

Simple approximate analytic expression for the electrophoretic mobility of a spherical colloidal particle in a mixed solution of 1:1 and 2:1 electrolytes

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Abstract Simple approximate analytic expressions are derived for the electrophoretic mobility of a spherical colloidal particle of radius a and zeta potential ζ in a mixed solution of 1:1 and 2:1 electrolytes with common anions on the basis of the general mobility expression previously derived by Ohshima (Colloids Surf A Physicochem Eng Asp 267:50, 2005). The obtained expressions, which are applicable for spheres of any ζ and large radii such that $\kappa a \geq \text{ca. } 30$ (where κ is the Debye-Hückel parameter), consist of Smoluchowski's equation and the correction term taking into account the relaxation effect.

Keywords Electrophoretic mobility · Spherical particle · Zeta potential · Relaxation effect

Introduction

The zeta potential of a charged colloidal particle in an electrolyte solution, which is usually estimated from its electrophoretic mobility, plays an essential role in determining its electrokinetic behaviors. A number of theoretical studies have been made on the electrophoretic mobility of spherical particles [1–22]. In particular,

approximate mobility expressions for charged spheres derived in Ref. [18] are applicable for all values of zeta potentials and large particle radii a such that $\kappa a \geq \text{ca. } 30$ (κ is the Debye-Hückel parameter) and have been applied to analyze the mobility of spherical particles with high zeta potentials [23–25]. The corresponding mobility expression for a cylindrical particle has also been derived [26]. However, simple mobility expressions for a sphere in a mixed electrolyte solution, so far, have not been available, since the general mobility expression given in Ref. [18] involves cumbersome numerical multiple integration, if applied for the case of mixed electrolyte solutions. The purpose of the present paper is to derive simple analytic mobility expressions of a charged sphere in a mixed solution of 1:1 and 2:1 electrolytes on the basis of the general mobility expression previously derived [18].

Theory

Consider a spherical particle of radius a and zeta potential ζ moving with a velocity \mathbf{U} under an external electric field \mathbf{E} in a liquid containing a general electrolyte composed of N ionic species with valence z_i and bulk concentration (number density) n_i^∞ and drag coefficient λ_i ($i=1, 2, \dots, N$). The electrophoretic mobility μ of the particle is defined by $\mu = U / E$, where $U = |\mathbf{U}|$ and $E = |\mathbf{E}|$. In a previous paper [18], we have derived the following general mobility expression, which is correct

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to the order of $\exp(z e |\zeta| / 2kT) / \kappa a$, where z is the valence of counterions, e is the elementary electric charge, k is Boltzmann’s constant, T is the absolute

temperature, and κ is the Debye-Hückel parameter, so that it is applicable for all values of ζ at large κa ($\kappa a \geq$ ca. 30):

$$\mu = -\frac{\varepsilon_r \varepsilon_0 kT}{3\eta a e} \sum_{i=1}^N z_i n_i^\infty \phi_i(a) \int_0^{\bar{\zeta}} \left\{ \int_0^y \frac{e^{-z_i y'} - 1}{\sqrt{\sum_{j=1}^N n_j^\infty (e^{-z_j y'} - 1)}} dy' \right\} \frac{1}{\sqrt{\sum_{j=1}^N n_j^\infty (e^{-z_j y} - 1)}} dy \tag{1}$$

with

$$\phi_i(a) = \frac{3a}{2} + \text{sgn}(\zeta) \frac{\phi_i(a)}{\kappa a} \left(\frac{1}{2} \sum_{j=1}^N z_j^2 n_j^\infty \right)^{1/2} \int_0^{\bar{\zeta}} \frac{1 - e^{-z_i y}}{\sqrt{\sum_{j=1}^N n_j^\infty (e^{-z_j y} - 1)}} dy + \text{sgn}(\zeta) \frac{3z_i m_i}{4\kappa a} \left(\frac{1}{2} \sum_{j=1}^N z_j^2 n_j^\infty \right)^{1/2} \int_0^{\bar{\zeta}} [(e^{-z_i y} - 1) \sum_{j=1}^N z_j n_j^\infty \phi_j(a) \times \int_{\bar{\zeta}}^y \left\{ \int_0^{y'} \frac{e^{-z_i y''} - 1}{\sqrt{\sum_{j=1}^N n_j^\infty (e^{-z_j y''} - 1)}} dy'' \right\} \frac{dy'}{\sqrt{\sum_{j=1}^N n_j^\infty (e^{-z_j y'} - 1)}} \Bigg] \frac{dy}{\sqrt{\sum_{j=1}^N n_j^\infty (e^{-z_j y} - 1)}} \tag{2}$$

