diffuse double layer

potential and distance from the surface and the effect of concentration and electrolyte valence on double-layer thickness.

The type of colloid (i.e., variable charge or constant charge) affects various double-layer parameters including surface charge, surface potential, and double-layer thickness (Fig. 5.10). With a variable charge surface (Fig. 5.10a) the overall diffuse layer charge is increased at higher electrolyte concentration (n'). That is, the diffuse charge is concentrated in a region that is closer to the surface when electrolyte is added and the total net diffuse charge, C′A′D′, which is the new surface charge, is greater than the surface charge at the lower electrolyte concentration, CAD. The surface potential remains the same (Fig. 5.10a) but since $1/\kappa$ is less, ψ decays more rapidly with increasing distance from the surface.

In variable charge systems the surface potential is dependent on the activity of PDI (potential determining ions, e.g., H^+ and OH^-) in the solution phase. The ψ_0 is not affected by the addition of an indifferent electrolyte solution (e.g., NaCl; the electrolyte ions do not react nonelectrostatically with the surface) if the electrolyte solution does not contain PDI and if the activity or concentration of PDI is not affected by the indifferent electrolyte.

In variable charge systems the surface charge (σ_v) is

$$\sigma_v = \left(\frac{2n\epsilon kT}{\pi}\right)^{1/2} \sinh\left(\frac{Ze}{2kT}\right) \text{(constant } \psi_0\text{)}, \qquad (5.10)$$

where sinh is the hyperbolic sin. If the PDI are H^+ and OH^-, the constant

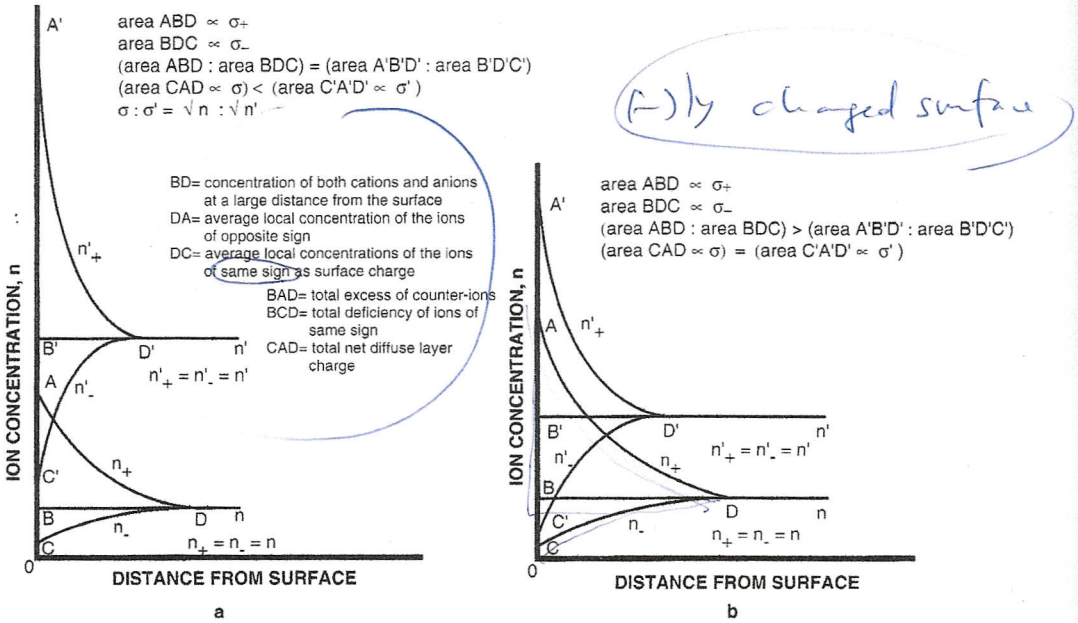

FIGURE 5.10. Charge distribution in the diffuse double layer of a negatively charged particle surface at two electrolyte concentrations, n (lower) and n' (higher). (a) Variable surface charge mineral. (b) Constant surface charge mineral. From van Olphen, H. "An Introduction to Clay Colloid Chemistry" 2nd ed. Copyright 1977 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.