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SHORT COMMUNICATION

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The electrophoresis of poly(*N*-isopropylacrylamide) microgel particles

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Abstract The electrophoretic mobility of a poly(*N*-isopropylacrylamide) microgel containing carboxylic groups has been measured as a function of the ionic strength, between 0.1 and 100 mM NaCl, over the temperature range 25–45 °C. The mobility data obtained have been evaluated using different models, including the porous-sphere, the soft-plate and the soft-sphere models as well as the hard-sphere model developed by Henry and later refined by O'Brien and White. The "porous" or "soft" behaviour is evident at lower temperatures, whereas at higher temperatures none of the models can fully explain the observed behaviour. It is suggested that the discrepancies at higher temperatures can be partly ascribed to the neglect of the relaxation effect in the "soft" models.

Key words poly(*N*-isopropylacrylamide) · Microgel · Electrophoretic mobility · Soft sphere · Relaxation effect

Introduction

In the 1950s, the theory of electrophoresis of a porous particle was developed [1–3]. The theory was used with limited success to explain some experimental data [4]. Some 20 years later theories for polymer-covered ("soft") particles started to appear [5–10]. Recently Ohshima [11] united the theories previously mentioned [1–10] with those for spherical hard colloidal particles [12–15] to account for the electrophoresis of porous/soft particles.

Experimentally, such "soft" behaviour has been observed for poly(*N*-isopropylacrylamide) (PNIPAM) and application [16–19] of the theory [2, 11] has, in general, produced good agreement with available experimental data. It has also been found that cationic starch can be described as a porous [20] or soft [21] particle.

Here, we present electrophoretic mobility data for a PNIPAM microgel containing carboxylic groups from the initiator used. The electrophoretic mobility was measured as a function of the ionic strength, between 0.1 and 100 mM NaCl, over the temperature range 25–45 °C.

Theory

The basic model is depicted in Fig. 1. Ohshima's porous-sphere model leads to the following expression for the electrophoretic mobility [11]

$$\mu = \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2}[1 + g + hp] \ , \tag{1}$$

where

$$g = \frac{1}{3}\left(\frac{\lambda}{\kappa}\right)^2\left[1 + \exp(-2\kappa b) - \left(\frac{1-\exp(-2\kappa b)}{\kappa b}\right)\right] \ , \tag{2}$$

$$h = \frac{1}{3}\left(\frac{\lambda}{\kappa}\right)^2\frac{1 + \left(\frac{1}{\kappa b}\right)}{\left[\left(\frac{\lambda}{\kappa}\right)^2 - 1\right]} \ , \tag{3}$$

$$p = \frac{\lambda}{\kappa}\frac{1 + \exp(-2\kappa b) - \frac{1-\exp(-2\kappa b)}{\kappa b}}{\left(\frac{1+\exp(-2\lambda b)}{1-\exp(-2\lambda b)} - \frac{1}{\lambda b}\right)} - [1 - \exp(-2\kappa b)] \ . \tag{4}$$

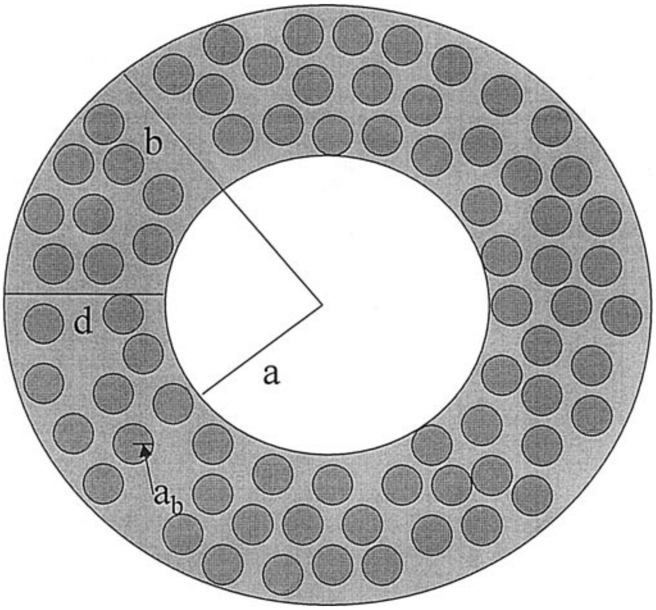

Fig. 1 Schematic representation of the soft-sphere model, where N polymer beads with radius a_b are enclosed within a spherical shell (the polymer layer) of radius d. a is the radius of the particle core, d is the radius of the polymer layer and b is the total radius. $a = 0$ for the porous sphere and $a \to \infty$ for the soft platelike particle

Here ρ_{fix} is the volume charge density, η is the viscosity of the solvent, λ is the frictional coefficient of the porous sphere, κ is the Debye–Hückel screening parameter and b is the radius of the porous sphere.

