

Chapter 5

Thermodynamic Considerations

As already discussed, interest of electrochemists is currently largely focused on polymer-modified (film) electrodes. Here, the conducting polymer is deposited on the surface of a substrate (usually a metal) and investigated or used in contact with an electrolyte solution that does not contain the polymer. Evidently, no equilibrium (adsorption equilibrium) will exist between the surface phase and the solution with respect to the polymer. The modified electrode can be used if the polymer is stably attached to the surface of the substrate. In most cases, no chemical bonds exist between the substrate and the polymer; the polymer layer remains at the surface due to the van der Waals forces between the substrate and the polymer, as well as between the polymer chains in multilayer films. The adsorption model of de Gennes [1] provides a description of this situation. It is based on the observation that the polymer sticks to the substrate surface and cannot be desorbed by washing with the pure solvent. This situation is expected when the surface tension of the pure polymer melt is lower than that of the pure solvent. Although the individual energy contribution of a segment of the polymer is small, the overall energy is large since the small energy contributions add up. An important consequence of this metastable adsorption is that the density of the polymer layer is usually not uniform. In fact, the behaviors of several polymer film electrodes [2–9] have been explained by the assumption of diminishing layer density from the metal surface. There is another problem with polymeric systems, especially with polyelectrolytes: a true equilibrium situation is seldom established within the time scale of the experiments since the relaxation process of the polymer network (gel) can be extremely long. This is true not only with respect to polymer morphology (conformation) but also with respect to membrane equilibria (in which ions and solvent molecules participate). Nevertheless, it is worth surveying the most important thermodynamic relationships for an idealized situation. The surface polymer layer will be treated as an amorphous swollen gel with a uniform structure and density in contact with a solution containing solvent molecules and ions. In this case, both nonosmotic and osmotic membrane equilibria, as well as the mechanical work done in swelling the polymer, must be taken into account. In most cases, the situation is even more complicated than that usually treated using a membrane equilibrium, since

the charge of the polymer changes during the redox reaction; in most cases, a neutral polymer is transformed into a polyelectrolyte, and vice versa.

5.1 Neutral Polymer in Contact with an Electrolyte Solution

We should consider the partitioning equilibria of the solvent molecules, the neutral salt, and the ions formed by dissociation. For all mobile species, the equilibrium condition is

$$\tilde{\mu}_i^\alpha = \tilde{\mu}_i^\beta, \quad \mu_i^\alpha + z_i F \varphi^\alpha = \mu_i^\beta + z_i F \varphi^\beta, \quad (5.1)$$

where $\tilde{\mu}_i^\alpha$ and $\tilde{\mu}_i^\beta$ are the electrochemical potentials of the i th species in phase α (film) and phase β (solution), respectively, z_i is the charge number of the species, and φ is the inner electric potential of the phase. For a neutral entity (solvent or salt molecules), $\tilde{\mu}_i = \mu_i$, where μ_i is the chemical potential.

The solvent (s) content in the polymer phase obviously depends on the difference between the standard chemical potentials (μ_i^\ominus) of the solvent molecules in the two contacting phases, since

$$\mu_s^\alpha = \mu_s^\beta = \mu_s^{\ominus\alpha} + RT \ln a_s^\alpha = \mu_s^{\ominus\beta} + RT \ln a_s^\beta \quad (5.2)$$

therefore

$$\Delta\mu_s^\ominus = \mu_s^{\ominus\alpha} - \mu_s^{\ominus\beta} = RT \ln \frac{a_s^\beta}{a_s^\alpha} = RT \ln K, \quad (5.3)$$

where a_s^β and a_s^α are the relative activities of the solvent in the respective phases, and K is the partitioning equilibrium constant.

If $\mu_s^{\ominus\alpha} > \mu_s^{\ominus\beta}$, $a_s^\beta > a_s^\alpha$, and taking the activity coefficients $\gamma_s^\alpha = \gamma_s^\beta = 1$ (dilute solutions, quasi ideal system), $c_s^\beta > c_s^\alpha$. This is the case when the polymer is hydrophobic and the solvent is hydrophilic. In other words, the interaction energies between the polymer segments and between the solvent molecules are higher than those between the polymer segments and the solvent molecules. In this case, the polymer segments are not solvated by the solvent molecules, and hence there is no solvent swelling of the polymer film. If the neutral polymer contains polar groups (e.g., $-\text{OH}$, $-\text{NH}_2$), water molecules will enter the polymer and the polymer phase will eventually contain substantial amounts of water. Other effects, however, may also be operative; e.g., the amount of cross-linking within the polymer.

Ions enter the film if their van der Waals and ion-dipole interactions with the polymer are large. Ions can be solvated (hydrated) by both the polymer and the solvent. A rough estimation can be achieved using Born's theory.

