

A CRITICAL APPRAISAL OF DEBYE LENGTH IN CLAY-ELECTROLYTE SYSTEMS

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Abstract—The equivalent diffuse double layer (DDL) thickness in clay-electrolyte systems is a very useful parameter for analyzing the engineering behavior of clays under different environmental conditions. The equivalent DDL thickness is generally assumed to be equal to the characteristic (Debye) length. The present work examined critically the applicability of characteristic length to define equivalent DDL thickness under various clay-surface and pore-fluid conditions. A critical analysis is presented of the changes in the equivalent DDL thickness and characteristic length under the influence of different clay-surface and electrolyte properties. The equivalent DDL thickness was found to be smaller than the characteristic length for a wide range of surface and pore-fluid parameters normally encountered in engineering practice. An accurate and simple power relationship was developed to predict the equivalent DDL thickness from the characteristic length, which is applicable to a wide range of clay-electrolyte systems.

Key Words—Clay-electrolyte System, Debye Length, Diffuse Double Layer.

INTRODUCTION

Plastic clays are of interest as buffer and backfill materials in toxic-waste and high-level nuclear-waste disposal facilities all over the world (JNC DI, 1999; Zheng *et al.*, 2011; Sellin and Leupin, 2014). Several natural and commercially available plastic clays (*e.g.* MX80, Febex, Montigel, and Kunigel V1) have been used widely in such applications. The application of DDL theory in the analysis of swelling pressures of compacted plastic clays is widely recognized (Tripathy *et al.*, 2004; Schanz and Tripathy, 2009; Baille *et al.*, 2010; Bharat *et al.*, 2013). The suitability of a given plastic clay for many engineering applications can be assessed easily and quickly using laboratory-based index tests, *e.g.* liquid limit and free swell ratio (Prakash and Sridharan, 2004). The relations between index and engineering properties are confirmed in the literature by analyzing the variations in the equivalent DDL thickness due to the changes in pore-fluid characteristics for given clay-electrolyte systems. The mechanisms by which equivalent DDL thickness influences the liquid limit (Sridharan *et al.*, 1986; Lambe and Whitman, 1979), sediment volume (Chen and Anadarajah, 1998; Sridharan and Prakash, 1999a), hydraulic conductivity (Fernandez and Quigley, 1985; Sridharan and Choudhury, 2002), and undrained shear strength (Sridharan and Prakash, 1999b) have been well documented. The relations between clay-surface properties and equivalent DDL thickness are also well known

(Muhunthan, 1994). Such correlations can be useful in predicting indirectly the clay-surface properties from knowledge of index properties by analyzing the equivalent DDL thickness which is commonly estimated (Mitchell and Soga, 2005) as:

$$1/\kappa = \sqrt{\frac{\epsilon KT}{8\pi e'^2 v^2 n}} \quad (1)$$

where e' is the elementary electric charge (esu), v is the valence of the ions, ϵ is the dielectric constant, K is thermal energy per ion in joules, T is the absolute temperature, and n is the molar concentration of the ions in bulk solution (mole/L). The quantity $1/\kappa$ (Å) is the characteristic length or 'Debye length' (Verwey and Overbeek, 1948). Equation 1 is used widely in many science and engineering applications as the equivalent DDL thickness (McBride, 1997; Poortinga *et al.*, 2002; Kitazumi *et al.*, 2013). There is no justification presented in the literature, however, to show that $1/\kappa$ is equal to the equivalent DDL thickness in non-interacting clay-electrolyte systems.

A critical appraisal of the characteristic length is provided here. The relevance of the equivalent DDL thickness was confirmed for different clay-surface and pore-fluid parameters. The condition at which the centroid distance deviates from the equivalent DDL thickness was investigated. The applicability of equivalent DDL thickness to determination of the theoretical water content of clays was analyzed qualitatively.

THEORY

The equivalent DDL thickness is considered as the distance of the centroid, d_c , of the electric potential distribution of clay-electrolyte systems, from the particle

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surface (Verwey and Overbeek, 1948) (Figure 1). The distribution of electric potential around a non-interacting and flat clay particle can be approximated using the following Poisson-Boltzmann equation (Mitchell and Soga, 2005):

$$\frac{d^2\phi}{dx^2} = \frac{8\pi nve'}{\epsilon} \sinh\left(\frac{ve'\phi}{KT}\right) \quad (2)$$

where x is the distance from the surface of the clay particle (Å) and ϕ is the electric potential (mV). The dimensionless form of equation 2 can be expressed as:

$$\frac{d^2y}{d\xi^2} = \sinh y \quad (3)$$

where $y = ve'\phi/KT$, $\xi = \kappa x$, and κ is the inverse of the characteristic length as defined in equation 1.