In a recent report [21], it has been explicitly shown that Ohshima's model can be related to Hermann and Fujita's porous-sphere model [1, 2], thus relating the following parameters.

$$\rho_{\mathrm{fix}} = \mathrm{DS}ev \ , \tag{5}$$

$$v = \frac{3N}{4\pi b^3} \ , \tag{6}$$

$$\sigma = \left(\frac{vfb^2}{\eta}\right)^{1/2} \ , \tag{7}$$

$$\lambda = \frac{\sigma}{b} \ , \tag{8}$$

$$f = 6\pi\eta a_{\mathrm{b}} \ , \tag{9}$$

where DS is the degree of dissociation, e is the elementary charge, N is the number of polymer beads within the porous sphere, σ is the Debye shielding parameter and a_{b} is the radius of one polymer bead as seen in Fig. 1.

Ohshima and Kondo [10] derived the following expression for a soft plate-like particle:

$$\mu = \frac{\varepsilon\varepsilon_0}{\eta}\frac{\frac{\psi_0}{\kappa_{\mathrm{m}}} + \frac{\psi_{\mathrm{DON}}}{\lambda}}{\frac{1}{\kappa_{\mathrm{m}}} + \frac{1}{\lambda}} + \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2} \ , \tag{10}$$

where

$$\kappa_{\mathrm{m}} = \kappa\left[1 + \left(\frac{\rho_{\mathrm{fix}}}{2zen_{\mathrm{salt}}}\right)^2\right]^{1/4} \ , \tag{11}$$

$$\psi_{\mathrm{DON}} = \frac{kT}{ze}\ln\left\{\frac{\rho_{\mathrm{fix}}}{2zen_{\mathrm{salt}}} + \left[1 + \left(\frac{\rho_{\mathrm{fix}}}{2zen_{\mathrm{salt}}}\right)^2\right]^{1/2}\right\} \ , \tag{12}$$

$$\psi_0 = \psi_{\mathrm{DON}} + \frac{2n_{\mathrm{salt}}kT}{\rho_{\mathrm{fix}}}\left\{1 - \left[\left(\frac{\rho_{\mathrm{fix}}}{2zen_{\mathrm{salt}}}\right)^2 + 1\right]^{1/2}\right\} \ , \tag{13}$$

$$n_{\mathrm{salt}} = IN_{\mathrm{A}} \ , \tag{14}$$

where ψ_0 is the potential at the surface of the polymer layer, ψ_{DON} is the Donnan potential in the polymer layer, κ_{m} is the Debye–Hückel parameter of the polymer layer, z is the valency of the electrolyte ions, I is the ionic strength and N_{A} is Avogadro's number.

Note that Eq. (1) as well as Eq. (10) contain the term $\rho_{\mathrm{fix}}/\eta\lambda^2$. This term does not vanish at high electrolyte concentrations, and therefore the mobility of soft (or porous) particles tends to a nonzero limiting value. This has in fact been observed experimentally [17–21]. For the platelike particle, the thickness of the polymer layer is $d = b - a$, where a is the radius of the particle core (Fig. 1). Since the geometry is platelike, $a \to \infty$, which means that only d is variable.

Ohshima [11] noticed that the difference between a porous platelike and a soft platelike particle with a low surface potential could be attributed to the presence of the particle core in the latter case. For hard particles, the difference of a factor of 2/3 between Smoluckowski's [12] and Hückel's [13] equations can be attributed to the distortion of the electric field created by the presence of the particle in the former case ($\kappa a \gg 1$). The difference between a porous platelike and a soft platelike particle is of the same nature. This can clearly be seen from the following expression for a soft spherical particle [11],

$$\mu = \frac{2}{3}\frac{\varepsilon\varepsilon_0}{\eta}\frac{\frac{\psi_0}{\kappa_{\mathrm{m}}} + \frac{\psi_{\mathrm{DON}}}{\lambda}}{\frac{1}{\kappa_{\mathrm{m}}} + \frac{1}{\lambda}}\left[1 + \frac{1}{2\left(1 + \frac{d}{a}\right)^3}\right] + \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2} \ , \tag{15}$$

