

APPENDIX

ELECTRIC DOUBLE LAYER AND CAPACITANCE RESPONSE

A.1. Models of the Electrical Double Layer

A.1.1. The Helmholtz model

In 1853 the first and simplest model of concept of the charge separation at interfaces was proposed by Helmholtz [1-3], who proposed that the interface between a metallic electrode and an electrolyte solution behaves like capacitor i.e. it is capable of storing electric charge. The proposed model was that the electrode possesses a charge density (q^m) arising from an excess (q^m negative) or deficiency (q^m positive) of electrons at the electrode surface. The charge on the electrode is exactly balanced in solution by an equal but oppositely charged amount of ions (q^s); a rigidly held layer exists in a plane parallel to the surface of the electrode and very close to it (Fig. A.1 (a) and (b)).

This charge originates from the arrangement of electrolyte ions at the interface and/or the reorientation of dipoles in solvent molecules. A potential difference occurs across the interface, forming an electric field gradient across the charge separation layer. Ions are electrostatically repelled or attracted towards the electrode surface and an excess of either anions or cations is created.

The attracted ion may approach the electrode only so far. The distance is limited by a monolayer of solvent molecules, which is assumed to exist between the ion and the electrode. The line drawn through the centre of such ions at a minimum distance from the electrolyte surface marks the boundary known as the 'Outer Helmholtz Plane' (OHP). The region within this plane Helmholtz is called the electrical double layer.

However, the interface cannot be represented simply by a parallel-plate capacitor, as shown experimentally by accurate measurements of real double layer capacitances [4]. The double layer capacitances are not linear as a function of potential i.e. the numerical value of the capacity depends on potential. In addition, the electrochemical double layer capacitors are "leaky" that is, they can be self-discharged by electrochemical reactions taking place across the interface. A more appropriate model would be a capacitor and resistor in parallel. Therefore, an integral capacitance K and a differential capacitance C need to be defined:

$K = \frac{q}{\Delta\phi}$ and $C = \frac{dq}{d(\Delta\phi)}$, where q is the charge held by the capacitor and $\Delta\phi$ is the potential drop across the interface. The ionic double layer capacity is dependent not only on the composition but also on the concentration of the electrolyte in a particular system. The double-layer capacitance per unit area, according to Helmholtz, is given as: $C_H = \frac{\epsilon}{4\pi d}$, where ϵ is the dielectric constant and d is the thickness of the double layer. The model does not account for the dependence of the measured capacity on potential or solution concentration, although the different values found in the presence of different electrolytes could be accounted for by the variation of d with ionic radius. The Helmholtz model of the double layer seems to be appropriate for polarizable electrodes in sufficiently high concentrations of electrolyte (> 1 M). At lower electrolyte concentrations (< 0.1 M), new features appear in the measurement of double layer capacitance as a function of potential which cannot be explained by the Helmholtz model.

A.1.2. The Gouy-Chapman model

between 1910-1913 Gouy [5,6] and Chapman [7], proposed the diffuse double layer model that predicted a dependence of the measured capacity on both potential and electrolyte concentration. They showed that the excess charge density in solution is not exclusively situated at the OHP, so that the double layer may be of variable thickness. In their view, a Helmholtz-type rigid double layer would not form because the attractive and repulsive electrostatic forces between the field and the charge on the ions are counteracted by random thermal motion in solution which tends to disperse the excess ions. In this model, the ions are considered as point charges contained within a single 'diffuse layer'.

The relationship between the excess surface charge density q^M on the metal, the differential capacity C_G of the diffuse double layer and the potential, ϕ_o , at the limit of the diffuse double layer is shown in Equation A. 1:

$$q^D = -\sqrt{8\epsilon RTc} \operatorname{Sin} h\left(\frac{zF\phi_o}{2RT}\right) = -q^M \quad (\text{A. 1})$$

Differentiation of Equation A.1 with respect to ϕ_o , leads to the capacitance of the diffuse layer C_G :

$$C_G = zF\sqrt{\frac{2\epsilon c}{RT}} \operatorname{Cos} h\left(\frac{zF\phi_o}{2RT}\right) \quad (\text{A. 2})$$

where F is the Faraday constant, c is the concentration, ϵ is the dielectric constant of the solvent, z is the magnitude of the ionic charge, and ϕ_0 is the potential of the outer Helmholtz plane.

The potential ϕ_0 was identified with the potential ϕ_M on the surface of the metal. That is, the notion of an ‘inner layer’ of ions strongly and rigidly adsorbed on the surface of the electrode as depicted by Helmholtz was incorrect. The model proposed by Gouy and Chapman, (Fig. A.2) represented substantial improvement over the Helmholtz model in that a dependence of the differential capacity on both potential and concentration was predicted (Equation A. 2). In this diffuse layer, the net charge density decreases with distance from the phase boundary. The Gouy-Chapman model fails to explain the actual capacity-potential curves found experimentally for all concentrations and measured capacity was much lower than that calculated from equation A. 2, except in very dilute solutions. The inverted “parabolas” (Fig. A.2 (b)) occur only in very dilute solution (< 0.001 M) and at potentials close to the potential of zero charge. The capacity-potential curves were incorrect and the predicted dependence on concentration was not observed.