$$m_i = \frac{2\varepsilon_r \varepsilon_0 kT}{3\eta z_i^2 e^2} \lambda_i = \frac{2N_A \varepsilon_r \varepsilon_0 kT}{3\eta |z_i| \Lambda_i^0} \tag{3}$$

where $\text{sgn}(\zeta) = +1$ if $\zeta > 0$ and -1 if $\zeta < 0$, ϕ_i is a function that is related to the deviation $\delta\mu_i$ of the electrochemical potential μ_i of the i -th ionic species from its equilibrium value due to the applied electric field E , $\phi_i(a)$ is its value at the sphere surface, $y = e\psi / kT$ is the scaled equilibrium electric potential (ψ is the equilibrium electric potential), $\bar{\zeta} = e\zeta / kT$ is the scaled zeta potential, λ_i is the drag coefficient of the i -th ionic species, m_i is its scaled drag coefficient, which is further related to the limiting conductance Λ_i^0 of that ionic species, N_A is Avogadro’s number, ε_r and η are, respectively, the relative permittivity and the viscosity of the electrolyte solution, and ε_0 is the permittivity of a vacuum.

Now, as a good approximation, we assume that the deviation of the electrochemical potential of the i -th ionic species is not influenced by those of other ionic species j ($j \neq i$). Under this approximation, the terms involving $\phi_j(a)$ ($j \neq i$) are neglected so that terms involving small quantities $m_i \times m_j$ may be dropped. This approximation holds good when $m_i \times m_j \ll 1$. We give below explicit expressions for the electrophoretic mobility μ of a spherical particle of radius a and zeta potential ζ in a mixed solution of 1:1 electrolyte of bulk concentration n_1 and 2:1 electrolyte of bulk concentration n_2 with common anions (where the Debye-Hückel parameter κ of this solution is given by $\kappa = \sqrt{2(n_1 + 3n_2)e^2 / \varepsilon_r \varepsilon_0 kT}$):

$$\mu = \frac{2\varepsilon_r \varepsilon_0}{3\eta} \left[\frac{\phi_{+1}(a)}{a} \left\{ \frac{\zeta}{2} - \left(\frac{kT}{e} \right) \ln \left(\frac{1+\beta}{2} \right) + \left(\frac{kT}{e} \right) H(\zeta, a) \right\} + \frac{\phi_{+2}(a)}{a} \left\{ \frac{\zeta}{2} - \left(\frac{kT}{e} \right) \ln \left(\frac{1+\beta}{2} \right) - \left(\frac{kT}{e} \right) H(\zeta, a) \right\} + \frac{2\phi_{-1}(a)}{a} \left(\frac{kT}{e} \right) \ln \left(\frac{1+\beta}{2} \right) \right] \tag{4}$$

with

$$H(\zeta, \alpha) = \frac{(1-\alpha)}{2} \sqrt{\frac{3}{\alpha}} \left\{ \left(\frac{e\zeta}{kT} \right) \ln \left[\left(\frac{1+\sqrt{\alpha/3}}{1-\sqrt{\alpha/3}} \right) \left(\frac{1-\beta}{1+\beta} \right) \right] - 2 \ln \left(\frac{\beta+\sqrt{\alpha/3}}{1+\sqrt{\alpha/3}} \right) \cdot \ln \left(\frac{1-\beta}{1+\beta} \right) - \text{Li}_2 \left(\frac{\beta+\sqrt{\alpha/3}}{1+\sqrt{\alpha/3}} \right) + \text{Li}_2 \left(\frac{\beta-\sqrt{\alpha/3}}{1-\sqrt{\alpha/3}} \right) - \text{Li}_2 \left(-\frac{\beta-\sqrt{\alpha/3}}{1+\sqrt{\alpha/3}} \right) + \text{Li}_2 \left(-\frac{\beta+\sqrt{\alpha/3}}{1-\sqrt{\alpha/3}} \right) - \text{Li}_2 \left(-\frac{1+\sqrt{\alpha/3}}{1-\sqrt{\alpha/3}} \right) + \text{Li}_2 \left(-\frac{1-\sqrt{\alpha/3}}{1+\sqrt{\alpha/3}} \right) \right\} - \frac{e\zeta}{2kT} + \ln \left(\frac{1+\beta}{2} \right) \tag{5}$$

$$\alpha = \frac{3n_2}{n_1 + 3n_2}, \quad \beta = \sqrt{\frac{\alpha}{3} + \left(1 - \frac{\alpha}{3}\right) \exp\left(\frac{e\zeta}{kT}\right)} \quad (6)$$

where $\text{Li}_2(z)$ is a dilogarithm function (defined by $\text{Li}_2(z) = \sum_{k=1}^{\infty} (z^k/k^2)$), which can easily be evaluated via, e.g., Mathematica.