According to the Born equation, the Gibbs free energy of solvation is

$$\Delta G_{\text{solv}} = -\frac{N_A z^2 e^2}{8\pi\epsilon_0 r} \left(1 - \frac{1}{\epsilon_r}\right), \quad (5.4)$$

and the Gibbs energy change when the ion is transferred from one solvent (phase α) to another solvent (phase β) is

$$\Delta G_{\text{solv}} = -\frac{N_A z^2 e^2}{8\pi\epsilon_0 r} \left(\frac{1}{\epsilon^\alpha} - \frac{1}{\epsilon^\beta}\right), \quad (5.5)$$

where N_A is the Avogadro constant, ϵ_0 is the permittivity of the vacuum, ϵ_r (as well as ϵ^α and ϵ^β) is the relative dielectric permittivity of the solvent (i.e., for phases α and β , respectively), e is the elementary electric charge, and z and r are the charge and the radius of the ion.

It follows that if ϵ_r is small, the Gibbs free energy of ion transfer is small, and if $\epsilon^\beta > \epsilon^\alpha$, ΔG_s becomes positive, and so the sorption of ions in phase α is less likely. If we assume that this electrostatic interaction dominates, i.e., $\Delta G_{\text{solv}} \cong \Delta\mu_{\text{ion}}^\ominus$, and taking into account that ϵ^β (water) is 78 at 25°C while ϵ^α (organic phase) is usually less than 10, the activity (concentration) ratio should be very small. Of course, $\Delta\mu_{\text{ion}}^\ominus$ may also depend on the differences between other interactions (e.g., van der Waals interactions) in the two phases.

By using (5.1) for a $K_{v_+}^+ A_{v_-}^-$ electrolyte that dissociates into $v_+ K^+$ and $v_- A^-$ ions (if the interface is permeable for both ions), we may write that

$$\tilde{\mu}_{K^+}^\alpha = \tilde{\mu}_{K^+}^\beta \quad \text{and} \quad \tilde{\mu}_{A^-}^\alpha = \tilde{\mu}_{A^-}^\beta, \quad (5.6)$$

and therefore the following equations can be obtained for the activities of ions in the polymer phase:

$$a_{K^+}^\alpha = a_{K^+}^\beta \exp\left(-\frac{\Delta\mu_{K^+}^\ominus}{RT}\right) \exp\left(-\frac{z_+ F \Delta\varphi}{RT}\right), \quad (5.7)$$

$$a_{A^-}^\alpha = a_{A^-}^\beta \exp\left(-\frac{\Delta\mu_{A^-}^\ominus}{RT}\right) \exp\left(-\frac{z_- F \Delta\varphi}{RT}\right), \quad (5.8)$$

where $\Delta\varphi = \varphi^\alpha - \varphi^\beta$, i.e., the interfacial potential drop, and $\Delta\mu_{K^+}^\ominus = \Delta\mu_{K^+}^{\ominus\alpha} - \Delta\mu_{K^+}^{\ominus\beta}$, $\Delta\mu_{A^-}^\ominus = \mu_{A^-}^{\ominus\alpha} - \mu_{A^-}^{\ominus\beta}$. The chemical potential of the electrolyte (μ_{KA}) should also be the same in both phases since it is a neutral entity:

$$\mu_{KA}^\alpha = \mu_{KA}^\beta = v_+ \tilde{\mu}_{K^+}^\alpha + v_- \tilde{\mu}_{A^-}^\alpha = v_+ \tilde{\mu}_{K^+}^\beta + v_- \tilde{\mu}_{A^-}^\beta = v\mu_\pm^\alpha = v\mu_\pm^\beta, \quad (5.9)$$

where μ_\pm is the mean chemical potential of the electrolyte, and $v = v_+ + v_-$. Since

$$\mu_{KA} = v\mu_{\pm} = v\mu_{\pm}^{\ominus} + RTv \ln a_{\pm}, \quad (5.10)$$

$$\ln \frac{a_{\pm}^{\alpha}}{a_{\pm}^{\beta}} = \frac{\mu_{\pm}^{\ominus\beta} - \mu_{\pm}^{\ominus\alpha}}{RT} = \ln K_{AB} = \ln \frac{c_{KA}^{\alpha}}{c_{KA}^{\beta}} + \ln \frac{\gamma_{\pm}^{\alpha}}{\gamma_{\pm}^{\beta}}, \quad (5.11)$$

where c_{KA} is the concentration of the electrolyte and γ_{\pm} is the mean activity coefficient.

