1 Theoretical model

The distribution of the potential (isodynamic curve) between two flat surfaces with dissimilar surface potentials is schematically illustrated in scheme 1. Φ_0 is the zeta potential. Subscripts 1 refers to the potential at the air/ solution interface and 2 to the potential of the solution/ solid interface. It was assumed that both potentials are negative and $\Phi_{01} > \Phi_{02}$. $\bar{\Phi}$ is a potential minimum between the two surfaces. Using the dimensionless form of the Poisson Boltzmann (PB) equation the dimensionless potential (Y) and distance (ξ) are defined by

$$Y = ze\Phi/kT \tag{1}$$

where z is the valence of the ion, e is the elemental charge, k is the Boltzmann constant, and T is the absolute temperature.

$$\xi = x\kappa \tag{2}$$

where κ is the reciprocal Debye length given by

$$\kappa = (2n^2e^2z^2/\epsilon_0\epsilon_r kT)^{\frac{1}{2}} \tag{3}$$

where n is the number concentration of electrolyte in the bulk solution, ϵ_0 is the permittivity of vacuum, and ϵ_r is the relative permittivity of the medium. It was assumed that the force of interaction per unit area, disjoing pressure Π, is equal to the osmotic pressure Π_{osm}. The PB equation in the dimensionless form for a symmetrical electrolyte and flat surface is given by

$$\frac{d^2Y}{d\xi^2} = sinhY \tag{4}$$

and the corresponding isodynamic curve and pressure by

$$\left(\frac{dY}{d\xi}\right)^2 = 2cosh(Y) + C \tag{5}$$

and

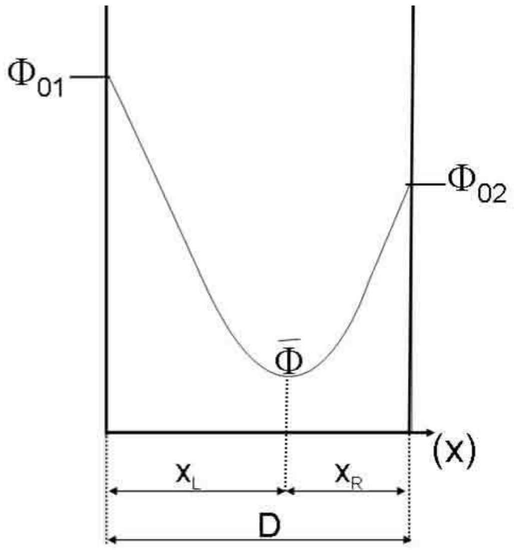
$$\Pi(D) = -nkT(C(D) + 2) \tag{6}$$

Analytical solution to Eq. (5) exist. The solution depends on whether for C≥2, |C|<2 or C≤-2. From Eq. (6) it is seen that Π is repulsive (positive) for C<-2 and attractive (negative) for C>-2. When a potential minimum exist as shown in scheme 1, C is given by

$$C = -2cosh(\bar{Y}) \tag{7}$$

The dimensionless surface separation is given by

$$\xi_D = \xi_L + \xi_R \tag{8}$$



Scheme 1: Schematic illustration of the potential distribution between two dissimilar charged flat surfaces.

by intergarting Eq. (5)

$$\xi_L = \int_{\bar{Y}}^{Y_{01}} \frac{dY}{(2coshY + C)^{0.5}} \tag{9}$$

$$\xi_R = \int_{\bar{Y}}^{Y_{02}} \frac{dY}{(2coshY + C)^{0.5}} \tag{10}$$

These integrals can be solved in terms of the elliptic integral of the first kind.

2 Zeta-potential measurements

The zeta-potential measurements were achieved by using a Zetasizer Nano ZS (Malvern Instruments, Germany). A defined electrical field is applied across a sample illuminated with two focused laser beams. Particles which move through the measuring volume scatter this light. The intensity of the scattered light fluctuates depending on the velocity of the particles. The mobility of the particles can be calculated from the frequency of the fluctuations and can be converted into the zeta-potential by using the Smoluchowski equation:

$$U_E = \frac{\epsilon\epsilon_0 \zeta f(ka)}{3\eta} \tag{11}$$

In this paper, zeta-potential measurements were used to ensure that for the used electrolytes, only a minor counterion adsorption at the solid substrate takes place within the considered concentration regime (see table 1). In all measurements the same amount of silica particles (0.001 w%)) have been investigated in the respective electrolyte solution.

Table 1: Experimental zeta-potential ζ of 0.001 w% of silica particle in water or in the repective electrolyte solution at a fixed concentration of 10^{-4} M.

	ζ [mV]
H_2O	-98.6±0.5
KI	-85.0±0.5
KCl	-84.6±0.5
KF	-78.3±0.5
NaI	-88.3±0.5
NaF	-80.7±0.5
CsI	-86.5±0.5
CsF	-74.9±0.5

Under this condition, the ζ-potential can be considered as more or less constant.