

**Figure 2.11** Interfacial tension of mercury in contact with various aqueous electrolyte solutions. The potential scale is adjusted so that zero potential occurs at the electrocapillary maximum for a capillary-inactive electrolyte. Reprinted with permission from D. C. Grahame, *Chem. Rev.* 1947, 41, 441, copyright 1947 American Chemical Society.

curves merge together, suggesting that cations (at least  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ ) do not specifically interact with the mercury surface, even when it is highly negatively charged.

It is commonly observed that the drop time of a dropping mercury electrode depends on potential, usually varying by a factor of 2 or more over the experimentally accessible range. More complex behavior is sometimes observed when surfactants are adsorbed on the electrode surface. Since adsorption is often potential dependent, very rapid changes in interfacial tension (and thus drop time) with potential are sometimes observed.

### Double-Layer Capacitance

When the potential applied to an electrode immersed in an electrolyte solution is decreased from zero, the surface charge becomes negative and the net space charge of the double layer must increase to maintain overall electrical neutrality. Similarly, an increase in electrode potential must induce a net negative space charge. From the point of view of the external electric circuit, the double layer thus behaves as a capacitor, serving to store electric charge.

Capacitance is defined as the ratio of charge stored to voltage applied, or, more appropriately in this case, as the derivative (the

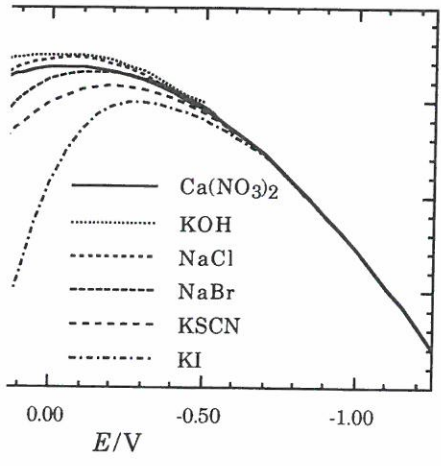


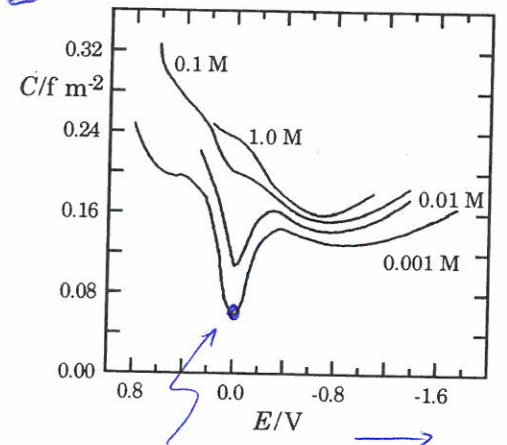
Figure 2.11 shows the differential capacitance of mercury in contact with various aqueous electrolyte solutions. The potential scale is adjusted so that zero potential corresponds to the electrocapillary maximum for a capillary-inactive electrode. Reprinted with permission from D. C. Grahame, *Chem. Rev.* 1947, 41, 441, copyright 1947 American Chemical Society.

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Unique metal-electrolyte interface. It is very hard to find ideal polarizable electrodes

Figure 2.12 Capacity of a mercury drop electrode in contact with aqueous NaF solutions, [NaF] = 0.001, 0.01, 0.1, and 1.0 M, as a function of potential measured vs. a normal (1 M KCl) calomel electrode. The potential of minimum capacity corresponds to the electrocapillary maximum (i.e., to maximum interfacial tension, see Figure 2.11). Reprinted with permission from D. C. Grahame, *Chem. Rev.* 1947, 41, 441, copyright 1947 American Chemical Society.



differential capacitance)

$$C = \frac{dQ}{d\Phi}$$

If we take  $C$  to be the capacitance per unit area (the capacity), then we can replace  $Q$  by the surface charge density  $\sigma$ . Consider first the capacity of the Gouy layer,  $C_G$ . Differentiating eq (2.13), we obtain

$$C_G = \frac{\epsilon\epsilon_0}{x_A} \tag{2.43}$$

A more exact calculation (see Problems) shows that  $C_G$  is a function of  $\Phi_a$  and that eq (2.43) represents the minimum capacity. Minima are observed experimentally and provide a way to determine the potential of zero charge for an electrode (20). The capacity vs. potential curves for some aqueous sodium fluoride solutions are shown in Figure 2.12.

**Example 2.6** Compute the Gouy layer capacity for a solution of a 1:1 electrolyte with concentrations of 0.001, 0.01, and 0.1 M.

The double-layer thicknesses for these concentrations are (Table 2.1) 9.6, 3.0, and 0.96 nm. Assuming the dielectric constant of pure water ( $\epsilon = 78.5$ ), eq (2.43) gives

$$C_G = 0.072, 0.23, \text{ and } 0.72 \text{ F m}^{-2}$$

for 0.001, 0.01, and 0.1 M solutions, respectively.

measure of  $C_G$

@ high voltage the charge goes into Helmholtz layer (2.42)

The curve for 0.001 M NaF solution in Figure 2.12 goes through a minimum of about  $0.06 \text{ F m}^{-2}$ , in excellent agreement with the value computed in Example 2.6 considering the simplicity of the theory. However, the minimum capacity of the 0.01 M NaF solution is about  $0.1 \text{ F m}^{-2}$  and for 0.1 M NaF the observed capacity at the electrocapillary maximum is only  $0.2 \text{ F m}^{-2}$ , rather less than the computed values, 0.23 and  $0.72 \text{ F m}^{-2}$ . Furthermore, the capacity minimum at  $\Phi = 0$  nearly disappears for concentrated solutions. The reason for these apparent discrepancies is not hard to find: we have neglected the effect of the immobilized ions and solvent dipoles on the surface which comprise the Helmholtz layer. These also contribute to the capacity. From the point of view of the external circuit, these two contributions— $C_H$  for the Helmholtz layer and  $C_G$  for the Gouy layer—behave like capacities in series. Thus the total observed capacity is given by

$$1/C = 1/C_H + 1/C_G$$

or

$$C = \frac{C_G C_H}{C_G + C_H} \quad (2.44)$$

For dilute solutions, the capacity of the diffuse layer  $C_G$  is small compared with the more or less constant Helmholtz layer contribution, so that  $C \approx C_G$ . When the diffuse layer becomes more compact and its capacity becomes large compared with that of the Helmholtz layer, then the latter contribution should dominate. Indeed, it is found that at zero potential the double-layer capacity initially increases with concentration and then levels off. In the case of NaF solutions in contact with mercury, the Helmholtz contribution to the double-layer capacity at  $\Phi = 0$  appears to be approximately  $0.29 \text{ F m}^{-2}$ .

## 2.6 DEBYE-HÜCKEL THEORY

In 1923 Debye and Hückel (21) found a way to calculate ionic activity coefficients for dilute electrolyte solutions. The basic idea of the theory is that, just as in the case of the charged surfaces we have been considering, individual ions possess an atmosphere of ions of opposite charge. By calculating the electrostatic free energy of interaction of an ion with its atmosphere, an estimate of the activity coefficient can be obtained. Debye-Hückel theory starts with the Gouy-Chapman description of the ion atmosphere derived from the linearized Poisson-Boltzmann equation.

Peter J. chemists Universit coming t contributi the Eidge Hückel ( through n in quanti

### Calcula

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