Consider first the case of $\zeta > 0$. In this case, the counterions are anions of valence -1 and we have

$$\frac{\phi_{-1}(a)}{a} = \frac{3}{2(1 + F_{-1})}, \quad \frac{\phi_{+1}(a)}{a} = \frac{\phi_{+2}(a)}{a} = \frac{3}{2} \quad (7)$$

with

$$F_{-1} = \frac{2(1 + 3m_{-1})}{\kappa a \sqrt{1 - \alpha/3}} \left\{ \exp\left(\frac{e\zeta}{2kT}\right) - 1 \right\}, \quad m_{-1} = \frac{2\varepsilon_r \varepsilon_0 kT}{3\eta e^2} \lambda_{-1} = \frac{2N_A \varepsilon_r \varepsilon_0 kT}{3\eta \Lambda_{-1}^0} \quad (8)$$

where λ_{-1} and Λ_{-1}^0 are, respectively, the drag coefficient and the limiting conductance of the counterions (anions) of valence -1 and m_{-1} is the corresponding scaled drag coefficient. Equation (4) thus becomes

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \left\{ \zeta - \frac{2F_{-1}}{1 + F_{-1}} \left(\frac{kT}{e}\right) \ln\left(\frac{1 + \beta}{2}\right) \right\} \quad (9)$$

In the limit of $n_2 \rightarrow 0$ ($\alpha \rightarrow 0$, pure 1:1 electrolyte), Eq. (9) tends to

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \left\{ \zeta - \frac{2F_{-1}}{1 + F_{-1}} \left(\frac{kT}{e}\right) \ln\left[\frac{\exp(e\zeta/2kT) + 1}{2}\right] \right\} \quad (10)$$

with

$$F_{-1} = \frac{2}{\kappa a} (1 + 3m_{-1}) \left\{ \exp\left(\frac{e\zeta}{2kT}\right) - 1 \right\} \quad (11)$$

In the limit of $n_1 \rightarrow 0$ ($\alpha \rightarrow 1$, pure 2:1 electrolyte), on the other hand, Eq. (9) tends to

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \left\{ \zeta - \frac{2F_{-1}}{1 + F_{-1}} \left(\frac{kT}{e}\right) \ln\left[\frac{1}{2} + \frac{1}{2} \sqrt{\frac{2}{3} \exp\left(\frac{e\zeta}{kT}\right) + \frac{1}{3}}\right] \right\} \quad (12)$$

with

$$F_{-1} = \frac{\sqrt{6}}{\kappa a} (1 + 3m_{-1}) \left\{ \exp\left(\frac{e\zeta}{2kT}\right) - 1 \right\} \quad (13)$$

Equations (10) and (12), respectively, agree with the previous results derived for pure 1:1 and 2:1 electrolytes [18].

Consider next the case of $\zeta < 0$. In this case, the counterions are cations of valence $+2$ and those of valence $+1$ and we have

$$\frac{\phi_{+1}(a)}{a} = \frac{3}{2(1 + F_{+1})}, \quad \frac{\phi_{+2}(a)}{a} = \frac{3}{2(1 + F_{+2})}, \quad \frac{\phi_{-1}(a)}{a} = \frac{3}{2} \quad (14)$$

with

$$F_{+1} = \frac{2}{\kappa a} (1 + 3m_{+1}) \left\{ \exp\left(\frac{e|\zeta|}{2kT}\right) - 1 \right\},$$

$$F_{+2} = \frac{\sqrt{3}}{\kappa a} (1 + 3m_{+2}) \left\{ \exp\left(\frac{e|\zeta|}{kT}\right) - 1 \right\} \quad (15)$$

$$m_{+1} = \frac{2\varepsilon_r \varepsilon_0 kT}{3\eta e^2} \lambda_{+1} = \frac{2N_A \varepsilon_r \varepsilon_0 kT}{3\eta \Lambda_{+1}^0},$$