The following analytical solution to equation 3 for obtaining scaled, non-linear potential distribution can be obtained by considering the boundary conditions: $\xi = \infty$, $y = 0$, and $dy/d\xi = 0$ for the first integration; $\xi = 0$ and $y = z$ for the second integration (Verwey and Overbeek, 1948):

$$y = 2 \ln \frac{\exp(\kappa x) + \tanh(z/4)}{\exp(\kappa x) - \tanh(z/4)} \quad (4)$$

where z is the scaled surface potential which is equal to $ve'\phi_0/KT$. The surface potential can be estimated using the following equation (van Olphen, 1977; Bharat *et al.*, 2013):

$$\phi_0 = 0.1725 \frac{T}{v} \sinh^{-1} \left(\frac{1256.81P}{\sqrt{n\epsilon T}} \right) \quad (5)$$

where ϵ is the dielectric constant, v is the valence, and P is the ratio of cation exchange capacity (CEC)

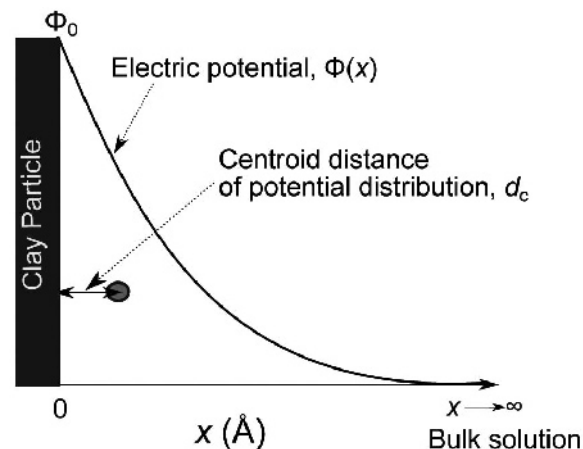


Figure 1. Conceptual diagram depicting the charge distribution around a clay particle.

(meq/100 g) to specific surface area (SSA) in m^2/g . According to the original discussion by Verwey and Overbeek (1948), the Debye length was defined in the context of $z \ll 1$ which is identical to $v\phi_0 \ll 25$ mV. The electric potential decreases exponentially and reaches a $1/e$ fraction of its value at the clay surface for small values of z ($z \ll 1$). The centre of gravity of the space charge also coincides with the plane $x = 1$ in the case $z \ll 1$. The 'equivalent' DDL thickness is, therefore, considered to be equal to the characteristic length of Debye ($= 1/\kappa$) in this particular case. This Debye length, a constant appearing in the dimensionless form of potential distribution in equation 3, is now used widely (Achari *et al.*, 1999; Poortinga *et al.*, 2002; Kitazumi *et al.*, 2013) as an equivalent DDL thickness for various clay-electrolyte systems, without attempting to understand its validity (*i.e.* $v\phi_0 \ll 25$ mV). The important and hitherto unanswered question is, therefore, whether the aforementioned definition is valid for equivalent DDL thickness for different clay-electrolyte parameters as the electric potential in the clay-electrolyte system is heavily dependent on the properties of the pore fluid for a given clay. The present study investigates the applicability of the Debye-length definition by comparing the centroid distance of the electric potential distribution around the particles with the characteristic length for different surface and pore-fluid parameters.

CENTROID DISTANCE CALCULATION

The centroid distance of a given clay-electrolyte system can be computed by considering either the variation of ion concentration or electric potential. The distribution of average local concentration of both counter-ions and co-ions at equilibrium must be considered when the concentration distribution is used (van Olphen, 1977). The original definition of Debye length by Verwey and Overbeek (1948) as an equivalent of $1/\kappa$ is given in the context of electric potential distribution only. The concentration is, therefore, expressed as a function of average electric potential according to the Boltzmann's theorem for centroid-distance computation. The electrostatic potential distribution around a clay particle was obtained by substituting the computed scaled surface potential, z , and the characteristic length, $1/\kappa$, into equation 4 for known properties of the clay surface and pore fluids. The centroid distance is computed using the following integral equation:

$$d_c = \frac{\int_0^\infty xy(x)dx}{\int_0^\infty y(x)dx} \quad (6)$$

where the centroid distance is measured in ångströms. The definite integral in equation 6 was solved numerically using the built-in 'quadv' function in MATLAB[®] (2012) which uses the recursive adaptive Simpson quadrature method. A very large value was assigned

for the upper boundary in the definite integral which varied between 5000 and 100,000 Å for each set of pore-fluid parameters to analyze the convergence of the numerical solution.