Taking into account the electroneutrality condition, i.e.,

$$z_+v_+ = z_-v_- \quad \text{or} \quad z_+c_{K^+} = z_-c_{A^-}, \quad (5.12)$$

$$\left(\frac{a_{K^+}^{\alpha}}{a_{K^+}^{\beta}} \right)^{v_+} = \left(\frac{a_{A^-}^{\beta}}{a_{A^-}^{\alpha}} \right)^{v_-} \quad (5.13)$$

or

$$\left(\frac{a_{K^+}^{\alpha}}{a_{K^+}^{\beta}} \right)^{1/z_+} = \left(\frac{a_{A^-}^{\alpha}}{a_{A^-}^{\beta}} \right)^{1/z_-}. \quad (5.14)$$

For an 1–1 electrolyte, and in dilute solutions ($\gamma_{\pm} = 1$),

$$\frac{c_{K^+}^{\alpha}}{c_{K^+}^{\beta}} = \frac{c_{A^-}^{\beta}}{c_{A^-}^{\alpha}}. \quad (5.15)$$

From (5.7) and (5.8), the interfacial electric potential drop can be expressed as follows:

$$\Delta\varphi = \frac{\Delta\mu_{A^-}^{\ominus} - \Delta\mu_{K^+}^{\ominus}}{F(z_+ - z_-)}. \quad (5.16)$$

It follows that the sign of the potential difference depends on the sign of the difference, $\Delta\mu_{A^-}^{\ominus} - \Delta\mu_{K^+}^{\ominus}$, which is determined by the different interactions between the polymer and the ions of opposite sign. For instance, a hydrophobic, nonpolar polymer will interact more strongly with a hydrophobic ion. If the latter is the cation (e.g., TBA^+), the surface charge of the polymer will be positive, which is compensated for by the excess negative charge of the anions in the solution phase. An illustration of this scenario is shown in Fig. 5.1.

A rough estimation of the formation of ion pairs (salt molecules) can be achieved using Bjerrum's theory. The probability of ions with charges of opposite signs associating increases with increasing ionic charge and with decreasing permittivity of the phase. For instance, the association of alkali halides is negligible in water at 25°C;

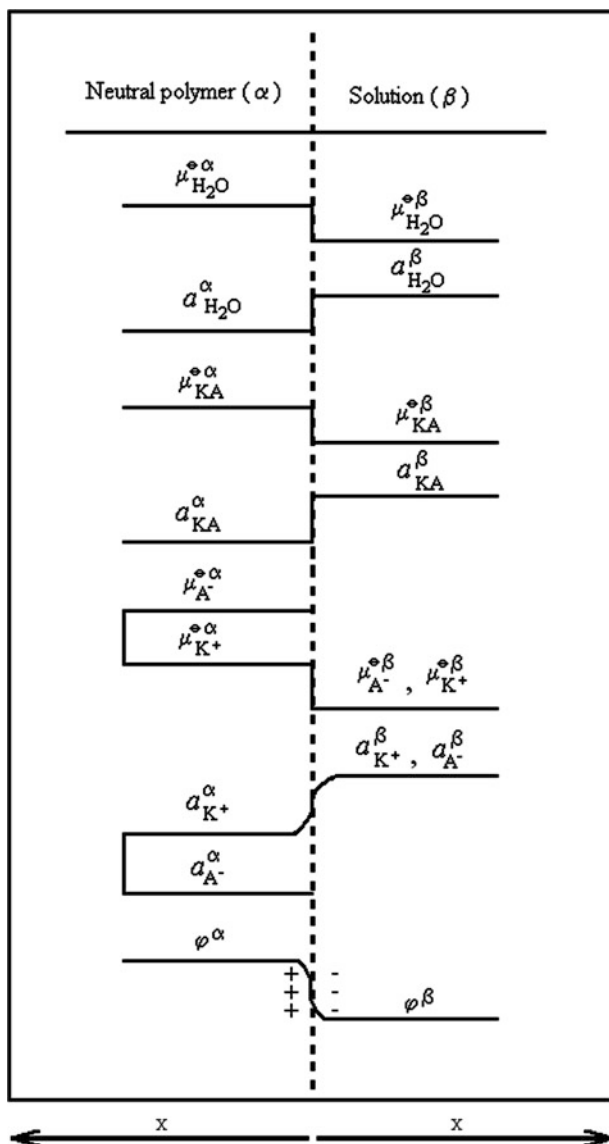


Fig. 5.1 The standard chemical potentials (μ_i^{\ominus}), the activities (a_i), and the inner potentials (φ) in the case of a neutral, hydrophobic polymer and an aqueous solution containing ($\text{KA} \rightleftharpoons \text{K}^+ + \text{A}^-$) electrolyte

however, it becomes significant upon the addition of dioxan when $\epsilon < 30$. The relationship between the logarithm of the association constant ($\log K_{\text{assoc}}$) and $1/\epsilon$ is approximately linear. This means that the formation of ion pairs within a polymer phase of low dielectric permittivity ($\epsilon = 2\text{--}10$) is expected. However, due to many other

possible interactions (e.g., complex formation), a rather detailed investigation is needed to estimate this effect for each system separately.

The situation is different when the interface is not permeable for one of the ions; i.e., the polymer film behaves like an ion-exchange membrane. This is the case when the polymer is charged, which is usually achieved by oxidation or reduction; however, this can also be the result of protonation.