where the term within the brackets tends to 1 if $d \gg a$ and to 1.5 if $d \ll a$. d/a is therefore analogous to κa, and Eq. (15) is analogous to the Henry equation [14],

$$\mu = \frac{\varepsilon\varepsilon_0\zeta}{\eta}f(\kappa a) \tag{16}$$

$$f(\kappa a) = \frac{2}{3}\left(1 + \frac{1}{2(1 + \{2.5/\kappa a[1 + 2\exp(-\kappa a)]\})^3}\right) , \tag{17}$$

where we have replaced Henry's original series expansion with Ohshima's [22] approximation (Eq. 17).

We will compare the three different models as expressed by Eqs. (1), (10) and (15) and see how they compare with experimental data. We also include the ordinary hard-sphere model [14, 15] as calculated using the MOBILITY program which is based on the calculations of O'Brien and White (OBW) [15]. For low ζ, the calculations agree with Henry's equation [14] and one can use the Loeb–Overbeek–Wiersema approximation [23]

$$\sigma_0 = \frac{\varepsilon\varepsilon_0 \kappa kT}{ze}\left(2\sinh\left(\frac{ze\zeta}{2kT}\right) + \frac{4}{\kappa a}\tanh\left(\frac{ze\zeta}{4kT}\right)\right) \tag{18}$$

in combination with Eqs. (16) and (17) to calculate the electrophoretic mobility for a given surface charge density.

Experimental

Aqueous dispersions of PNIPAM microgel particles were produced by emulsion polymerisation as described in Ref. [24] using 4,4/-azobis(4-cyanopentanoic acid) as the initiator. For this particular batch 0.38 g initiator was used compared to the 0.5 g stated in Ref. [24]. The effect of temperature on the hydrodynamic radius was measured using a Brookhaven Instruments Zeta Plus fitted with a 635 nm He-Ne laser and a detector at 90°. The result can be seen in Fig. 2. The "collapse" temperature is somewhere between 35 and 40 °C.

Measurement of the electrophoretic mobility was performed at pH 6 (±0.05) using a Phase Analysis light-scattering apparatus [25]. Some of the measurements were checked using a Laser Doppler Penkem "System 3000" apparatus. The agreement between the two techniques was good (within 5%).

The electrophoretic mobility data as a function of the ionic strength at five different temperatures is shown in Fig. 3. It can be observed that the mobility tends to a nonzero limiting value independent of temperature (over the range studied) at high ionic strength, as expected for a soft particle. At higher temperatures, the magnitude of the mobility continuously decreases with increasing ionic strength, which implies that the particle is "harder" under these conditions. It is interesting to note that a maximum in the mobility is observed around 0.3 mM NaCl at all the temperatures studied, except 45 °C. This maximum is also observed for normal polystyrene latices, but generally at somewhat higher ionic strength values (1–10 mM) [26]. Suffice to say the soft-sphere model does not predict this maximum, but it is worth noting that the maximum seems to disappear at 45 °C, indicating more ideal behaviour.

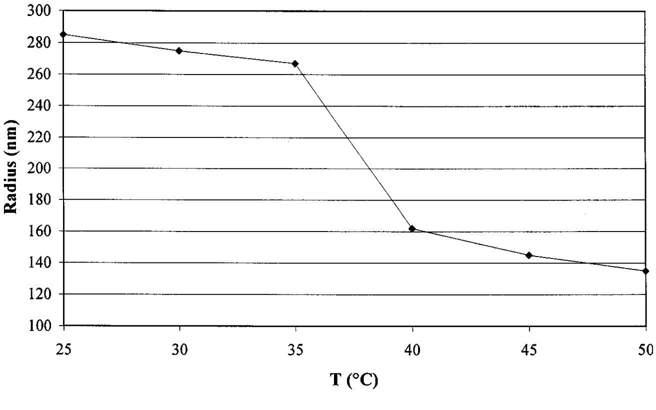

Fig. 2 The radius of the microgel particle as a function of temperature as determined by photon correlation spectroscopy (PCS)