RESULTS AND DISCUSSION

The results of equivalent DDL thickness were analyzed by plotting the variation of the characteristic

length, $1/\kappa$, and the centroid distance, d_c , separately and also as a ratio of $1/\kappa d_c$ for different pore-fluid and clay-surface properties (Figures 2–6). Details of the pore-fluid and clay-surface properties used in the theoretical calculations are listed in Table 1. The variations in both the characteristic length and the centroid distance are presented for different electrolyte concentrations varying between 10^{-7} M and 10 M (Figure 2a). The surface potentials for concentrations between 10^{-6} M and

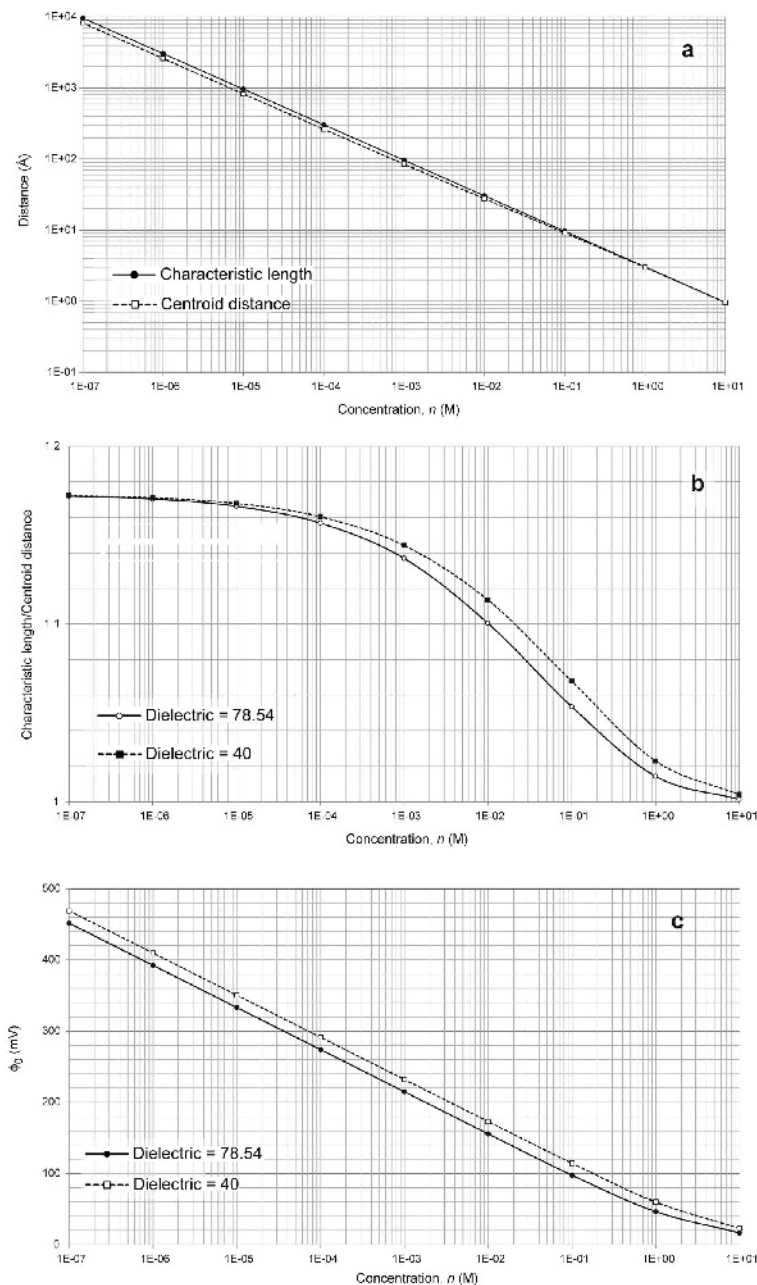


Figure 2. The influence of electrolyte concentration on (a) the characteristic length and centroid distance from the clay surface, (b) the ratio of characteristic length to the centroid distance for different dielectric media, and (c) surface potential for different dielectric media.