5.2 Charged Polymer in Contact with an Electrolyte Solution

Two cases should be considered (1) nonosmotic membrane equilibrium and (2) osmotic membrane equilibrium. In the latter case, where solvent molecules can enter the surface layer or the membrane, the situation is more complicated since mechanical equilibria are also involved. We will start by considering nonosmotic equilibrium.

5.2.1 Nonosmotic Membrane Equilibrium

For the sake of simplicity, we will consider a negatively charged polymer film (negative sites are formed as a result of a reduction process) in contact with a K^+A^- electrolyte. The concentration of the negatively charged sites (X^-) is c_{X^-} , the value of which depends on the potential according to the Nernst equation. At fixed potential and a concentration of c_{KX} , the partitioning equilibrium (γ_{\pm} is taken to be 1) is

$$c_{K^+}^{\alpha} c_{A^-}^{\alpha} = c_{K^+}^{\beta} c_{A^-}^{\beta} = \left(c_{KA}^{\beta}\right)^2. \quad (5.17)$$

Because of the electroneutrality condition

$$c_{K^+}^{\alpha} = c_{A^-}^{\alpha} + c_{X^-}^{\alpha}, \quad (5.18)$$

$$c_{K^+}^{\beta} = c_{A^-}^{\beta} = c_{KA}^{\beta}. \quad (5.19)$$

From (5.17)–(5.19), it follows that

$$c_{K^+}^{\alpha} = 0.5c_{X^-}^{\alpha} + \left[(0.5c_{X^-}^{\alpha})^2 + \left(c_{KA}^{\beta}\right)^2 \right]^{1/2}, \quad (5.20)$$

$$c_{A^-}^{\alpha} = -0.5c_{X^-}^{\alpha} + \left[(0.5c_{X^-}^{\alpha})^2 + \left(c_{KA}^{\beta}\right)^2 \right]^{1/2}. \quad (5.21)$$

When $c_{KA}^\beta/c_{X^-}^\alpha \ll 1$, $c_{K^+}^\alpha \approx c_{X^-}^\alpha$, and $c_{A^-}^\alpha = 0$; i.e., the membrane behaves as a cation exchanger. This condition is usually fulfilled, since the concentration of the negatively charged sites in fully reduced polymer film is 1–5 mol dm⁻³, while the concentration of the contacting solution is usually 0.1–1 mol dm⁻³. However, in the beginning of the reduction (e.g., in a cyclic voltammetric experiment), $c_{X^-}^\alpha$ might be smaller than c_{KA}^β , or when a concentrated electrolyte is applied ($c_{KA}^\beta > 5 - 15$ mol dm⁻³), the sorption of co-ions (anions in this case) should also be considered (see Fig. 5.2). In the very beginning of the redox transformation, (5.3) may also be operative if the neutral polymer has a low dielectric permittivity and both $\Delta\mu_s^\ominus$ and $\Delta\mu_{ion}^\ominus$ also change during the redox transformation. The Donnan potential between the polymer membrane and the solution is

