

An approach to estimate the position of the shear plane for colloidal particles in an electrophoresis experiment



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ARTICLE INFO

Article history:

Received 6 June 2014

Accepted 25 August 2014

Available online 1 September 2014

Keywords:

Shear layer thickness

Zeta potential

Charged particles

Surface potential

Mixtures of electrolyte

ABSTRACT

The existence of the shear layer has great influence on the stability of colloidal systems and it is an important physicochemical parameter in the field of colloid and interface chemistry. However, to date, people do not know the actual position of the shear plane, and there is no theory to calculate the shear layer thickness. Conventionally, it is thought that the shear plane is very close to the Stern plane. In this study, a new theory for calculating the thickness of the shear layer for a planar charged colloidal particle in an aqueous solution was established; the shear layer thickness can be obtained based on the surface potential (the potential at the original plane of diffusion layer) and zeta potential of colloidal particles. The results showed that the surface potential of montmorillonite in various electrolyte solutions was approximately 3 to 6 times larger than the corresponding zeta potential. The thickness of the shear plane was dependent on the surface potential in the aqueous solution, and the shear plane was located far from the Stern plane but close to the Gouy plane, contradicting the widely accepted, erroneous placing of the shear plane close to the Stern plane. This study also showed that, ionic polarization in the electric field of the diffuse layer will significantly decrease the surface potential and the position of the shear plane.

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1. Introduction

When a colloidal particle carrying surface charge is dispersed in an aqueous solution there will be an electric double layer (EDL) surrounding the particle due to dissociation of the surface ions and adsorption and redistribution of the ions from the bulk solution near the particle surface [1]. The electric double layer adjacent to a charged surface is very vital to many interfacial phenomena [2,3]. The thickness of shear layer is the distance between the shear plane and the particle surface from the theory of electric double layer [3]. The shear layer thickness is an important physicochemical parameter in the field of colloid and interface chemistry [1,4–14]. The existence of the shear layer has a great influence on the stability of colloidal systems; specifically, it influences the hydrodynamic motion of the suspended particles, and is closely related to electrochemical phenomena such as electrodialysis and electrophoresis, and electrochemical properties such as the streaming potential and the sedimentation potential [1,15–18]. The position of the shear plane has therefore been a subject of great interest for many investigators [1,4–14].

Many authors hold that the shear plane is very close to the surface of planar colloidal particles, and that its position is roughly equal to that of the Stern plane or the outer Helmholtz plane (see Fig. 1) [4,5,8,12,13,18]; this would mean that the thickness of the shear layer would be approximately two to three water molecule diameters, smaller than the thickness of the Gouy plane (the Debye–Hückel length κ^{-1}). Additionally, some researchers argue that the shear plane in the electrical double layer is close to the Gouy plane [10], and others argue that the thickness of the shear plane is greater than the Debye–Hückel length κ^{-1} [6]. It is therefore non-trivial to question the true location of the shear plane.

Li et al. discussed the position of the shear plane based on the Poisson–Boltzmann equation in a single electrolyte [10]. The Gouy–Chapman theory was originally applied to symmetric ions [19,20]. The extension to 2:1 and 1:2 electrolytes was obtained by Grahame [21]. Of course, Valleeu and Torrie have applied the modified Gouy–Chapman theory to ions which are symmetric in charge and asymmetric in diameter in the early 1980s [22], while that for both asymmetric valencies and ionic sizes was solved by Bhuiyan et al. [23]. Classically, ionic size, hydration and dispersion forces between ion and surface will influence potential distribution in the diffuse layer, those are referred to as specific ion effects or Hofmeister effects [24]. However, only under relatively high electrolyte concentrations would those effects become significant [25–28]. In dilute solutions, Liu et al. found another important effect-

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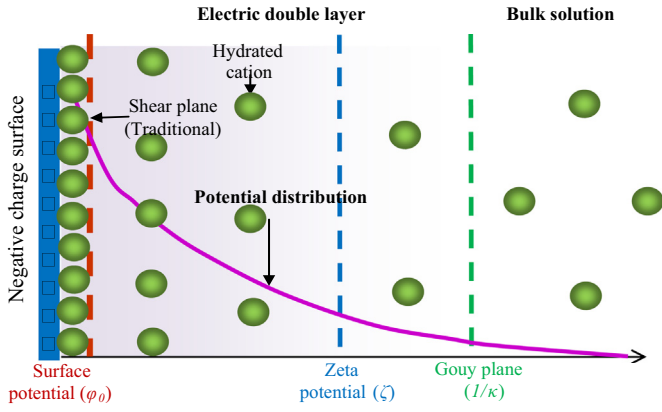


Fig. 1. A diagram of the position of the shear plane in the electric double layer.

strong polarization presented for adsorbed ions in the strong electric field in the diffuse layer [28]. Therefore, even in dilute solutions, the classical Gouy–Chapman theory is incorrect. Obviously, all the above effects as well as ion–ion interactions will influence the surface potential ψ_0 and potential distribution $\psi(x)$. However, if we employ the method suggested by Liu et al. [29], we could use a modified $\varphi_0 = \beta\psi_0$ and $\varphi(x) = \beta\psi(x)$ instead of the classic ψ_0 and $\psi(x)$ in the Poisson–Boltzmann equation, and as the result the mathematic expressions of the analytic solutions in the classical Gouy–Chapman theory were still correct. Therefore, for this approach, the key is how to obtain the *modified surface potential*. Li et al. and Liu et al. have developed a method to determine the modified surface potential [28–30]. Here we should note that, the experimentally determined surface potential is actually the true potential at the surface because it includes all the above effects. In summary, if the *true surface potential* was used, the mathematic expressions in the classical Gouy–Chapman theory could be directly employed in this study. The analytical solutions of the Poisson–Boltzmann equation in a single 1:1, 2:1, 1:2, and 2:2 electrolyte were derived [31], and the potential distributions in the electrical double layer could then be described. By combining the zeta potential with the potential distribution, the shear plane could be investigated theoretically.