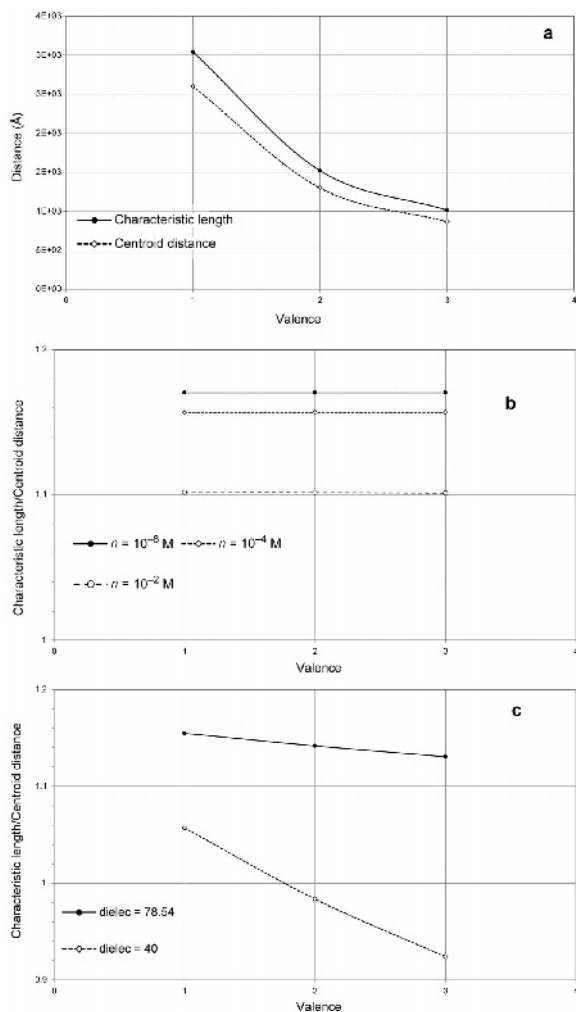


Figure 3. The influence of valence on (a) the characteristic length and centroid distance from the clay surface, (b) the ratio of characteristic length to the centroid distance for different electrolyte concentrations, and (c) the ratio of characteristic length to the centroid distance for different dielectric media.

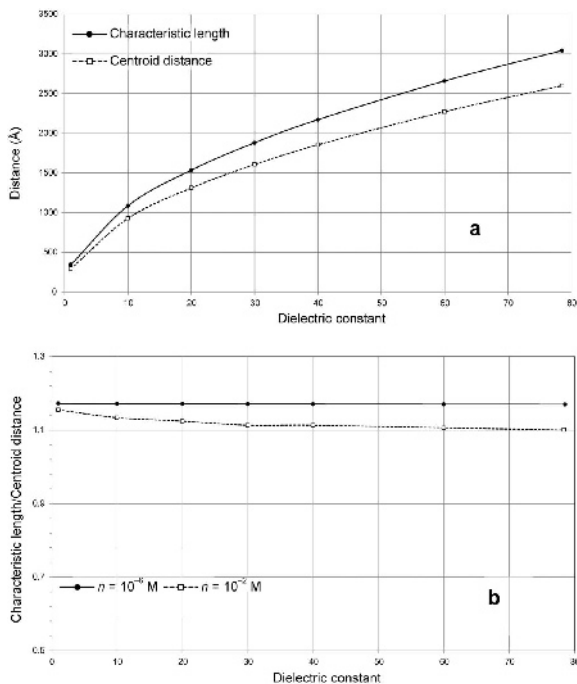


Figure 4. The influence of dielectric constant on (a) the characteristic length and centroid distance from the clay surface and (b) the ratio of characteristic length to the centroid distance for different electrolyte concentrations.

10^{-7} M were observed to be very large, *i.e.* $\phi_0 \geq 360$ mV. The commonly encountered surface potentials of clay minerals in engineering applications may be <360 mV (van Olphen, 1977), but in many science disciplines the surface potentials of charged metal surfaces can be as high as 400 mV (Scruton and Blott, 1973). A wide range of electrolyte concentrations was, therefore, selected in the present study in order to analyze the conditions under which the characteristic length, $1/\kappa$, becomes equal to the equivalent DDL thickness, d_c . Both characteristic length and centroid

Table 1. Details of the electrolyte and clay-surface properties in the sensitivity analysis for DDL thickness calculations.