A.1.3. The Stern model

A simple development of the double-layer theory was suggested by Stern in 1924 [8] as a more realistic way of describing the physical situation at the interface. Stern [8] combined the two previous models, with some of the ions adhering to the electrode as suggested by Helmholtz and some forming a Gouy-Chapman type diffuse layer (Figs. A.3 (a) and (b)).

Stern adapted the Gouy-Chapman model to take into account the fact that ions have finite size, and consequently have a closest approach a to the electrode of the order of the ionic radius. Thus the potentials are given by: $\phi_0 = \phi_a < \phi_m$. Under all conditions, the interface is assumed to be neutral i.e. $-q^m = q^s$. Stern assumed the charge q_s on the solution side resided partially in a compact layer, q_H (the Helmholtz charge), and the remainder q_G in a diffusely region (as in the Gouy-Chapman models) in the solution i.e. $q_s = q_H + q_G$. There are therefore two regions of charge separation. When charges are separated, a potential drop results. In the Stern model, two capacitors are effectively operating in determining the total

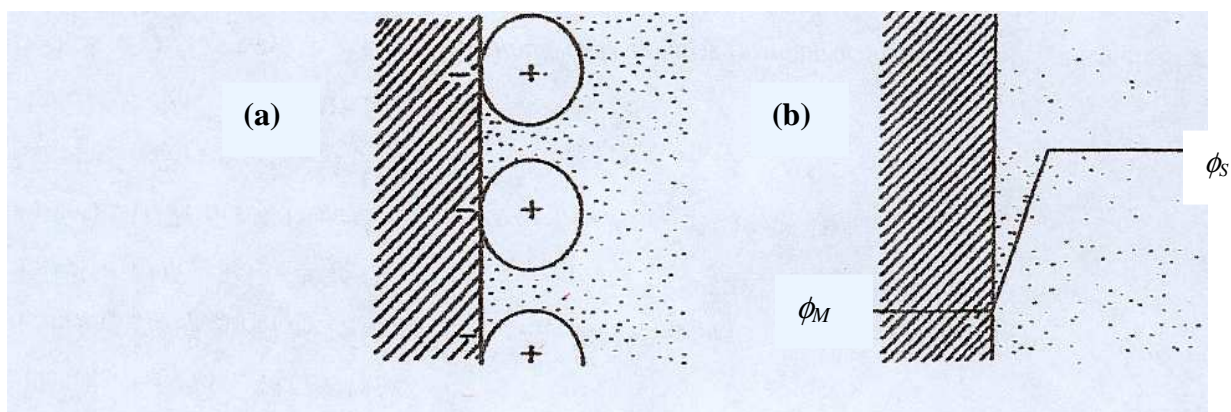


Fig. A.1. (a) The Helmholtz model of the rigid ionic double layer.
 (b) The potential profile of the Helmholtz model, where ϕ_M is the potential at the metal surface and ϕ_S is the potential of the bulk solution. Reprinted from [9].

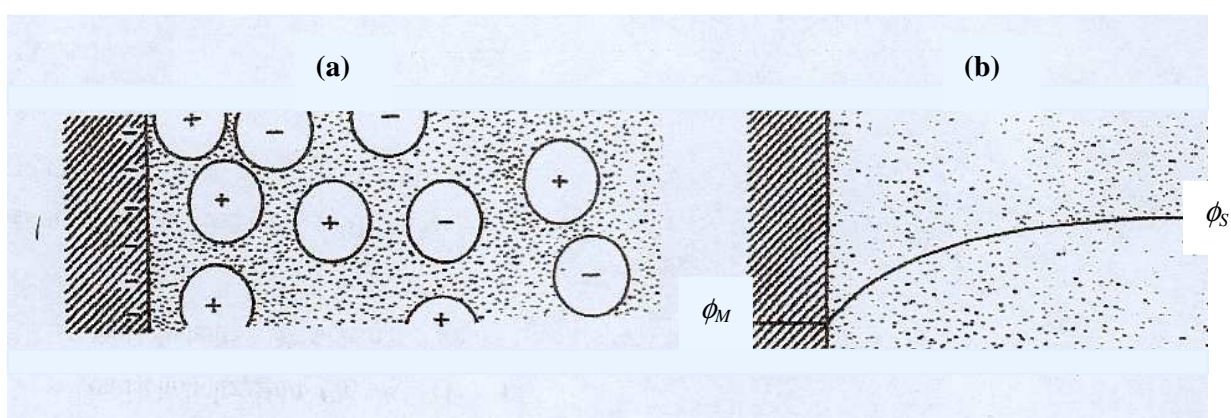


Fig. A.2. (a) The Gouy-Chapman model of the diffuse ionic double layer.
 (b) The potential profile for the Gouy-Chapman model. Reprinted from [9].