$$E_D = \frac{RT}{F} \ln \frac{a_{K^+}^\beta}{a_{K^+}^\alpha}. \quad (5.22)$$

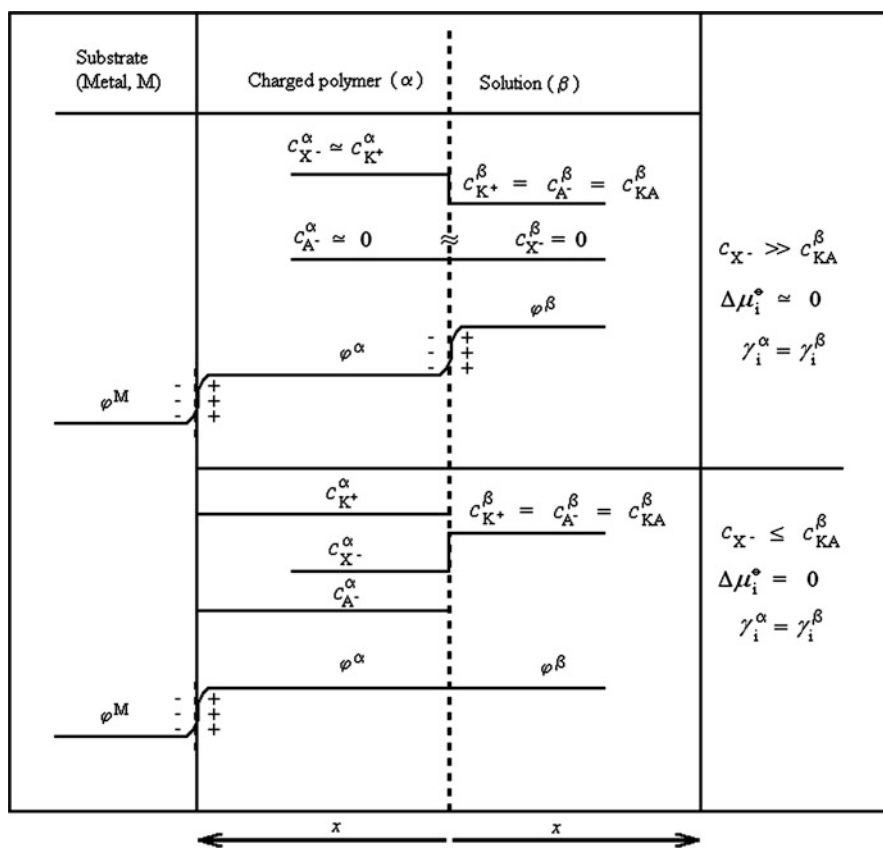


Fig. 5.2 The concentrations of the ions and the inner potentials in the different phases of a modified electrode arrangement

The dependence of the Donnan potential on the electrolyte concentration can be obtained by combining (5.20) and (5.22) and taking the value of the activity coefficient of K^+ to be 1 or $\gamma_{K^+}^\alpha = \gamma_{K^+}^\beta$. In fact, the terms containing the activity coefficients $[RT \ln(\gamma_{K^+}^\alpha/\gamma_{K^+}^\beta)]$ and $\Delta\mu_{K^+}^\ominus$ are usually treated together, since they are not accessible separately by any measurements. Additional hypotheses are needed to assign the deviation from the ideal behavior either to the solvation effect, specific interactions between the ions and the polymer, or to the interactions between charged entities.

In the true membrane arrangement, when the conducting ion-exchange polymer is situated between two solutions (I and II) of different concentrations, a Donnan potential also arises at the other membrane–solution interface, which can be expressed similarly; however, no equilibrium exists in this case.

A diffusion potential ($\Delta\varphi_{\text{diff}}$) arises within the membrane which depends on the concentrations and mobilities of the ions within the membrane. For a perfectly selective membrane (e.g., $c_A^\alpha \approx 0$),

$$\Delta\varphi_{\text{diff}} = \frac{RT}{F} \ln \frac{c_{K^+}^\alpha(\text{I})}{c_{K^+}^\alpha(\text{II})}, \quad (5.23)$$

and the Donnan potential

$$E_D = \frac{RT}{F} \ln \frac{a_{K^+}(\text{I})}{a_{K^+}(\text{II})}. \quad (5.24)$$

If more than one cation is present, due to the specific interactions between the polymer and ions, a selectivity can be observed. Only electrostatic interactions were considered above, which, of course, involve the differences between the charges of the ions, which were not treated in our derivations but can easily be included. The specific interactions are due to other forces (dipole, van der Waals, hydrogen bonding, etc.).

If we consider two electrolytes (KA, BA) and the polymer film electrode arrangement, we can write (5.1) for both K^+ and B^+ , and the different specific interactions can be expressed by different $\Delta\mu_i^\ominus$ values according to (5.3). Introducing the ion-exchange equilibrium constant (K_{KB}),

$$RT \ln K_{KB} = \mu_{K^+}^{\ominus\alpha} + \mu_{B^+}^{\ominus\beta} - (\mu_{K^+}^{\ominus\beta} + \mu_{B^+}^{\ominus\alpha}), \quad (5.25)$$

$$K_{KB} = \frac{a_{K^+}^\beta a_{B^+}^\alpha}{a_{K^+}^\alpha a_{B^+}^\beta}. \quad (5.26)$$

It follows that the $a_{K^+}^\alpha/a_{B^+}^\alpha$ ratio (i.e., the distribution within the polymer phase) will depend on the difference in $\Delta\mu_i^\ominus$ values, and K_{KB} is a selectivity constant.

When the membrane is in contact with solutions of different concentrations of KA and BA on both sides, $K_{KB} = (u_{K^+}/u_{B^+})K'_{KB}$, where u_{K^+} and u_{B^+} are the mobilities of the respective ions.

For the potential difference ($\Delta\varphi = \Delta_I^\beta\varphi + \Delta_{II}^\beta\varphi + \Delta\varphi_{\text{diff}}$)

$$\Delta\varphi = \frac{RT}{F} \ln \frac{a_{K^+}^I + K'_{AB} a_{B^+}^I}{a_{K^+}^{II} + K'_{AB} a_{B^+}^{II}} \quad (5.27)$$

is obtained.

The membrane properties of electrochemically active polymer films, including several examples, have been compiled by Doblhofer and Vorotyntsev [10–12].

5.2.2 Osmotic Membrane Equilibrium and Electrochemical and Mechanical Equilibria

During the redox transformations and the incorporation of ions and solvent molecules into the polymer phase, a swelling of the polymer layer occurs; i.e., the state of the polymer phase depends on the potential. A volume change may also take place when the molar volumes of the reduced and oxidized forms differ. To obtain a thermodynamic description of the expansion or contraction of the polymer network, a mechanical work term must be added to the equations used so far. We may consider a polymer network where the chains are kept together by interchain cross-links based on chemical bonds or weaker (e.g., van der Waals) forces. When the interchain forces are weak, the sorption of solvent molecules may lead to infinite swelling (i.e., to dissolution).