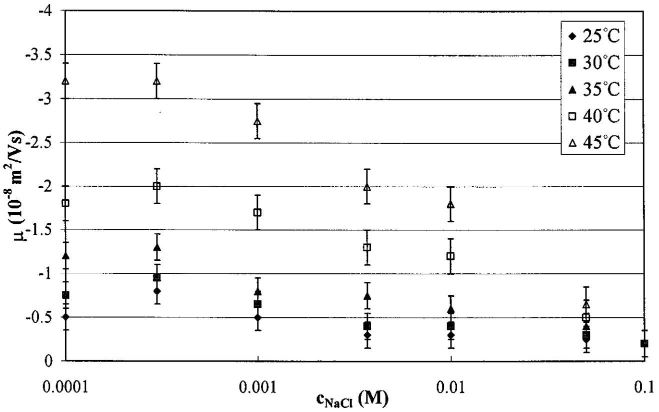

Fig. 3 The measured electrophoretic mobility as a function of ionic strength at five different temperatures

Comparison with theory

The soft sphere

Previous fits to PNIPAM microgel mobility data [17–19] suggest a volume charge density (ρ_{fix}) of about 5–6.5 × 10^4 C/m^3 at 25 °C. Pelton et al. [16] performed a conductometric titration and found that the number of sulfate groups corresponded to a ρ_{fix} of about 5 × 10^4 C/m^3 at 25 °C.

λ characterises the degree of friction exerted on the liquid flow in the polymer layer. λ depends on ρ_{fix}, b and a_{b}, as can be seen from Eqs. (5)–(9). Typically, $1/\lambda$ (the softness of the polymer layer) decreases from about 3 nm at 25 °C to 1 nm at 40 °C for a pure PNIPAM layer [18].

We first focus on the porous-sphere model. We assume that the radius obtained from photon correlation spectroscopy (PCS) is identical to b, the radius of the porous sphere. Further, we expect that the degree of dissociation is 1 in these lowly charged systems. The remaining parameters are then the number of polymer beads, N, and the radius of a polymer bead, a_{b}. By setting a_{b} to 4.5 nm and N to 3.5 × 10^4, we obtained a good fit to the mobility data, as can be seen from Fig. 4a. $1/\lambda$ is 5.7 nm at 25 °C according to Eq. (8). From Fig. 5 it can be seen that $1/\lambda$ reflects the decrease in the PCS radius with increasing

