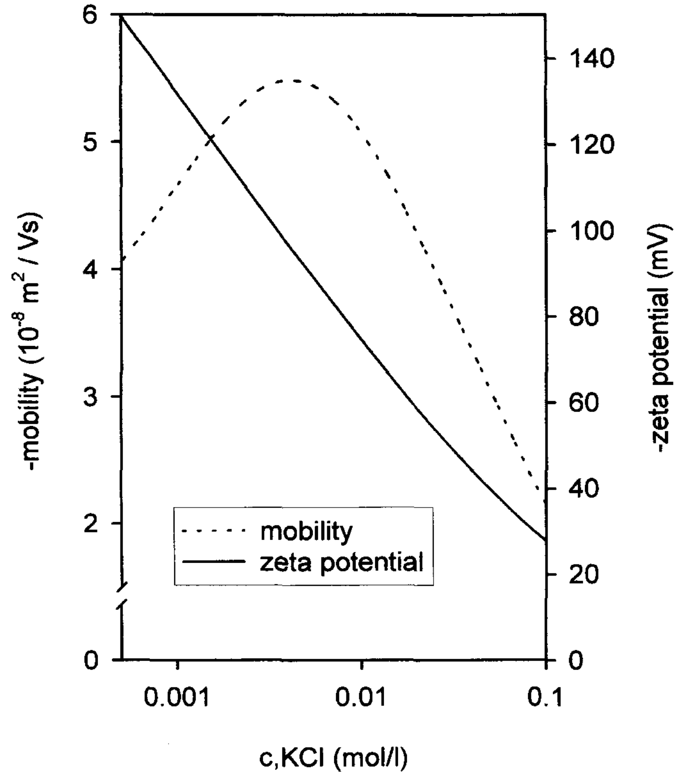

Fig. 1 Calculated values of the electrophoretic mobility and the zeta potential for PS2

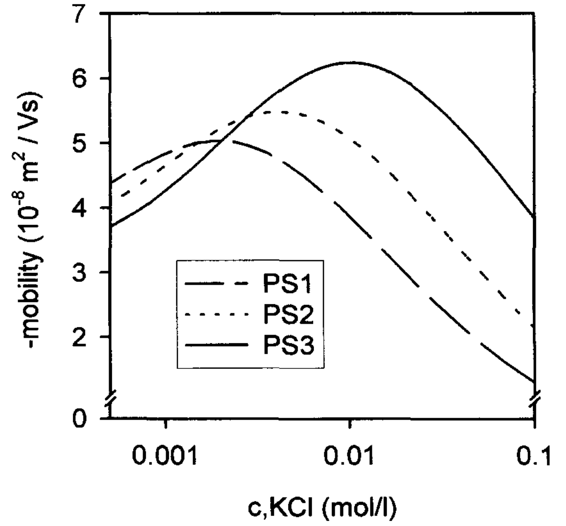

Fig. 2 Theoretical curves for the variation of mobility with electrolyte concentration calculated for the three samples PS1, PS2, PS3

with different surface charge, respectively. Both sets of curves have several characteristic features in common:

- With increasing surface-charge density the maximum possesses higher mobility values.

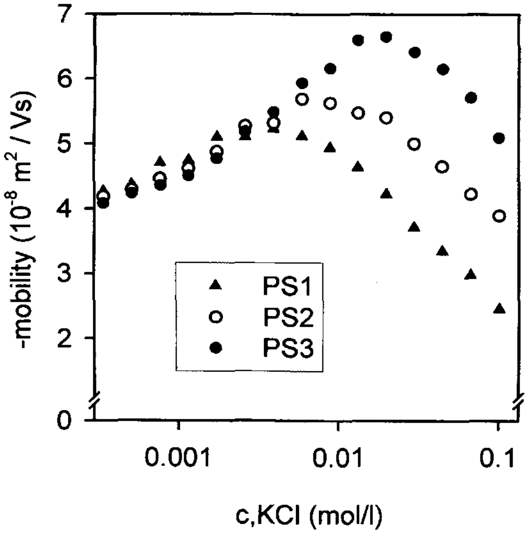

Fig. 3 Measured values for the variation of mobility with electrolyte concentration for the three samples PS1, PS2, PS3

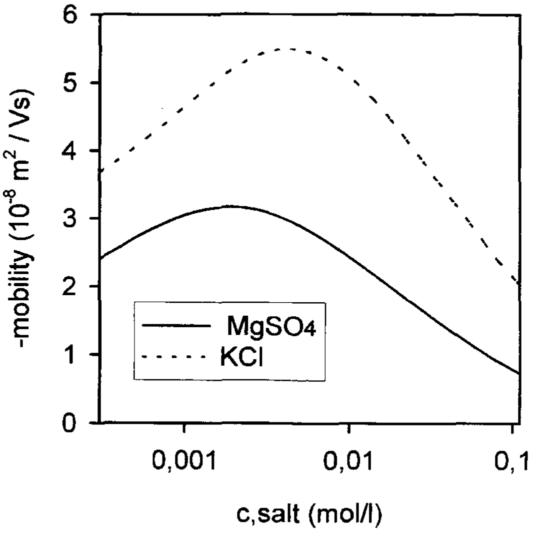

Fig. 4 Calculated values for the variation of mobility with electrolyte concentration for sample PS2 computed for two electrolytes with different valence

- Higher charge density shifts the maximum in the curve toward higher electrolyte concentrations.
- The curves intersect; at low ionic strength the order of mobility values is reversed, i.e. the latex bearing the highest charge density is slowest in this regime.