Figure #	Variables	Details of the clay surface and electrolyte parameters
2a	N	CEC = 100 meq/100 g, SSA = 800 m ² /g, $\nu = 1$, $\epsilon = 78.54$, and $T = 298$ K
2b	n, ϵ	CEC = 100 meq/100 g, SSA = 800 m ² /g, $\nu = 1$, and $T = 298$ K
2c	n, ϵ	CEC = 100 meq/100 g, SSA = 800 m ² /g, $\nu = 1$, and $T = 298$ K
3a	V	CEC = 100 meq/100 g, SSA = 800 m ² /g, $n = 10^{-6}$ M, $\epsilon = 78.54$, and $T = 298$ K
3b	n, ν	CEC = 100 meq/100g, SSA = 800 m ² /g, $\epsilon = 78.54$, and $T = 298$ K
3c	ϵ, ν	CEC = 100 meq/100 g, SSA = 800 m ² /g, $n = 10^{-6}$ M, and $T = 298$ K
4a	ϵ	CEC = 100 meq/100g, SSA = 800 m ² /g, $\nu = 1$, $\epsilon = 78.54$, and $T = 298$ K
4b	ϵ, n	CEC = 100 meq/100 g, SSA = 800 m ² /g, $\nu = 1$, and $T = 298$ K
5a	CEC/SSA	$\nu = 1$, $\epsilon = 78.54$, $n = 10^{-6}$ M, and $T = 298$ K
5b	$n, \text{CEC/SSA}$	$\epsilon = 78.54$, $\nu = 1$, and $T = 298$ K
5c	$n, \text{CEC/SSA}$	$\epsilon = 78.54$, $\nu = 1$, and $T = 298$ K
6a	T	CEC = 100 meq/100 g, SSA = 800 m ² /g, $\nu = 1$, $\epsilon = 78.54$, $n = 10^{-6}$ M, and $T = 298$ K
6b	T, n	CEC = 100 meq/100 g, SSA = 800 m ² /g, $\nu = 1$, $\epsilon = 78.54$, $n = 10^{-6}$ M, and $T = 298$ K

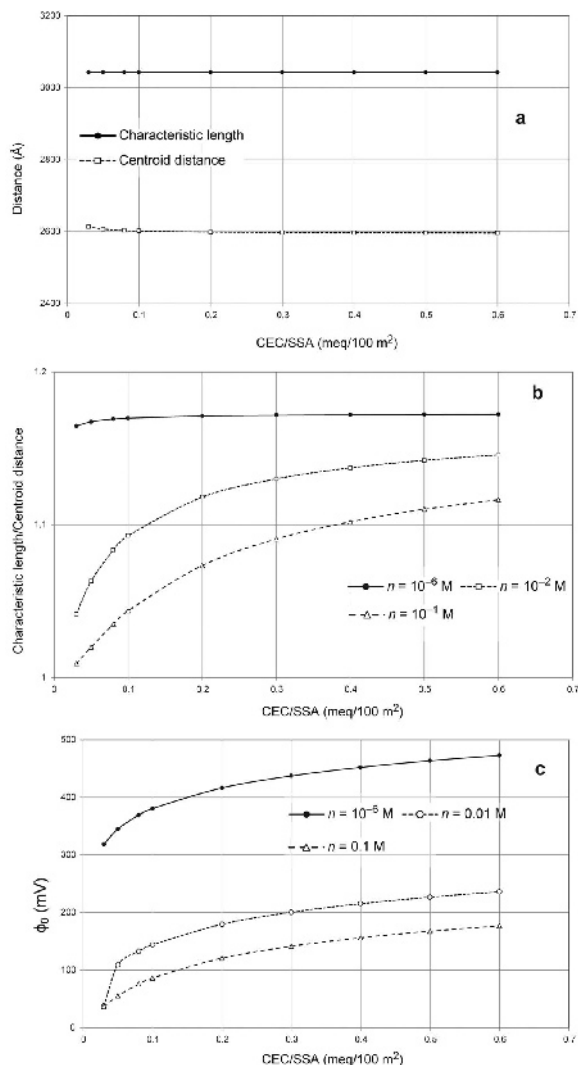


Figure 5. The influence of clay-surface properties on (a) the characteristic length and centroid distance from the clay surface, (b) the ratio of characteristic length to the centroid distance for different electrolyte concentrations, and (c) surface potential for different dielectric media.

distance decreased with the increase in the electrolyte concentration (Figure 2a).