$$m_{+2} = \frac{\varepsilon_r \varepsilon_0 kT}{6\eta e^2} \lambda_{+2} = \frac{N_A \varepsilon_r \varepsilon_0 kT}{3\eta \Lambda_{+2}^0} \quad (16)$$

where λ_{+1} and Λ_{+1}^0 are, respectively, the drag coefficient and limiting conductance of counterions (cations) of valence $+1$, λ_{+2} and Λ_{+2}^0 are those of counterions (cations) of valence $+2$, and m_{+1} and m_{+2} are the corresponding scaled drag coefficients. The electrophoretic mobility μ is thus given by

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \left[\zeta + \left(\frac{1}{1 + F_{+1}} + \frac{1}{1 + F_{+2}} - 2\right) \left\{ \zeta - \left(\frac{kT}{e}\right) \ln\left(\frac{1 + \beta}{2}\right) \right\} + \left(\frac{1}{1 + F_{+1}} - \frac{1}{1 + F_{+2}}\right) H(\zeta, \alpha) \right] \quad (17)$$

Note that

$$H(\zeta, \alpha) \rightarrow \frac{e\zeta}{2kT} - \ln\left(\frac{1 + \beta}{2}\right) \quad \text{as } n_2 \rightarrow 0 \text{ and} \quad (18)$$

$$H(\zeta, \alpha) \rightarrow -\frac{e\zeta}{2kT} + \ln\left(\frac{1 + \beta}{2}\right) \quad \text{as } n_1 \rightarrow 0$$

In the limit of $n_2 \rightarrow 0$ ($\alpha \rightarrow 0$, pure 1:1 electrolyte), in which case, Eq. (17) tends to

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \left\{ \zeta + \frac{2F_{+1}}{1 + F_{+1}} \left(\frac{kT}{e}\right) \ln\left[\frac{\exp(e|\zeta|/2kT) + 1}{2}\right] \right\} \quad (19)$$

while in the limit of $n_1 \rightarrow 0$ ($\alpha \rightarrow 1$, pure 2:1 electrolyte), Eq. (17) tends to

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \left\{ \zeta + \frac{2F_{+2}}{1+F_{+2}} \left(\frac{kT}{e} \right) \ln \left[\frac{1}{2} \exp \left(\frac{e|\zeta|}{2kT} \right) + \frac{1}{2} \sqrt{\frac{1}{3} \exp \left(\frac{e|\zeta|}{kT} \right) + \frac{2}{3}} \right] \right\} \quad (20)$$

Equations (18) and (19), respectively, agree with the previous results derived for pure 1:1 and 2:1 electrolytes [18]. Note that F_{+1} , F_{+2} , and F_{-1} in the above equations correspond to Dukhin's number, expressing the relaxation effect.

Results and discussion

We have derived approximate analytic expressions Eqs. (4) and (17) for the electrophoretic mobility μ of a spherical particle of radius a and zeta potential ζ in a mixed solution of 1:1 and 2:1 electrolytes with common anions. The relaxation effect, which becomes appreciable for high zeta potentials, is taken into account. Equations (4) and (17) are approximate equations applicable for all values of ζ at large κa . Since these equations are derived by neglecting terms of the order of $1/\kappa a$, they are expected to be applicable for $\kappa a \geq$ ca. 30 with tolerable errors. Some examples of the calculation of the electrophoretic mobility μ for a positively (Fig. 1) or negatively (Fig. 2) charged spherical particle for $\kappa a = 50$ in an