The deformation of the polymer layer may be plastic or elastic. Plastic deformation occurs during the break-in period when a freshly deposited film (e.g., the polymer is deposited from an organic solvent solution using an evaporation technique) is placed in an aqueous electrolyte and the incorporation of ions and solvent molecules is completed after many potential cycles. The elastic deformation is usually reversibly coupled to the redox reaction.

5.2.2.1 Osmotic Membrane Equilibrium and Incorporation of Solvent Molecules

In this case, the osmotic equilibrium is reached when

$$\mu_s^\alpha = \mu_s^\beta, \quad (5.28)$$

where μ_s is the chemical potential of the solvent (s).

The activity of the solvent in the polymer phase differs from that of the electrolyte

$$\mu_s = \mu_s^\ominus + RT \ln a_s + PV_s, \quad (5.29)$$

where P is the pressure relative to the standard pressure p^\ominus used to define the standard chemical potential, and V_s is the partial molar volume of the solvent.

If we assume that P^α is higher than P^β (i.e., there is an osmotic pressure drop across the film/solution interface but the partial molar volume of the solvent molecules is the same in both phases), then:

$$\mu_s^\alpha - \mu_s^\beta = \Delta\mu_s = \mu_s^{\ominus\alpha} - \mu_s^{\ominus\beta} + (P^\alpha - P^\beta)V_s + RT \ln \frac{a_s^\alpha}{a_s^\beta}, \quad (5.30)$$

$(P^\alpha - P^\beta)V_s$ is the work needed to expand the polymer network, which is still maintained by cross-links. This means that (5.3) or (5.11) must be extended with this term.

5.2.2.2 Mechanical–Electrochemical Equilibrium and Incorporation of Counterions

Of course, if the pressure difference exists, this mechanical work term is operative for all species, including the freely moving ions and the redox sites. For each charged species, (5.29) can be written as follows:

$$\tilde{\mu}_i^\alpha = \mu_i^{\ominus\alpha} + RT \ln a_i^\alpha + z_i F \varphi^\alpha + P^\alpha V_i. \quad (5.31)$$

The equilibrium situation between the surface film and the solution for ions that enter the film from the solution can be expressed by taking into account the mechanical free energy associated with the incorporation of counterions. Considering an anion exchanger (i.e., when the redox sites are positively charged),

$$\tilde{\mu}_{A^-}^\alpha = \tilde{\mu}_{A^-}^\beta, \quad (5.32)$$

and so the expression for the potential drop at this interface will be

$$\varphi^\alpha - \varphi^\beta = \frac{\mu_{A^-}^{\ominus\alpha} - \mu_{A^-}^{\ominus\beta}}{F} + \frac{RT}{F} \ln \frac{a_{A^-}^\alpha}{a_{A^-}^\beta} + \frac{V_A(P^\alpha - P^\beta)}{F}, \quad (5.33)$$

when the charges of both the anion and the redox sites are $|z_i| = 1$, and assuming that V_A is independent of composition and pressure. At the substrate (metal, M) and

film interface, where only electron transfer occurs, the equilibrium can be represented by the equality of the electrochemical potential of the electron:

$$\tilde{\mu}_{e^-}^M = \tilde{\mu}_{e^-}^\alpha. \quad (5.34)$$

In the polymer phase (α), the following electron exchange reaction takes place:



Therefore,

$$\tilde{\mu}_e^\alpha = \tilde{\mu}_{\text{Red}}^\alpha - \tilde{\mu}_{\text{Ox}}^\alpha \quad (5.36)$$

and consequently the potential drop at this interface

$$\varphi^M - \varphi^\alpha = \frac{\mu_{\text{Ox}}^{\ominus\alpha} - \mu_{\text{Red}}^{\ominus\alpha} + \mu_e^{\ominus M}}{F} + \frac{RT}{F} \ln \frac{a_{\text{Ox}}^\alpha}{a_{\text{Red}}^\alpha} + \frac{P^\alpha (V_{\text{Ox}}^\alpha - V_{\text{Red}}^\alpha)}{F}, \quad (5.37)$$

assuming that the partial volumes of the oxidized and reduced forms are different, and neglecting the activity and volume changes (as usual) in the metal phase.

The addition of (5.33) and (5.37) gives the total potential difference between the metal and the electrolyte solution.