However, both in scientific research and in chemical engineering, people often meet mixed electrolyte solutions rather than a single electrolyte solution. Fortunately, Liu et al. recently determined the analytical solutions of the PB equation in mixed electrolytes with monovalent and bivalent ions [32]. Hence, in the present study, theoretical expressions for the thickness of the shear layer on planar surfaces in a mixed solution (i.e., 1:1 + 2:1, 1:1 + 1:2, 1:1 + 2:2, 2:1 + 1:2, 2:1 + 2:2 and 1:2 + 2:2 electrolytes) could be derived. It would expand the function of zeta potential instrument, namely the zeta potential instrument would determine surface potential that is the potential at the outer Helmholtz plane.

2. Theoretical analysis

Here we just give the results in Z:Z and 1:2/2:1 electrolyte solutions, the expressions in all mixture electrolyte solutions are in the Appendix A.

2.1. The shear layer thickness for colloidal particles in Z:Z electrolyte

2.1.1. The shear layer thickness for colloidal particles in 1:1 electrolyte

Although the actual position of the shear plane is unknown, it is not in doubt that the shear plane must be situated in the domain beyond the outer Helmholtz or the Stern plane; therefore, the Gouy–Chapman theory can be used in a discussion of the position of the shear plane under

the given conditions. For a 1:1 electrolyte solution (i.e., an AB electrolyte, for example, NaCl), considering a planar surface, the potential distribution can be expressed as Eq. (1):

$$\varphi(x) = \frac{2RT}{F} \ln \left(\frac{1 - \lambda_1 e^{-\kappa x}}{1 + \lambda_1 e^{-\kappa x}} \right). \quad (1)$$

In a 1:1 electrolyte solution, the distance from a particle surface is obtained from Eq. (1) as:

$$x = -\frac{1}{\kappa} \ln \left[\frac{1 - e^{\varphi(x)F/2RT}}{(1 + e^{\varphi(x)F/2RT})\lambda_1} \right]. \quad (2)$$

The shear plane thickness is defined as the distance from a particle surface to the shear plane; then, at the shear plane, a zeta potential ζ can be determined from electrophoretic measurements. By substituting $\varphi(x) = \zeta$ into Eq. (2), we can obtain an equation to calculate the shear plane thickness (x_s):

$$x_s = -\frac{1}{\kappa} \ln \left[\frac{1 - e^{\zeta F/2RT}}{(1 + e^{\zeta F/2RT})\lambda_1} \right] \quad (3)$$

where the F is Faraday constant ($F = 96,490$ C/mol), R is the molar gas constant ($R = 8.314$ J/mol K), T is the absolute temperature (K), Z is the valence of the ions, $\lambda_{1:1}$ is a constant, and κ is the Debye–Hückel parameter. $\lambda_{1:1}$ and κ can be expressed as Eqs. (4) and (5):

$$\lambda_1 = \frac{1 - e^{F\varphi_0/2RT}}{1 + e^{F\varphi_0/2RT}} \quad (4)$$

$$\kappa = \sqrt{\frac{8\pi F^2 Z_A^2 f_A}{\varepsilon RT}} = \sqrt{\frac{8\pi F^2 (0.5 \sum Z_i^2 f_i)}{\varepsilon RT}} \quad (5)$$

where φ_0 is the surface potential (the potential at original plane of diffusion layer), ε is the dielectric constant of the medium (for water, $\varepsilon = 8.9 \times 10^{-9}$ C²/J m), and f_A is the cationic concentration in a 1:1 electrolyte in the bulk solution.

2.1.2. The shear layer thickness for colloidal particles in 2:2 electrolyte

For a 2:2 electrolyte (i.e., CD electrolyte, for example, CaSO₄), considering a planar surface, the potential distribution be expressed as Eq. (6).

$$\varphi(x) = \frac{RT}{F} \ln \left[1 - \frac{16\lambda_2 e^{\kappa x}}{(\lambda_2 e^{\kappa x} + 4)^2 - 16} \right] \quad (6)$$

The distance from a particle surface is obtained from Eq. (6) as follows.

$$x = \frac{1}{\kappa} \ln \left[\frac{8 + 8e^{\varphi(x)F/RT}}{(1 - e^{\varphi(x)F/RT})\lambda_2} \right] \quad (7)$$

By substituting $\varphi(x) = \zeta$ into Eq. (7), we can obtain the equation to calculate the shear plane thickness (x_s).

$$x_s = \frac{1}{\kappa} \ln \left[\frac{8 + 8e^{\zeta F/RT}}{(1 - e^{\zeta F/RT})\lambda_2} \right] \quad (8)$$

where

$$\lambda_2 = \frac{8 + 8e^{F\varphi_0/RT}}{1 - e^{F\varphi_0/RT}} \quad (9)$$

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