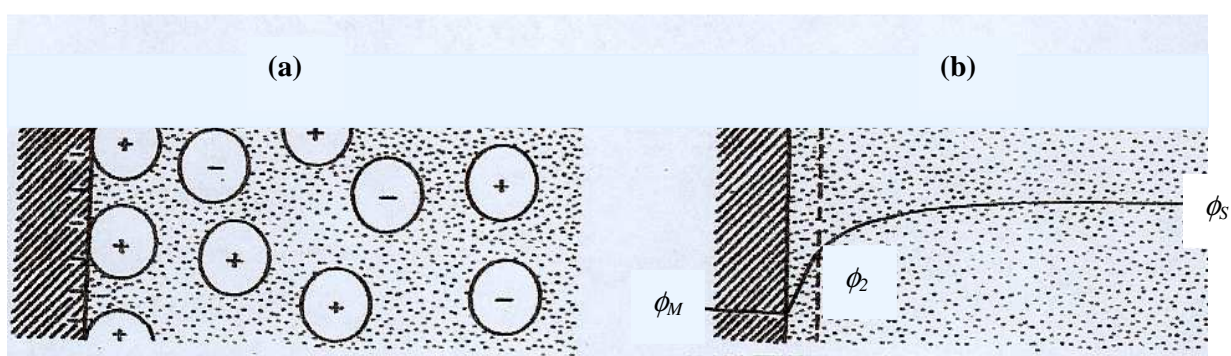


Fig. A.3. (a) The Stern model of the ionic structure at the interphase.
 (b) The potential profile of the Stern model, where ϕ_2 is the potential at the outer Helmholtz plane (OHP). Reprinted from [9].

differential capacity of the interface, C_H due to the Helmholtz layer and C_G due to the diffuse layer. The total capacity of the interface C is therefore given by:

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G} \quad (\text{A. 3})$$

The two adjacent regions act like capacitors in series. This proved to be a significant result since it indicates the smaller of the two capacitances determines the overall capacitance. In very low dilute solutions and close to the potential of zero charge, when $q_M \cdot \phi_0$ and ϕ_a are relatively small C_G should dominate. Stern also recognised the effect of specific interactions between ions and suggested a distinction between ions which were adsorbed on the electrode and those which merely approached it to the distance of the closest approach. This idea was later developed by Grahame [10].

A.1.4. The Grahame model

In 1947, Grahame [10] proposed that, although the closest approach to the electrode is occupied by solvent molecules, it may also be possible for some ionic or uncharged species to penetrate into this region. This could come about if the ion possessed no solvation shell, or if the solvation shell was lost when the ion came close to the electrode. Ions in direct contact were deemed to be ‘specifically adsorbed’.

This model for the electrode/electrolyte interface (Fig. A.4) proposed the existence of three regions. First, the inner Helmholtz plane (IHP) (potential ϕ_1) extends from the electrode to a plane passing through the centres of the specifically adsorbed ions. Second, the outer Helmholtz plane (OHP) passes through the centres of hydrated ions at their distance of closest approach to the electrode. Third, the diffuse layer i.e. the region that lies beyond the OHP. The potential at the OHP is denoted by ϕ_2 . Potential changes linearly with distance up to the outer Helmholtz plane and then exponentially through the diffuse double layer region. Diffuse double layer effects decrease with increasing concentration in solution (equations A.2, A.3).

A.1.5. The Bockris, Devanathan and Muller model

Clearly, in dipolar solvents, such as water, interactions exist between the electrode and the dipoles of the water molecules. Furthermore, the concentration of the solvent is always much higher than that of the solute. In the Gouy-Chapman model, the diffuse part of the double layer is similar to the ionic environment around an ion, the electrode being thought of as an infinite radius. One would consequently expect to find a layer of solvent molecules attached

to the electrode surface in fixed orientation and a few more layers of solvent in orientation intermediate between that of the first layer and that in the bulk-like arrangement corresponding to the primary and secondary solution shells around an ion.

In 1963, Bockris, Devanathan and Muller [11] proposed a model of the double-layer which clearly takes into account the predominant role of the solvent in the interface. They suggested that reorientation of solvent molecules would occur depending on the excess charges at the electrode and the presence or absence of specifically adsorbed ions at the surface. The proposed variation of the electrostatic potential with distance is qualitatively similar to that of the Grahame model. At present, this seems to be the best model to demonstrate the role of the solvent in the double layer. However, the distribution of electronic charges on the side of the electrode has not been fully clarified and requires further analysis using surface analytical techniques. Fig. A.5 shows the effect of water molecules according to this model. The water molecules cover most of the electrode with an oriented layer of water molecules. At certain sites, the water molecules are replaced by a specifically adsorbed ion (usually an anion) that has shed its hydration shell. The plane going through the centres of these ions is defined as the inner Helmholtz plane. Ions that carry a primary hydration shell are found next and are situated outside the first layer of water molecules adsorbed on the electrode surface. The plane going through the centres of these ions constitutes the outer Helmholtz plane. For contact adsorption of an ion to occur, chemical work must be done in order to rid the ion of its primary hydration sheath and to remove one or more of the surface water molecules at the electrode surface. The final state is then stabilised by the specific interactions between the ion and the surface. These effects are absent for ions adsorbed in the outer Helmholtz plane where interactions are mainly electrostatic in origin.

A.2. Capacitance

An electrode-solution interface is analogous to a capacitor composed of two metal sheets separated by a dielectric material (Fig. A.6 (a)), whose behaviour is represented by the following equation: $C = q/E$ where C is the capacitance in Farads, q is the charge in Coulombs and E is the potential across the capacitor in volts. When a potential is applied across a capacitor, charge accumulates on its metal plates until the charge q satisfies the equation $C = q/E$. During this charging process, no current will flow. The charge on the capacitor arises as a result of an excess of electrons on one plate and a deficiency of electrons on the other plate (Fig. A.6 (b)). The electrode-solution interface behaves as a leaky capacitor.

