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ELECTROPHORETIC MOBILITY

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SUMMARY

The contributions of local field and dielectric friction to the electrophoretic mobility in an electrophoresis system are calculated for the simple model of spherical ions. These effects are important in a fluid with a large dielectric constant.

INTRODUCTION

In electrophoresis experiments, electrophoretic mobility (EM) is a fundamental characteristic parameter which is measurable. There have been several theories[1–5] for the calculation of EM from special simple models. The main forces which have been considered are: (a) the electric attraction force $e\vec{E}$ (e is the charge of migrating particles and $\vec{E}$ the electric field in the system), which is responsible for the observed migration; (b) the Stokes friction due to viscosity of the fluid; and two relatively less important forces; (c) electroosmotic retardation; and (d) the relaxation effect. It is shown that EM is dependent on the dielectric constant ε and viscosity η of the fluid.

In this paper we shall show two additional contributions to EM which might be important in a charge liquid such as an electrophoresis system.

LOCAL FIELD EFFECT

The true electric force acting on a particle is not the averaged Maxwell electric field $\vec{E}$. The acting field (local field) differs from the Maxwell field by a modification factor $r(\varepsilon)$, which is a function of the dielectric constant ε of the surrounding medium

$$\vec{E}_{\mathrm{loc.}} = r(\varepsilon)\,\vec{E} \tag{1}$$

This effect is important in any "dense" system, such as a liquid or a solid[6,7]. For an isotropic liquid, we have[7]

$$r(\varepsilon) = \frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} \tag{2}$$

where ε_∞ is the optical dielectric constant of the liquid.

DIELECTRIC FRICTIONAL EFFECT

In addition to the Stokes friction, there is an extra frictional force on a moving charge particle in a fluid

$$\vec{F}_f = -\zeta_0 \vec{v} - \zeta_D \vec{v}, \tag{3}$$

where $\vec{v}$ is the averaged velocity of the charged particle, ξ_0 the Stokes friction constant and ζ_D the dielectric frictional constant

$$\zeta_D = \zeta_D(\varepsilon) \tag{4}$$

which is dependent on the dielectric constant of the fluid.

For a spherical charged particle of radius a, the Stokes frictional constant has the form

$$\zeta_0 = \begin{Bmatrix} 6\pi\eta a, \text{ stick} \\ 4\pi\eta a, \text{ slip} \end{Bmatrix} \text{ ion-fluid boundary condition} \tag{5}$$

and ζ_D was calculated by Zwanzig[8]

$$\zeta_D = C \frac{\varepsilon - \varepsilon_\infty}{2\varepsilon + 1} \tag{6}$$

where

$$C = \frac{3e^2\tau}{4a^3} \times \begin{Bmatrix} 2, \text{ stick} \\ 1, \text{ slip} \end{Bmatrix} \text{ ion-fluid boundary condition} \tag{7}$$

τ being the dielectric relaxation time.

Next, we shall consider the contributions of these two effects to EM. In steady state, the electric force is balanced by the frictional force

$$e\vec{E}_{\text{loc.}} - (\zeta_0 + \zeta_D)\vec{v} = 0 \tag{8}$$

Then, from the definition of EM (μ),

$$\vec{v} = \frac{e}{|e|} \mu \vec{E} \tag{9}$$

and eqns. 1 and 8 we have

$$\mu(\varepsilon) = |e| \frac{r(\varepsilon)}{\zeta_0 + \zeta_D(\varepsilon)} \tag{10}$$

For an analytical study, we consider the special case of spherical ions. Substituting eqns. 2 and 6 into eqn. 10, we obtain the expression for EM

$$\mu(\varepsilon) = \mu_0 \left(\frac{3\varepsilon}{2\varepsilon + 1}\right)\left(\frac{1}{1 + A\,\dfrac{\varepsilon - \varepsilon_\infty}{2\varepsilon + 1}}\right) \tag{11}$$

where

$$\mu_0 = \frac{|e|}{\zeta_0} \tag{12}$$

is the value of EM in the absence of both effects. In eqn. 11

$$\frac{3\varepsilon}{2\varepsilon + 1}$$

is the factor due to the local field effect and

$$\frac{1}{1 + A\,\dfrac{\varepsilon - \varepsilon_\infty}{2\varepsilon + 1}}$$

the factor due to the dielectric friction.

$$A = \frac{C}{\zeta_0} = \frac{e^2\tau}{8\pi\eta a^4} \times \begin{Bmatrix} 2, \text{ stick} \\ 1, \text{ slip} \end{Bmatrix} \text{ ion-fluid boundary condition} \tag{13}$$

is a dimensionless dielectric friction parameter dependent on the ion particle size a, the viscosity η, and the relaxation time τ of the fluid.