The variation of $1/\kappa d_c$ with respect to the electrolyte concentration in the presence of two different dielectric media (Figure 2b) showed that the ratio $1/\kappa d_c$ changed non-linearly from 1.18 to 1 when the concentration increased from 10^{-7} to 10 M. This was because the surface potential decreased from 452 mV ($z \approx 18$) to 16 mV ($z < 1$) with the increase in the electrolyte concentration (Figure 2c). This observation was consistent with the definition of equivalent DDL thickness by van Olphen (1977). The classical definition of equivalent DDL thickness is, therefore, valid for electrolyte concentrations beyond 1 M where the surface potential dropped below 25 mV (Figure 2c).

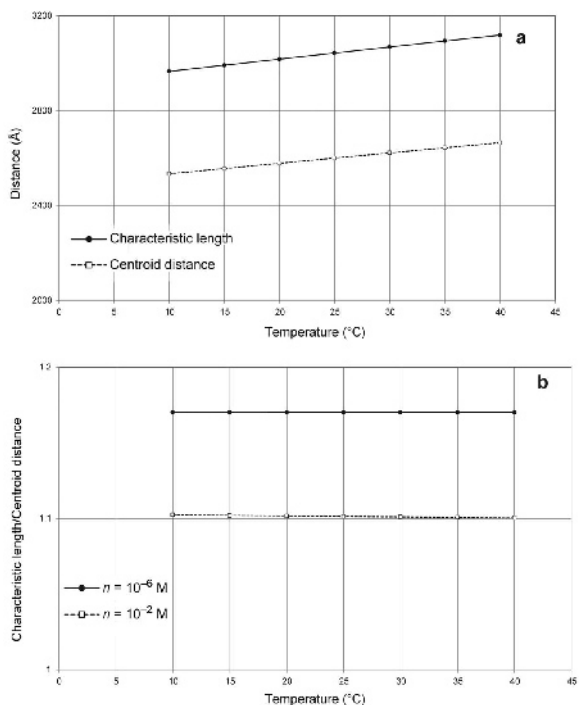


Figure 6. The influence of temperature on (a) the characteristic length and centroid distance from the clay surface and (b) the ratio of characteristic length to the centroid distance for different electrolyte concentrations.

The variation of the characteristic length and the centroid distance due to changes in the electrolyte valence was also analyzed (Figure 3a). A deviation of ~17% was observed between the characteristic length and the centroid distance in the presence of monovalent cations. The deviation decreased slightly in the presence of divalent and trivalent cations, even though both $1/\kappa$ and d_c decreased with increase in the cation valence. The influence of electrolyte concentration on the variation of $1/\kappa d_c$ was identified by analyzing the relationship of $1/\kappa d_c$ against the cation valence in the presence of three different electrolyte concentrations (Figure 3b). The ratio was consistent with the valence, but approached unity with increasing concentration. The influence of dielectric medium on the variation of $1/\kappa d_c$ was identified by analyzing the relationship of $1/\kappa d_c$ vs. the cation valence in the presence of two different dielectric media (Figure 3c). The ratio ($1/\kappa d_c$) was found to decrease with valence. The decreasing trend was more pronounced for smaller dielectric constants, e.g. the ratio approached unity when the surface potential dropped below 25 mV, which corresponds to the presence of a very large cationic valence and small dielectric constant.

The variations of the characteristic length and of the centroid distance were analyzed using different dielectric media (Figure 4a). The deviation of the characteristic length from the centroid distance was ~17% when water was used as the pore-fluid medium. The deviation

decreased slightly with decrease in the dielectric constant and approached zero at very small values of the dielectric constant. The influence of electrolyte concentration on the relationship between the ratio $1/\kappa d_c$ and the dielectric constant was confirmed (Figure 4b). The ratio $1/\kappa d_c$ remained nearly constant for different dielectric media. The ratio did become almost equal (~ 1.16) in the presence of a very low dielectric pore medium such as $\epsilon = 1$. The ratio did not converge to unity (i.e. $\phi_0 > 25$ mV) for the entire range of dielectric constants (1–78.54) encountered in engineering applications.