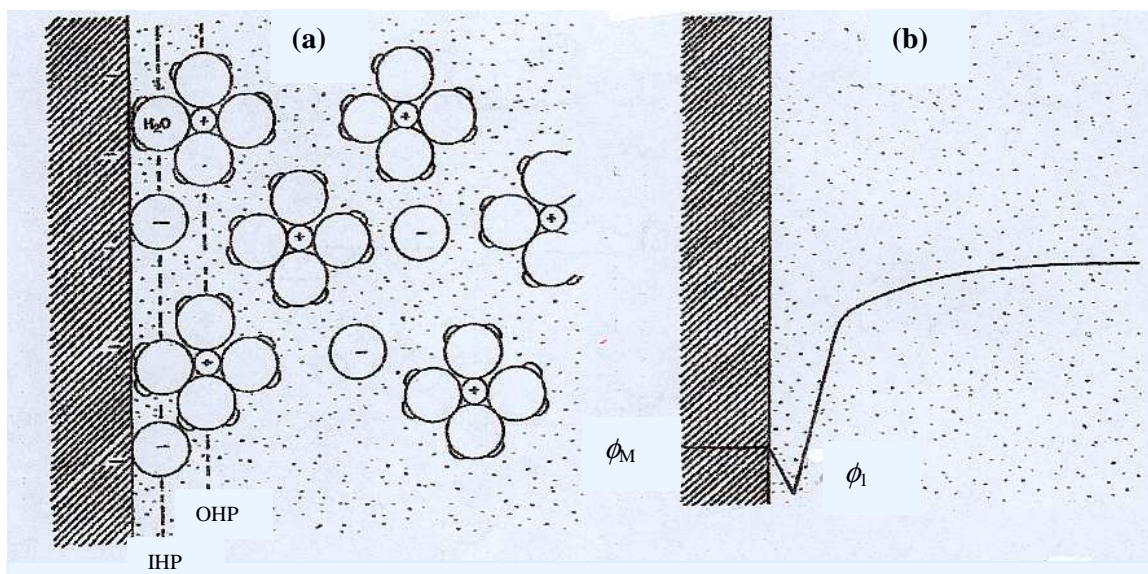


Fig. A.4. (a) The Grahame model indicating the specific adsorption of ions within the IHP and hydrated ions at the OHP.
 (b) The potential profile of the Grahame model, where ϕ_1 is the potential at the inner Helmholtz plane (IHP). Reprinted from [9].

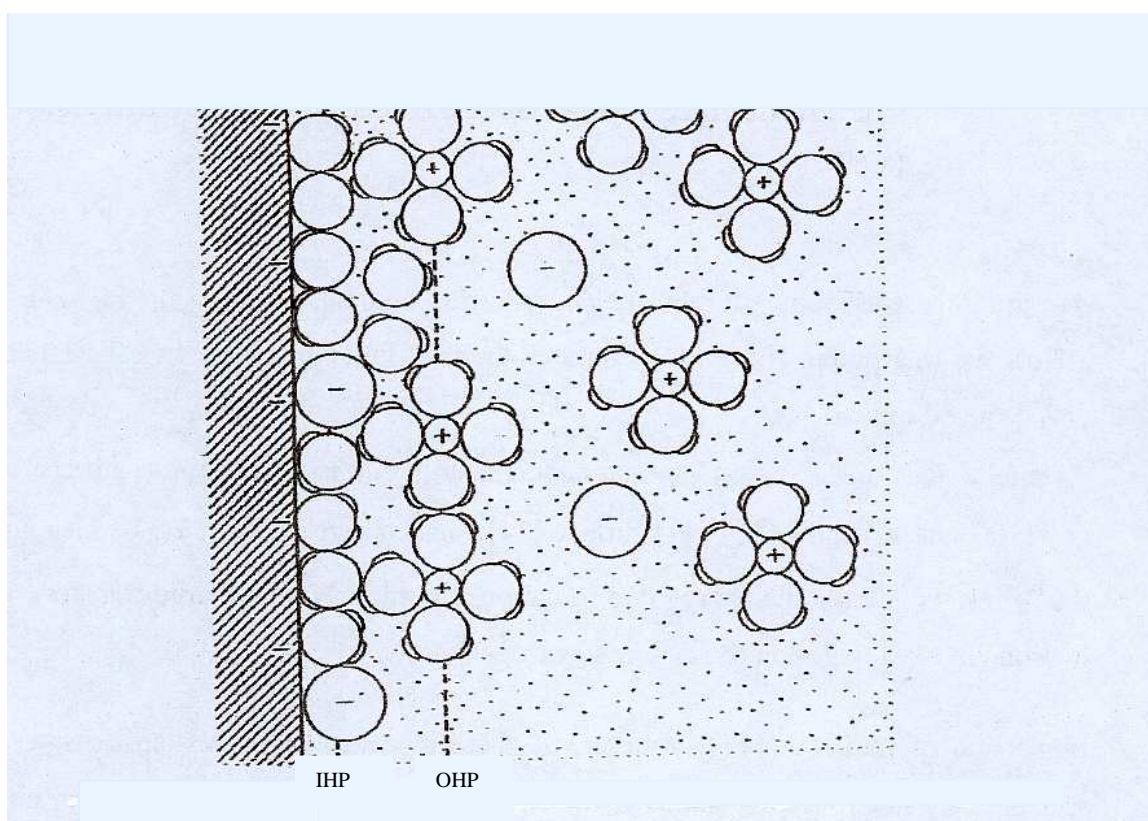


Fig. A.5. The model of Bockris, Devanathan and Muller. Reprinted from [9].