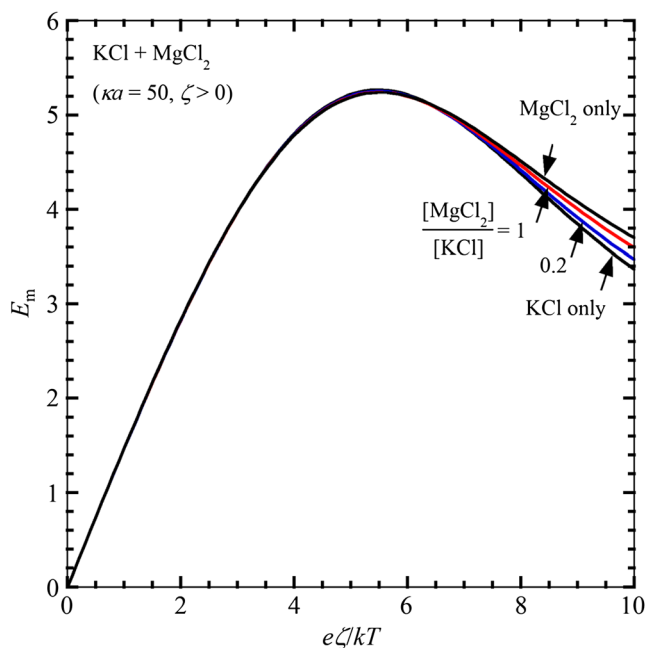


Fig. 1 Scaled electrophoretic mobility $E_m = (3\eta e / 2\varepsilon_r \varepsilon_0 kT) \mu$ of a positively charged spherical particle of radius a and zeta potential $\zeta > 0$ in an aqueous mixed solution of KCl and MgCl_2 as functions of scaled zeta potential $e\zeta/kT$. Calculated with $\kappa a = 50$ at 25 °C

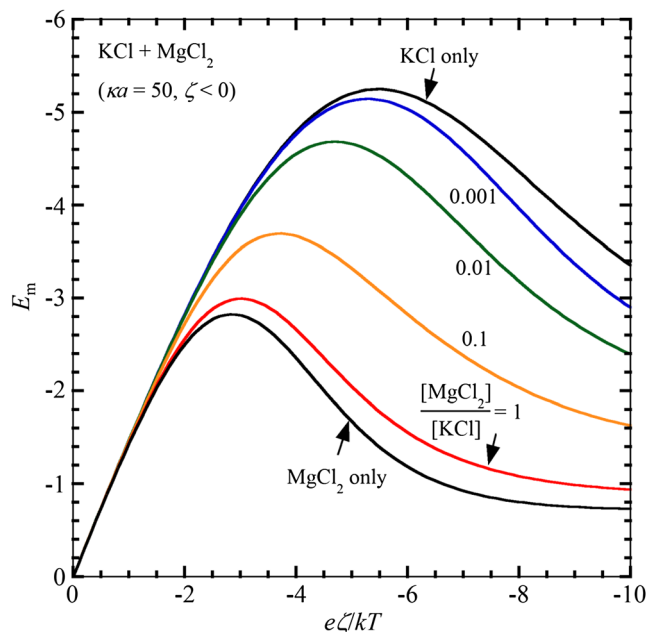


Fig. 2 Same as Fig. 1 but for a negatively charged spherical particle with $\zeta < 0$

aqueous mixed solution of KCl and MgCl_2 at 25 °C for several values of the concentration ratio $[\text{MgCl}_2] / [\text{KCl}]$ are shown in Figs. 1 and 2 in comparison with the results for pure 1:1 or 2:1 electrolytes. These figures show the scaled electrophoretic mobility $E_m = (3\eta e / 2\varepsilon_r \varepsilon_0 kT) \mu$ plotted as functions of the scaled zeta potential $e\zeta/kT$. For $\zeta > 0$ (Fig. 1), in which case the counterions are Cl^- ($\Lambda_{-1}^0 = 76.3 \times 10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$ and $m_{-1} = 0.169$), the mobility μ for a mixed solution slightly differs from those for pure electrolytes. For $\zeta < 0$ (Fig. 2), however, in which case the counterions are K^+ ions ($\Lambda_{+1}^0 = 73.5 \times 10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$ and $m_{+1} = 0.176$) and Mg^{2+} ions ($\Lambda_{+2}^0 = 106.1 \times 10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$ and $m_{+2} = 0.061$), the mobility μ for a mixed solution considerably differs from those for pure electrolytes. This difference comes from the fact that in this example, there are two kinds of counterions with different valences for $\zeta < 0$, but just one kind of counterion for $\zeta > 0$.

Conclusion

We have derived simple approximate analytic expressions Eqs. (4) and (17) for the electrophoretic mobility μ of a charged spherical colloidal particle of radius a and zeta potential ζ in an mixed solution of 1:1 and 2:1 electrolytes with common anions by taking into account the relaxation effects. These expressions, which are obtained by neglecting terms of order $1/\kappa a$ in the general mobility expression and correct to the order of $\exp(ze|\zeta|/2kT) / \kappa a$ (where z is the valence of counterions), are applicable for all values of zeta potential at large κa ($\kappa a \geq$ ca. 30).

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