Using an appropriate reference electrode, the Galvani potential difference $\Delta\varphi = \varphi^M - \varphi^\alpha$ can be measured against this reference potential, and the electrode potential (E) can be given as follows:

$$E = E^\ominus + \frac{RT}{F} \ln \frac{\gamma_{\text{Ox}}^\alpha c_{\text{Ox}}^\alpha}{\gamma_{\text{Red}}^\alpha c_{\text{Red}}^\alpha} + \frac{RT}{F} \ln \frac{\gamma_{\text{A}^-}^\alpha c_{\text{A}^-}^\alpha}{\gamma_{\text{A}^-}^\beta c_{\text{A}^-}^\beta} + \frac{\mu_{\text{A}^-}^{\ominus\alpha} - \mu_{\text{A}^-}^{\ominus\beta}}{F} + \frac{(P^\alpha + P^\beta)V_{\text{A}}}{F} + P^\alpha (V_{\text{Ox}}^\alpha - V_{\text{Red}}^\alpha), \quad (5.38)$$

where the standard electrode potential (E^\ominus) belongs to reaction (5.35), the second term is the Nernstian activity ratio term where the relative activities are expressed by the product of the respective activity coefficients and concentrations, the third term and the fourth term give the potential difference resulting from a Donnan-type ionic equilibrium at the polymer film–solution interface, and the last two terms express the mechanical equilibria. The fifth term is of importance when P^α differs from P^β and its value increases when the partial molar volume of the counterion increases. The sixth term should be taken into account if the internal pressure of the polymer film is significant and the partial molar volumes of the oxidized and reduced forms of the electrochemically active species differ substantially from each other.

Equation (5.38) must be extended with (5.30) when solvent sorption plays a significant role.

When the activity coefficients are unknown, the formal potential ($E_c^{\circ'}$) is used in electrochemistry [13]. This approach, in principle, could also be followed in the case of polymer film electrodes. However, the activity coefficients should be independent of the potential—a requirement which is not fulfilled for these systems. It is evident that during charging, both the electrostatic interactions and the chemical environment will change substantially, which will influence the values of the activity coefficients to a great extent. In many cases, the concentration of charged sites is as high as $1\text{--}5 \text{ mol dm}^{-3}$ after complete oxidation or reduction, and consequently it is expected that the values of $\gamma_{\text{Ox}}^\alpha$, $\gamma_{\text{Red}}^\alpha$, and $\gamma_{\text{A}^-}^\alpha$ (or $\gamma_{\text{K}^+}^\alpha$) will increase significantly. Because we usually have no information on the function $\gamma_i^\alpha(E)$, in order to elucidate the nonideal electrochemical behavior (e.g., the shape of the cyclic voltammogram), an “interaction” parameter is introduced that relates to the variations in the activity coefficients of the redox sites [second term in (5.38)].

Beside the excess internal pressure originating from osmotic phenomena due to the transport of solvent molecules, the incorporation of counterions also contributes to the development of a pressure difference, because the cross-linked polymer network must expand to accommodate counterions. Evans et al. [14, 15] have dealt with this problem and proved that for poly(vinylferrocene) (PVF) films the latter is the important pressure-generating mechanism. Furthermore, in the case of PVF, the term $P^\alpha(V_{\text{Ox}}^\alpha - V_{\text{Red}}^\alpha)$ can be neglected since $V_{\text{Ox}} \sim 1.02 V_{\text{Red}}$, and the effect of the incorporation of counterions dominates.

They considered only the elastic deformation of the polymer network, which is reversibly coupled to the redox reaction. On the basis of this simplified model, the following relationship for the electrode potential as a function of the fraction of oxidized sites, f , was derived:

$$E = E_c^{\circ'} + \frac{RT}{nF} \ln \frac{f}{1-f} + \frac{nV_{\text{A}}^2 c K f}{Fz^2}, \quad (5.39)$$

where the mechanical work term contains the modulus of elasticity, K , the molar volume of the anion, V_{A} , the redox site concentration, c , the charge of the counterion, z , and the number of electrons transferred from the film to the electrode substrate, n .

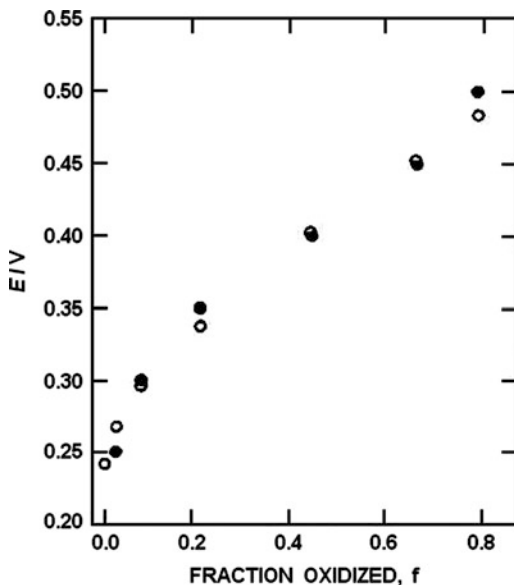
Despite the rather simplified nature of the model, the deviation of the experimental data obtained for different PVF films from the ideal Nernstian response without a mechanical contribution was nicely described (see Fig. 5.3).

The nonideality of the electrochemically active polymer film has also been explained by the interactions of the redox sites [16] and the heterogeneity [17] of the polymer layer.