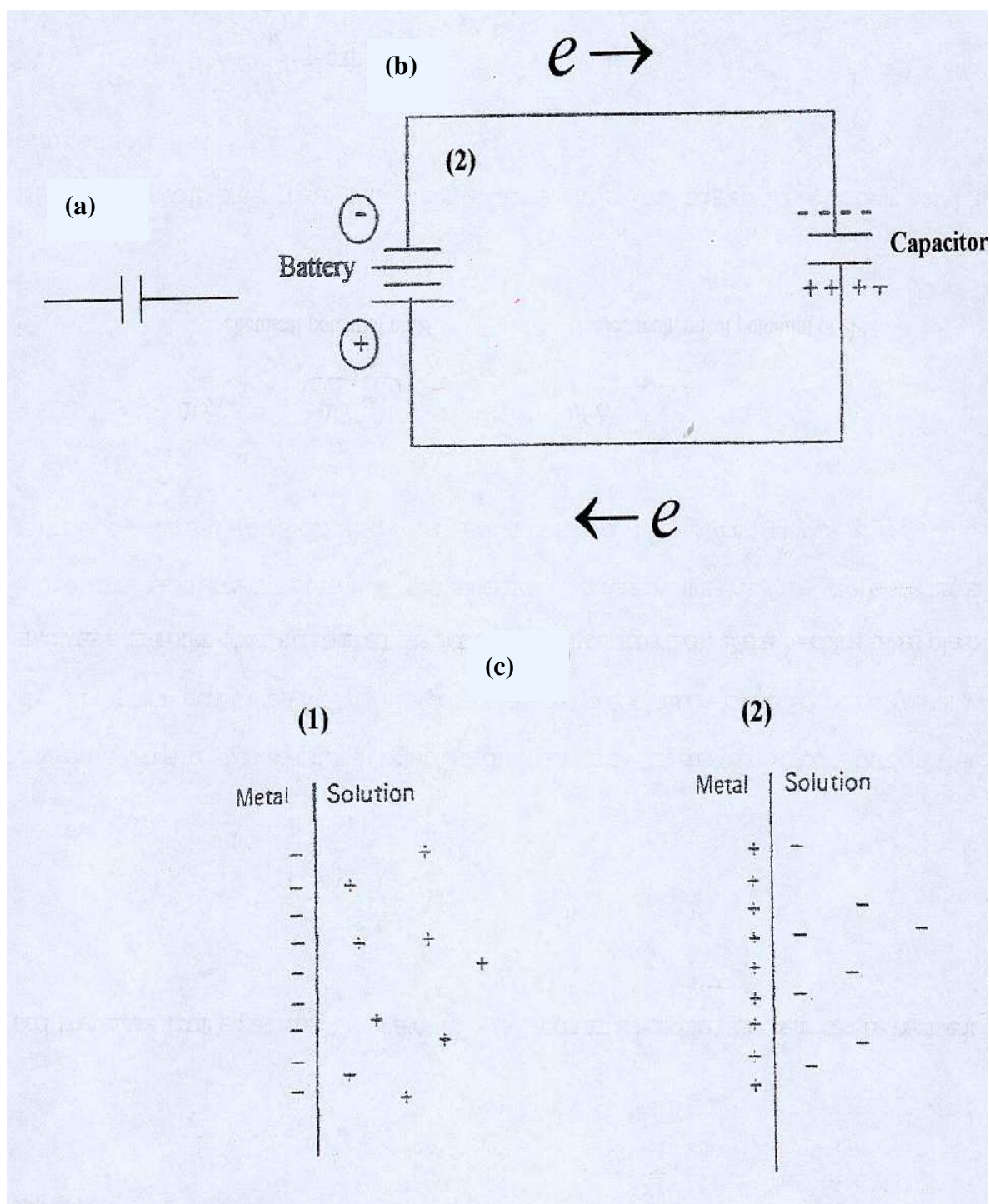


Fig. A.6. (a) a capacitor, (b) charging a capacitor with a battery. (c) The metal-solution interface as a capacitor with a charge on the metal, q^M , (1) negative and (2) positive. Reprinted from [4].

At a given potential there will exist a charge on the metal electrode, q^M , and a charge in the solution, q^S (A.6 (c)).

Whether or not the charge on the metal is negative or positive with respect to the solution depends on the potential across the interface and the composition of the solution. However, at all times $q^M = -q^S$. The charge on the metal q^M represents an excess or deficiency of electrons and resides in a very thin layer on the metal. The charge in solutions q^S is made up of an excess of cations or anions in the vicinity of the electrode surface. The charges q^M and q^S are often divided by the electrode area and denoted as charge densities, σ^M , $\sigma^M = q^M / A$, having the units of $\mu C cm^{-2}$.