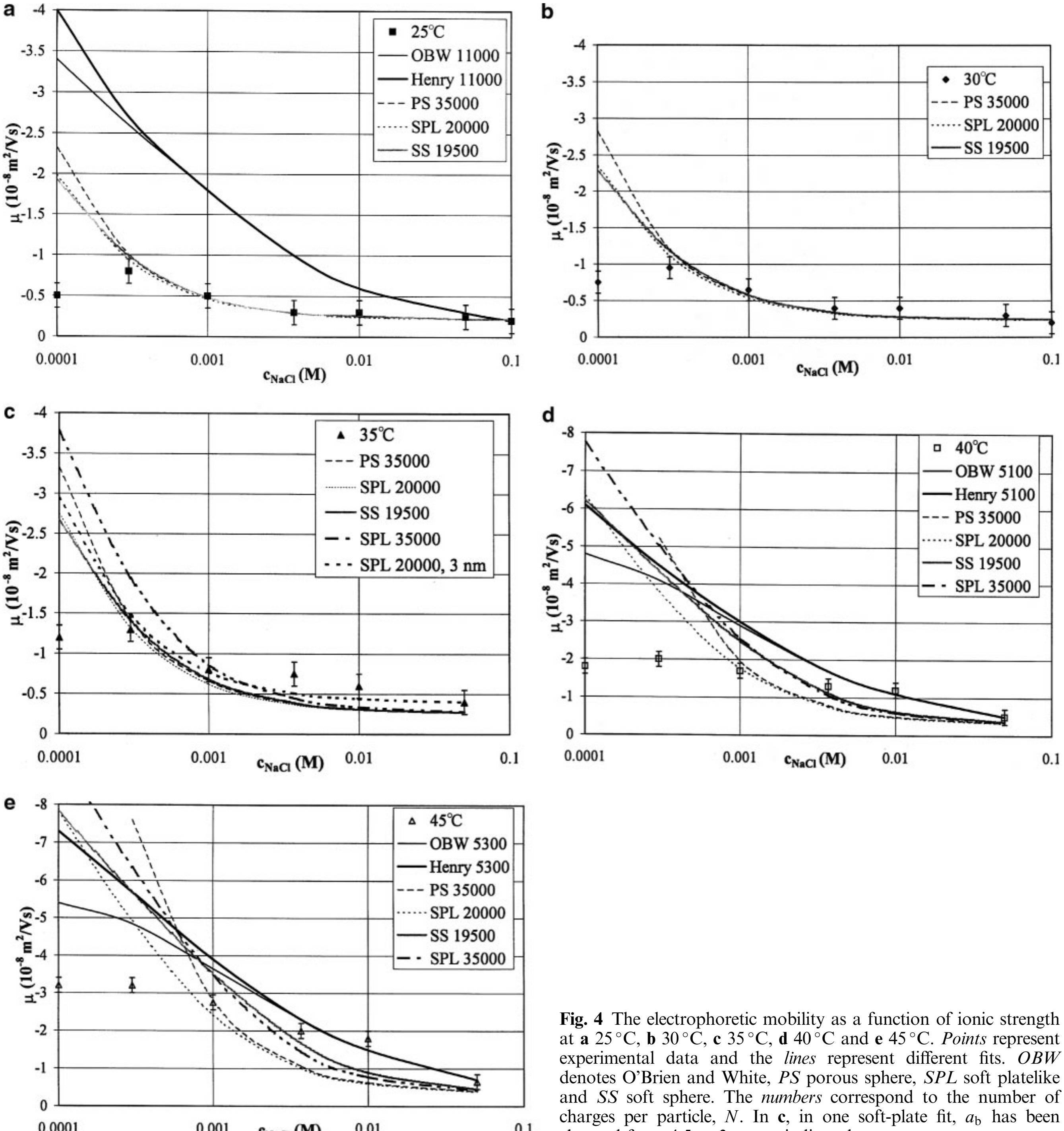

Fig. 4 The electrophoretic mobility as a function of ionic strength at **a** 25 °C, **b** 30 °C, **c** 35 °C, **d** 40 °C and **e** 45 °C. *Points* represent experimental data and the *lines* represent different fits. *OBW* denotes O'Brien and White, *PS* porous sphere, *SPL* soft platelike and *SS* soft sphere. The *numbers* correspond to the number of charges per particle, *N*. In **c**, in one soft-plate fit, a_b has been changed from 4.5 to 3 nm as indicated

temperature. $N = 3.5 \times 10^4$ corresponds to a ρ_{fix} of about 5.8×10^4 C/m^3 at 25 °C, in good agreement with the values cited previously.

How then does the porous-sphere model behave with increasing temperature? The fits in Fig. 4b and c are reasonable, but it is clear that at 40 and 45 °C (Fig. 4d, e) the microgel cannot be regarded as porous anymore. Furthermore, the porous-sphere model involves the Debye–Hückel approximation, and as such it breaks down when the mobility (i.e. potential) is increasing. We therefore turn our attention to the soft platelike model, which does not suffer from this drawback.

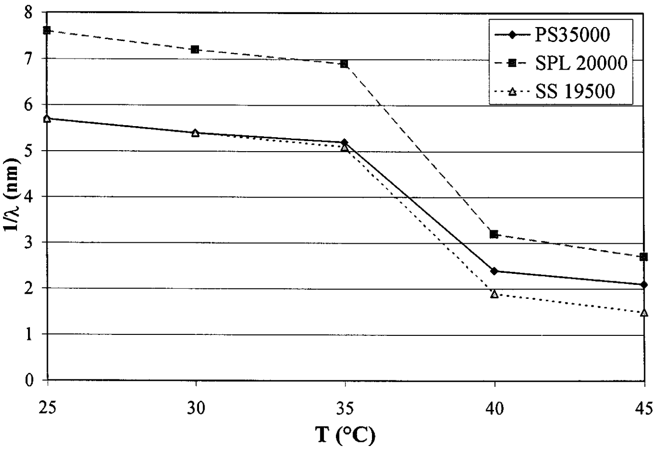

Fig. 5 $1/\lambda$ (the softness of the polymer layer) as a function of temperature for three different models. Same notation as in Fig. 4a