The most salient discrepancy between experimental and theoretical data lies in the magnitude of the mobilities at high ionic strengths, in this limit the experimental values are clearly above the theoretical ones.

Another sensitive test of this concept is given by variation of the valence of the electrolyte. Figure 4 shows the calculated values for the sample PS2 obtained for the 1.1-electrolyte KCl and the 2.2-electrolyte $MgSO_4$, respectively. For the calculation of the dimensionless ionic mobility m for $MgSO_4$ according to Eq. (5) the arithmetic mean of the Λ^0-values for the two ions was used.

In Fig. 5 the corresponding measured values are shown. In both diagrams the curves for $MgSO_4$ are below the KCl-curves, and the maximum is less pronounced for the 2.2-electrolyte. This finding is also in agreement with experimental results reported previously in the literature [13].

However, the theoretical description is still far from being complete: for $MgSO_4$, the experimental values present their maximum at higher ionic strength than the calculated ones, and as with KCl the measured values deviate significantly from the predicted ones in the high-concentration regime.

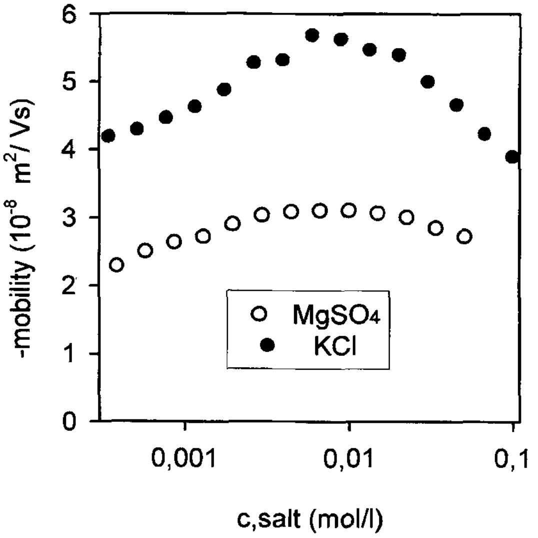

Fig. 5 Measured values for the variation of mobility with electrolyte concentration for sample PS2 obtained for two electrolytes with different valence

This is possibly due to the fact that several serious simplifications were employed in the model in order to keep the number of unknown parameters describing the movement of the particle in the electric field as low as possible:

- The Poisson–Boltzmann equation holds down to the surface of the particle; no stern layer was assumed.
- Anomalous surface conductance i.e. ionic conduction inside the plane of shear [6–8] is neglected.
- A constant value of x = 0.3 nm was more or less arbitrarily chosen.

- The charge density is "smeared out" on the surface of the particle; no account to consider the discrete nature of single-point charges was performed.

Despite these shortcomings, it is nevertheless worth underlining that the model can correctly describe all qualitative features of the experimental results without involving any further assumption, e.g. concerning the presence of a hairy layer or adsorption of ions on the surface.

Because of the mobility–zeta potential maximum for constant values of κa, the O'Brian–White theory relates two possible zeta potentials to a given mobility, one low and the other high [3, 11]. The calculations of the mobility from zeta potential values presented in this paper have shown that at lower salt concentration a decreasing mobility might still be related to an increasing zeta potential, when the higher of the two possible solutions is taken. Good results using the upper branch of the mobility–zeta potential relation were already obtained by Gittings and Saville [14], who compared the ζ-values from dielectric measurements and electrophoresis. Therefore, it seems to be appropriate to take the second, higher zeta potential branch into account when mobilities in the low-salt region are converted into zeta potentials by the O'Brian–White theory.

In order to describe the observed deviations between experimental and theoretical values in the high electrolyte concentration regime, the presented model is without doubt too simple, and further sophistication of the model is necessary.

Conclusions

Using a simple model based on the O'Brian–White theory it is possible to show that lowering the electrolyte concentration leads to a steadily increasing zeta potential and a maximum of the electrophoretic mobility of the particle. No assumptions about adsorption of ions, shift of the plane of shear or anomalous surface conductance were made.

Comparison with experimental data reveals that this simple model describes qualitatively the variation of the electrophoretic mobility with electrolyte concentration of polystyrene latices having different charge densities. The difference in mobility values between 1.1- and 2.2-electrolytes is also correctly predicted by this approach.

These results show that the so-called atypical behavior of the electrophoretic mobility is not atypical at all, but a direct consequence of the structure of the physics involved.

List of symbols

c	electrolyte concentration
D	dielectric permittivity of the continuous phase
ε_0	dielectric vacuum permittivity
η	viscosity of the continuous phase
κ	reciprocal of the double-layer thickness
Λ^0	limit equivalence conductance
μ	electrophoretic mobility
Ψ	diffuse layer potential
R	gas constant
σ	surface-charge density
T	absolute temperature
z	valency of ions
ζ	electrokinetic potential

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