The entire arrangement of charged species and oriented dipoles existing at the metal-solution interface is called “the electrical double layer”. At a particular potential the electrode-solution interface is characterised by a double-layer capacitance, C_d , which has values in the range of 10 to 40 $\mu F/cm^2$. Unlike real capacitors, whose capacitances are independent of the voltage across them, C_d is often a function of potential. The capacitance of an interface characterises its ability to store charge in response to a change in potential. One definition is based on the small change in charge density that results from a small alteration in potential. The differential capacitance, C_d , is given by $C_d = (\partial\sigma^M / \partial E)$, i.e. by the slope of σ^M vs. E at any point (Fig. A.7 (a)). Since C_d is not constant with E (see Fig. A.7 (b) for some experimental examples) its variation leads to the concept of integral capacitance, C_i defined as the ratio of the total charge density σ^M at potential E to the total potential difference leading to the accumulation of charge, that is; $C_i = \sigma^M / (E - E_Z)$ where E_Z denotes the potential of zero charge (PZC), and C_i is related to C_d via the equation:

$$C_i = \frac{\int_{E_Z}^E C_d dE}{\int_{E_Z}^E dE}. \text{ Thus, } C_i \text{ is an average of } C_d \text{ over the potential range from } E_Z \text{ to } E.$$

The differential capacitance is a useful parameter since it is precisely measurable by impedance techniques [4].

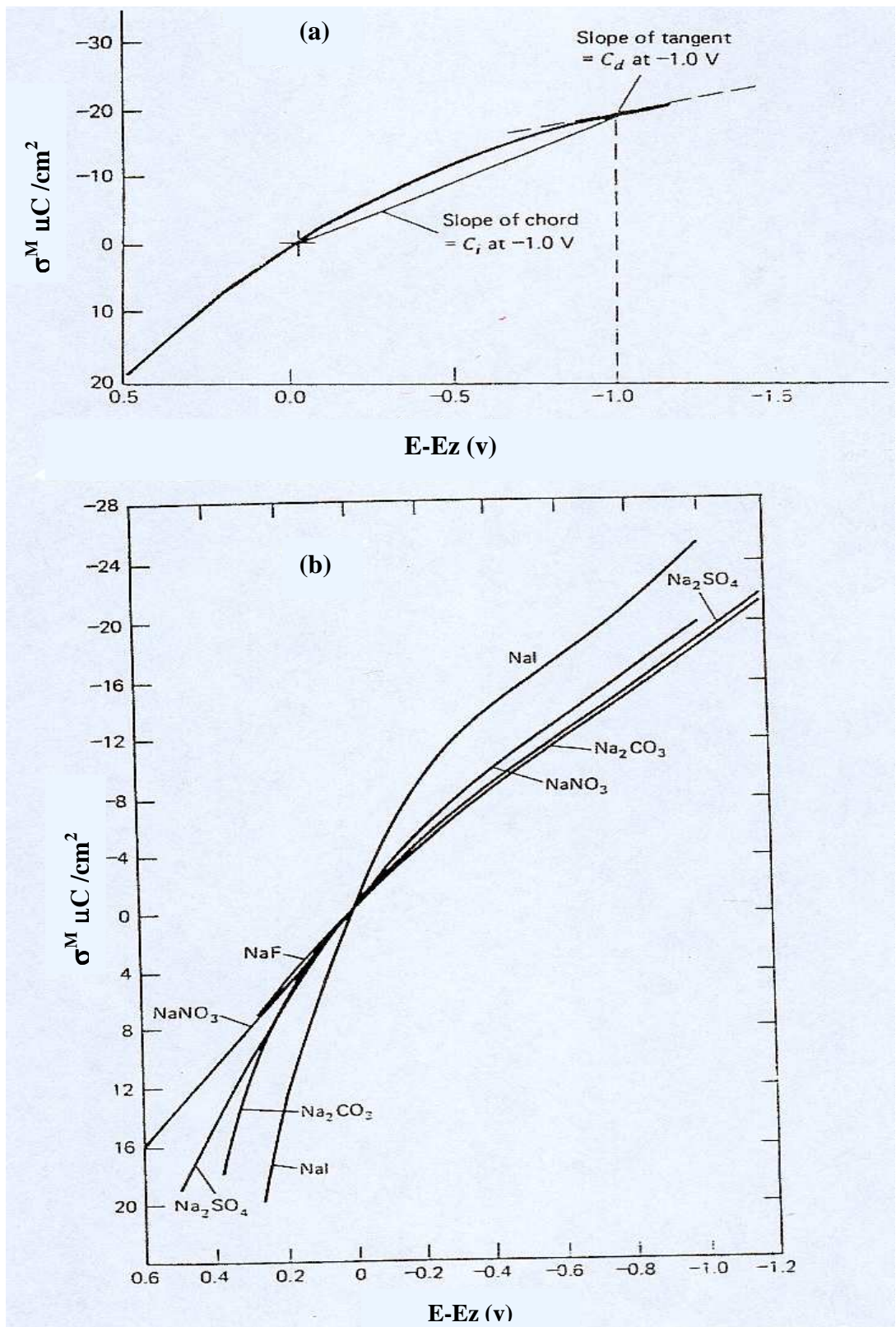


Fig. A.7. (a) Schematic plot of charge density *versus* potential illustrating the definitions of the integral and differential capacitancies. (b) Charge density on the electrode *versus* potential for mercury immersed in 1 M solutions of the indicated electrolytes at 25 °C. The potentials are plotted with respect to the PZC for each electrolyte. Reprinted from [4].