The soft platelike model is somewhat akin to the Smoluchowski equation in that the presence of a particle core distorts the electric field. In essence, we are assuming a very large particle coated with a thinner polymer layer which is still thick enough to satisfy the conditions $\lambda d \gg 1$ and $\kappa d \gg 1$. To facilitate comparison with the Hückel-like porous-sphere model, we simply set $b = d$ and adjusted N until a good fit was obtained at 25 °C. It turns out that setting $N = 2 \times 10^4$ produced almost the same fit as the porous-sphere model with 3.5×10^4 charges. By decreasing N, $1/\lambda$ increased somewhat as can be seen from Fig. 5. The resulting soft-plate fits can be seen in Fig. 4a–e. For mobility magnitudes larger than 2, the porous-sphere and the soft-plate models start to diverge, which is an indication that the Debye–Hückel approximation starts to break down. However, the soft-plate-like model fits at 40 and 45 °C are not much better than the porous-sphere fits. The discrepancy between theory and experiment can therefore not be ascribed to the Debye–Hückel approximation.

The soft-sphere model requires a, the radius of the hard core, as an additional fitting parameter. Equation (15) is derived under the assumptions $\lambda a \gg 1$, $\kappa a \gg 1$, $\lambda d \gg 1$ and $\kappa d \gg 1$, so the parameter space is somewhat restricted in this case. a was set to 50 nm and d was therefore $(b - a)$, where b again is the PCS radius at a given temperature. N was adjusted to 1.95×10^4 so that ρ_{fix} equalled 5.8×10^4 C/m^3 at 25 °C, just as in the porous-sphere case. The results can be seen in Fig. 4a–e. Below the collapse temperature, the soft-sphere fit coincides with the soft-plate fit at the lowest ionic strength and with the porous-sphere fit at the higher ionic strengths. Above the collapse temperature, the soft-sphere fit again coincides with the soft-plate fit at the lowest ionic strength, but at intermediate ionic strengths the soft-sphere model predicts substantially higher mobilities than the other two models.

Can we improve the fit by adjusting the parameters slightly at a given temperature? In Fig. 4c–e, we have also included a soft-plate fit with 3.5×10^4 charges. By increasing the number of charges, the magnitude of the mobility increases more dramatically with decreasing ionic strength. The fit is close to the soft-sphere fit down to about 0.001 M in Fig. 4d and e. In Fig. 4c, we also show a soft-plate fit with 2×10^4 charges, where the friction (Eq. 20) is decreased by changing the radius of a polymer bead from 4.5 to 3 nm. The magnitude of the mobility increases at all ionic strengths because the term $\rho_{\mathrm{fix}}/\eta\lambda^2$ in Eq. (10) increases in magnitude.

The hard sphere

In Fig. 4a, d and e, the hard-sphere model [14, 15] has also been included. The fits are made to coincide with the data point at the highest ionic strength at each temperature, keeping $\sigma_0(N)$ constant at a given temperature. Notice that the hard-sphere fit requires fewer charges and that the number of charges is lower at 40 and 45 °C than at 25 °C.

The difference between the OBW calculation [15] and the Henry equation (Eq. 16) can be attributed to the neglect of the relaxation effect in the latter case. It is therefore interesting to compare Eqs. (15) and (16), since they are at the same level of approximation. Notice that the OBW fit captures the general trend of the data at 40 and 45 °C, even though the fit is far from good. It would be interesting to extend the temperature range up to 50 or even 55 °C and see if the agreement between the OBW fit and the data improved even further. Nevertheless, it may be that the discrepancy between the soft-sphere fit and the data at elevated temperatures can partly be ascribed to the neglect of the relaxation effect in the model.

Conclusions

- Between 25 and 35 °C, the electrophoretic mobility of a carboxyl-initiated PNIPAM microgel can be interpreted in terms of the soft-sphere model as proposed by Ohshima [11].
- At 40 and 45 °C, the electrophoretic mobility pattern does not fit the soft-sphere or the hard-sphere model. A maximum in the mobility is observed at 0.3 mM NaCl at all temperatures, except at 45 °C. This maximum is also observed for normal polystyrene latices, but it is then shifted to a higher ionic strength (1–10 mM) [26].
- It is suggested that the discrepancies at 40 and 45 °C can partly be ascribed to the neglect of the relaxation effect in the soft-sphere model. Also, Eq. (15) has

been derived under the assumptions $\kappa a \gg 1$ and $\kappa d \gg 1$, but this is not really true at low ionic strengths ($\kappa a \approx 5$ at 1 mM NaCl).

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