The variations in the characteristic length and the centroid distance were plotted vs. the cation exchange capacity and surface area of the clay (CEC/SSA) (Figure 5a). The characteristic length was observed to be insensitive to CEC/SSA because the equation describing the characteristic length does not contain the surface properties of the clay. The clay-surface properties do influence the centroid distance, however. A significant deviation ($\sim 17\%$) of the characteristic length from the centroid distance was observed, therefore. The variation of the ratio $1/\kappa d_c$ with CEC/SSA in the presence of three different electrolyte concentrations (Figure 5b) showed that the ratio $1/\kappa d_c$ remained constant in the presence of low electrolyte concentrations, but the ratio approached unity for a small value of CEC/SSA, i.e. 0.03 meq/100 m² in the presence of high electrolyte concentrations. The effect of CEC/SSA on the ratio between centroid distance and characteristic length was found to be significant only at very high concentrations. The centroid distance decreased by 10% with increase in the ratio of CEC/SSA (for a change of CEC/SSA ratio from 0.03 to 0.6 meq/100 m²) when $n = 0.01$ M. The distance decreased by just 0.7% with increase in CEC/SSA when $n = 10^{-6}$ M, however. This can be analyzed easily using equations 4–6. At very small ratios of CEC/SSA (i.e. < 0.03) and under high electrolyte concentrations, the surface potential dropped below 25 mV and the centroid distance was equal to the characteristic length (Figure 5c).

The variation of the characteristic length and the centroid distance with temperature (Figure 6a) showed a deviation of 17% between characteristic length and centroid distance. The deviation remained nearly constant with increase in the temperature, even though both $1/\kappa$ and d_c increased with increase in the ambient temperature. The influence of electrolyte concentration on the variations of characteristic length and the centroid distance was confirmed by plotting the $1/\kappa d_c$ vs. the temperature in the presence of two different electrolyte concentrations (Figure 6b). The ratio $1/\kappa d_c$ remained constant for different temperatures, but decreased with increase in the electrolyte concentration.

The dependency of centroid distance on the characteristic length was very complex as many pore-fluid and clay-surface parameters influence the two thicknesses. The $1/\kappa$ value was observed to be consistently

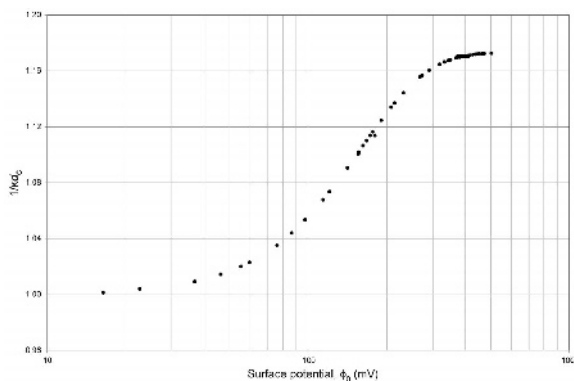


Figure 7. The variation of characteristic length to centroid distance ratio with surface potential.

greater than d_c , $\sim 17\%$ for different pore-fluid and clay-surface parameters. The values of characteristic length and equivalent DDL thickness converged only under uncharacteristic surface and pore-fluid conditions at which the surface potential dropped below 25 mV (Figure 7). The relationship followed an S curve and the maximum value of $1/\kappa d_c$ was ~ 1.18 . The value became equal to unity with extreme pore-fluid and surface properties. The application of characteristic length as an equivalent DDL thickness is questionable, therefore.

A generalized relationship was confirmed between $1/\kappa$ and d_c for predicting the equivalent DDL thickness from the characteristic length by plotting the data of $1/\kappa$ and d_c obtained for the same pore-fluid and clay-surface parameters (Figure 8). The results followed a power relationship which can be expressed as:

$$d_c = 0.95(1/\kappa)^{0.986} \quad (7)$$

where both $1/\kappa$ and d_c were measured in ångströms. The data fit was good with $R^2 = 0.999$. The accuracy of the proposed equation was verified by plotting the computed centroid distance (equation 6) and predicted distance (equation 7), which provided an accurate equivalent DDL thickness for all of the data (not shown here). The

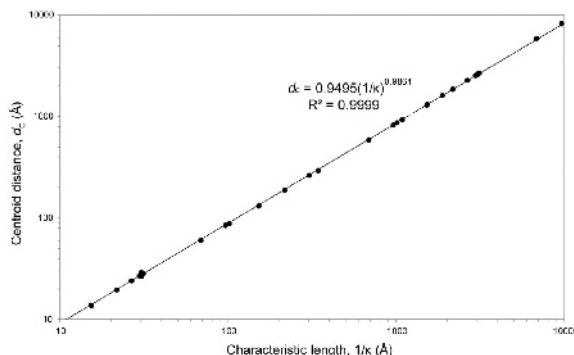


Figure 8. Power fit to the theoretical data between centroid distance and characteristic length for different pore-fluid characteristics.

proposed equation is applicable to a wide range of clay-surface and pore-fluid parameters that are commonly encountered in engineering and science applications.