According to the Helmholtz model, C_d should be a constant, however, in real systems this is not the case. Fig. (A.8 (a)) shows a dramatic illustration for interfaces between mercury and sodium fluoride solutions of various concentrations. C_d varies with both potential and concentration [10]. According to the Gouy-Chapman model, as the electrode becomes more highly charged, the diffuse layer should become more compact and C_d should increase. Likewise when the concentration of the electrolyte increases, a similar compression of the diffuse layer should occur, producing a consequent increase in capacitance. These qualitative trends are actually represented in the data of Fig. A.8 (a). The predicted differential capacitance from the Gouy-Chapman theory is shown in Fig. A.8 (b). Thus, C_d varies with potential, and there is a minimum PZC.

The predicted "V shaped" capacitance function resembles the observed behaviour of mercury in NaF at low concentrations and at potentials (near to the PZC) (Fig A.8 (a)). However, real interfaces display a flattening in capacitance at more extreme potentials, and the valley ("V-shape") at the PZC disappears altogether at high electrolyte concentrations. Also, the actual capacitance is normally much lower than the predicted value.

In a real system, according to the Gouy-Chapman-Stern (GCS) model, the capacitance consists of two components can be expressed as: $\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}$ (see Fig. A.9 (a)) where C_H is the capacitance of the charges held at the OHP and C_D is the capacitance of the truly diffuse charge. C_H is independent of potential but C_D is potential dependent. The composite capacitance, C_d shows a complex behaviour and is governed by the smaller of the two components. Near the PZC in systems with low electrolyte concentration, the V-shaped function characteristic of C_D is expected. At large concentrations C_D becomes so large that it is no longer contributes to C_d and one sees only the constant capacitance of C_H is observed. Fig. A.9 (c)) shows a schematic representation of this behaviour. In this model there are still discrepancies in that C_H is not truly independent of potential. Various methods can be used to measure the double layer capacity. The impedance technique is the most common, and is applicable to most types of electrode, solid or liquid. The electrocapillary measurement method is only applicable to liquid electrodes (for example, mercury) [12].