The ε dependence of μ/μ_0 is calculated and shown in Fig. 1. Bigger additional dielectric friction (*i.e.*, a bigger value of A) will effectively reduce the electrophoretic mobility.

For a typical electrophoresis system, we have
$\eta \approx 10^{-1}$ P
$\tau \approx 10^{-5}$ sec
$e^2 \approx 10^{-19}$ e.s.u.^{2}

Then, from eqn. 13, the constant A is critically dependent on the ionic size and can be estimated, as shown in Table I.

We see that the ionic size-dependent effect on EM is rather sensitive. A smaller ion will have a bigger dielectric friction. The dielectric friction on large ions (with $a > 10^{-6}$ cm) will be unimportant.

If we neglect the dielectric friction (or in the case $A \ll 1$), the local field factor

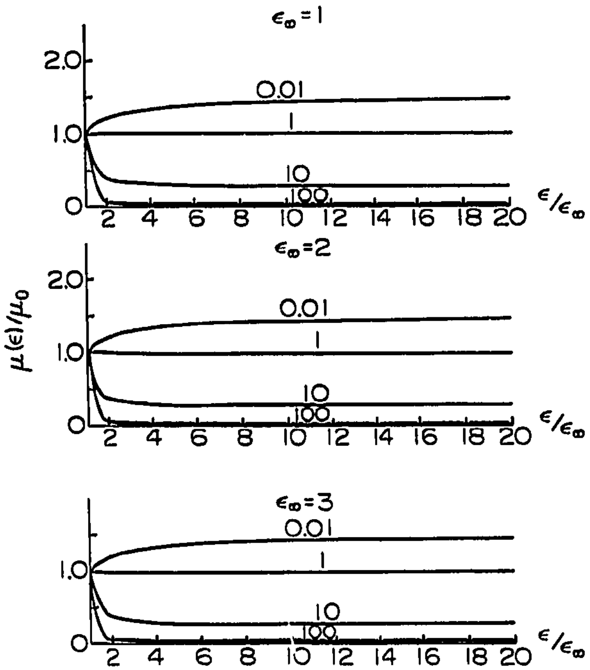

Fig. 1. Modification of electrophoretic mobility. The cases with an optical dielectric constant ε_∞ = 1, 2, 3 and the dielectric frictional parameter A = 0.01, 1, 10, 100 are shown.

$3\varepsilon/(2\varepsilon + 1)$ ranges between 1, for small ε, and 3/2, for large ε. Then, in the case of stick ion-fluid boundary conditions, the EM has the limiting expressions

$$\mu = \begin{cases} \dfrac{|e|}{6\pi\eta a} & \varepsilon \approx 1 \\ \dfrac{|e|}{4\pi\eta a} & \varepsilon \gg 1 \end{cases} \tag{14}$$

The result reduces to the Helmholtz-Smoluchowski (H–S) expressions[3,4] for light dielectric fluid ($\varepsilon \approx 1$) and the Debye–Hückel form[5] for strong dielectric fluid ($\varepsilon \gg 1$). This is physically expected. The H–S expression[3,4] is the result when the ion is bigger than the double layer size, *i.e.* the electrostatic screening effect is small[2]. This corresponds to a light dielectric medium. Similar arguments can be applied to the other limit —the Debye–Hückel case[2,5].

TABLE I

IONIC SIZE DEPENDENCE OF THE DIELECTRIC FRICTION PARAMETER A

a (cm)	A
10^{-7}	10^{4}
10^{-6}	1
10^{-5}	10^{-4}

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