The equivalent DDL thickness was observed to be the controlling parameter for analyzing the engineering behavior of clays. The influence of equivalent DDL thickness computation on the theoretical water content of the clay minerals was verified using the following equation (Lambe and Whitman, 1979):

$$w = t \times SSA \times \rho_w \quad (8)$$

where w is the gravimetric water content, t the equivalent DDL thickness, SSA is the specific surface area, and ρ_w the density of water. The equation represents the water content of a clay sample under stress-free conditions, *i.e.* an approximately 'liquid-limit' water content. The osmotic pressures due to the interacting diffuse double layers are negligibly small in the stress-free state. The theoretical water contents obtained by two different thicknesses (equations 1 and 6) were compared (Figure 9). An electrolyte concentration of 0.001 M, $v = 1$, and a specific surface area of 800 m²/g were used for the theoretical calculation of water content of the clay minerals. The water-content values observed here were comparable to the water contents reported by Low (1980) for sodium bentonite clays at a consolidation pressure of 2.5 kPa. The computed water content from the two different thicknesses differed by ~13% for the reported clay surface and electrolyte properties. The characteristic length over-predicted the clay water contents and the deviation from the actual values increased even beyond 20% with the decrease in the electrolyte concentration. A detailed error analysis of variation in water contents with clay surface and electrolyte parameters, however, was outside

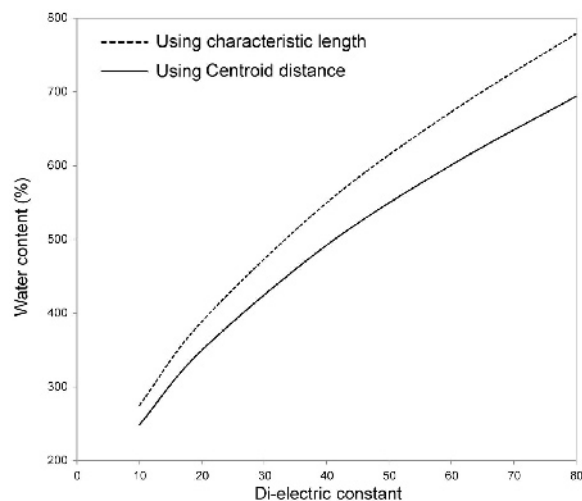


Figure 9. Comparison of the predicted clay-water contents in the presence of different dielectric media using characteristic length and centroid distance.

the scope of this study. The water content of the clay is inter-related to the surface properties and many other engineering properties. The relevance of the proposed equation to the equivalent DDL thickness computation in understanding the engineering behavior of clays and for applications in other, allied disciplines is yet to be explored. The convention of the characteristic length being equivalent to DDL thickness is, nevertheless, invalid.

CONCLUSIONS

The equivalent DDL thickness was observed to be the centroid distance, d_c , of the electric potential distribution around the clay particle in a clay-electrolyte system. On the other hand, $1/\kappa$ was simply an 'equation constant' which appeared in double-layer theoretical equations. The suggestion in the literature that $1/\kappa = d_c$ was valid only at very high electrolyte concentrations (1 M) and for very small CEC/SSA ratios (<0.03 meq/100 m²). Such extreme surface and pore-fluid conditions are encountered rarely in engineering and scientific applications. Use of characteristic length to represent the equivalent DDL thickness, therefore, is incorrect except within a very narrow zone of parameter space. The equivalent DDL thickness was smaller than the characteristic length (by as much as 17%) for a wide range of pore-fluid and surface properties. A new power relationship is proposed here to predict the equivalent DDL thickness from the characteristic length. This equation was not only valid over a wide range of pore-fluid and surface parameters, but was also capable of predicting the equivalent DDL thickness to a very high degree of accuracy. The proposed equation is useful for analyzing the influence of DDL thickness computation on many engineering parameters.

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