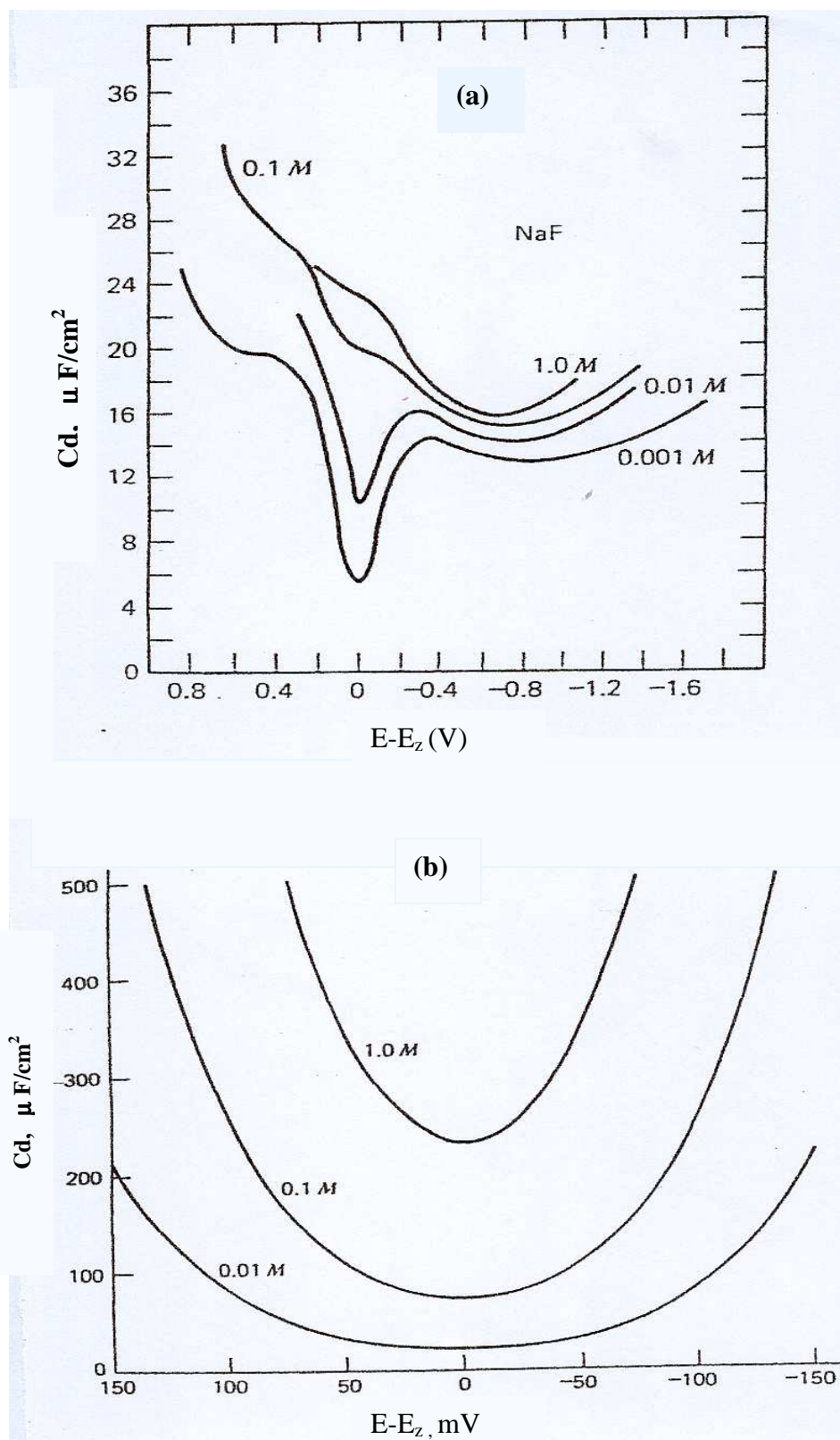


Fig. A.8. (a) differential capacitance versus potential for NaF solutions in contact with mercury at 25 °C. Reprinted from [9].
 (b) predicted differential capacitancies from the Gouy-Chapman theory. Calculated for the indicated concentrations of a 1:1 electrolyte in water at 25 °C. Reprinted from [4].

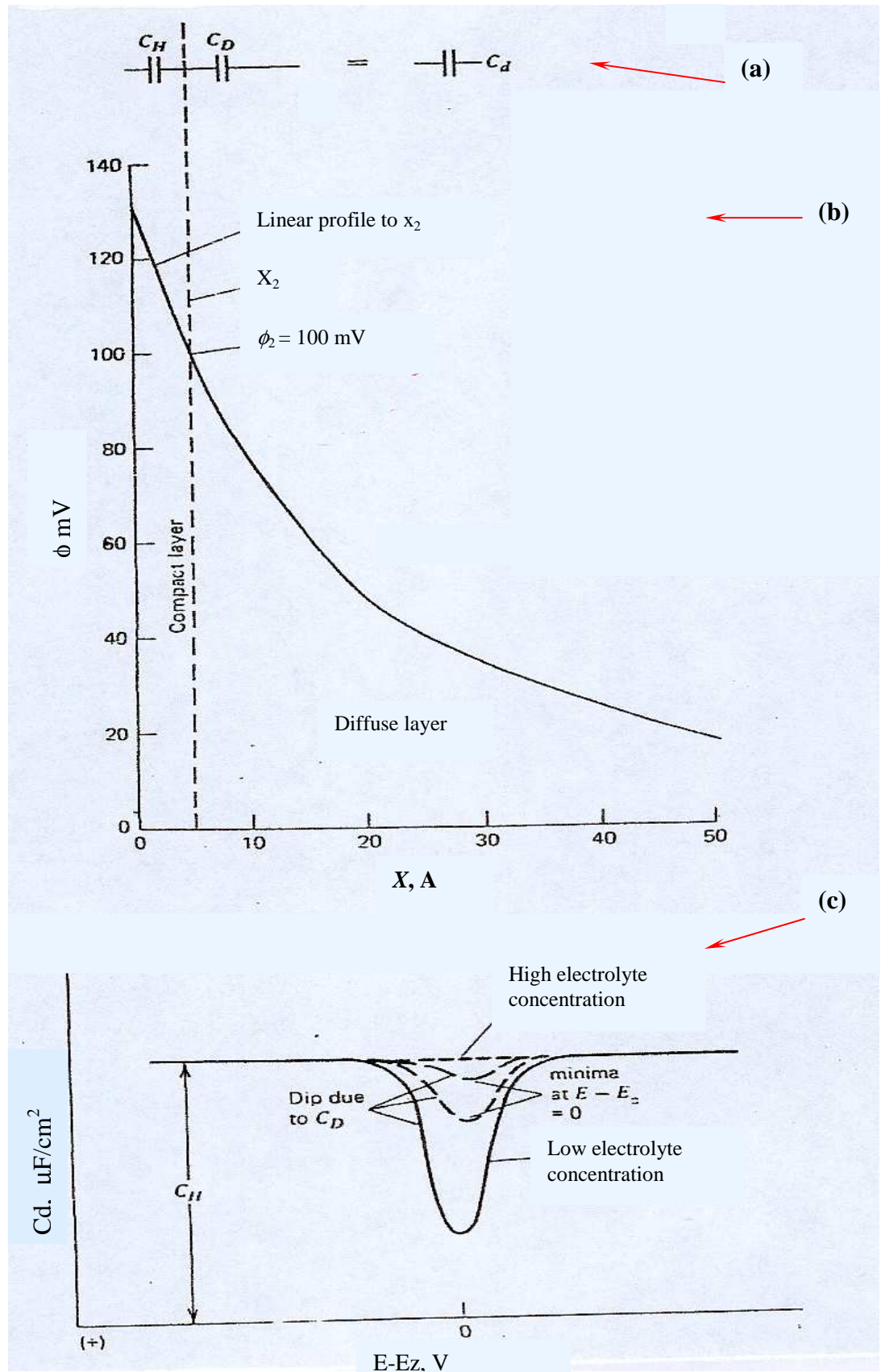


Fig. A.9. (a) a view of the differential capacitance in the GCS model as a series network of the Helmholtz layer and the diffuse layer capacitances.
 (b) Calculated potential profile through the solution side of the double layer, according to CGS theory.
 (c) Schematic representation of the expected behaviour of C_d (according to GCS theory) as the electrolyte concentration changes. Reprinted from [4].

A.4. References

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