Brown and Anson [16] assumed that the degree of interaction between the redox sites depends on the concentrations of the reduced (c_{A}) and oxidized (c_{B}) sites, and so the activity coefficients can be expressed as follows:

$$\gamma_{\text{A}} = \exp[-(r_{\text{AA}}c_{\text{A}} + r_{\text{AB}}c_{\text{B}})], \quad (5.40)$$

Fig. 5.3 Comparison of experimental data obtained for plasma-polymerized vinylferrocene (*solid circles*) and the theoretical calculation (*open circles*) according to (5.39) (Reproduced from [14] with the permission of Elsevier.)



$$\gamma_B = \exp[-(r_{BB}c_B + r_{BA}c_A)], \quad (5.41)$$

where r_{AA} , r_{AB} , r_{BB} , and r_{BA} are the respective interaction parameters. Repulsive interactions have $r < 0$, while attractive ones have $r > 0$. This approach has been used in several papers [18, 19]. Albery et al. assumed a Gaussian distribution of the standard potentials of the redox sites [17].

The concept of distributed formal redox potentials was introduced by Posadas et al. [20] for the thermodynamic description of conducting polymers. The distribution of the formal redox potentials was derived from the experimental data obtained for PANI, POT, POAP, PBD, and polybenzidine polymers. In all cases, a sigmoidal distribution function was found. The shape of the distribution function was explained by a mechanical stress effect generated by the contraction and expansion of the polymer film during the redox transformations.

The most comprehensive thermodynamic model that describes the redox switching of electroactive polymers has appeared recently. Posadas and Florit [21] considered the following phenomena: conformational changes; swelling due to the sorption/desorption of solvent molecules; injection/ejection of ions that specifically bind to the polymer; and ion ingress/egress in order to maintain electroneutrality inside the polymer. Both the oxidized and reduced forms of the polymer are considered to be polyelectrolytes; however, they have different chemical natures. The polymer was treated as a separate phase in contact with an electrolyte solution on one side (where the ionic exchange processes occur), and with a metallic conductor on the other side (where the electron exchange takes place). The apparent formal potential was calculated by taking into account the different contributions to the free energy. The model was applied to the redox transformation of polyaniline (PANI).

The free energy of mixing the polymer with the solvent (ΔA_m) was calculated based on the theory of Flory [22].

$$A_m = kT(N_1 \ln \phi_1 + N_2 \ln \phi_2) + \chi M_t \phi_1 \phi_2, \quad (5.42)$$

where ϕ_1 and ϕ_2 are the volume fractions of the solvent and the polymer, respectively; N_1 is the number of solvent molecules inside the polymer phase; N_2 is the number of chains; $M_t = N_1 + N_2 M$ (M is the average number of monomer units); and χ is the interaction parameter. The phase behavior of the polymer is governed by χ ($\chi < 0$ for a good solvent, i.e., when interactions between the polymer segments and the solvent molecules are larger than the segment–segment interactions, and $\chi > 0.5$ for bad solvents, i.e., when the interactions between the segments are stronger than the solvent–segment interactions).

The swelling equilibrium is established when the deformation of the polymer network equals the osmotic pressure of the solvent. The corresponding free energy change (ΔA_d) is purely entropic [23–25].

$$\Delta A_d = -T\Delta S_d = \nu M kT \left[\ln \phi_2 + 3 \left(\phi_2^{-2/9} - 1 \right) \right], \quad (5.43)$$

where νM is the number of monomer units that are participating in the deformation process.

The change in the binding free energy (A_b) was described by a Langmuir isotherm:

$$\Delta A_b = kTB \left\{ \ln(1-f) + f \ln \left[\frac{f}{q(1-f)} \right] \right\}, \quad (5.44)$$

where B is the total number of binding sites (for PANI there are two types of binding site: amine and imine groups), f is the fraction of the bound sites, and q is the partition function of occupied sites.

The free energy change due to the incorporation of counterions into the polymer phase to maintain the electroneutrality (A_{el}) is:

$$A_{el} = \frac{z_{ad}^2 M f^2 \phi^2}{2\nu_0 I}. \quad (5.45)$$

The total free energy change of the polymer is

$$\Delta A_{pol} = \Delta A_m + \Delta A_d + \Delta A_b + \Delta A_{el}. \quad (5.46)$$

The chemical potentials corresponding to the different free energy contributions of the polymer are the corresponding derivatives with respect to M , which are dependent only on ϕ_2 :

$$M_m = \left[\frac{1 - \phi_2}{\phi_2} \right] \ln(1 - \phi_2) + \chi(1 - \phi_2), \quad (5.47)$$

($N_2 = 1$ for a polymer network)

$$M_d = \nu kT \left[\ln \phi_2 + 3 \left(\phi^{-2/9} - 1 \right) \right], \quad (5.48)$$

$$M_b = gkT \left\{ \ln(1 - f) + f \ln \left[\left(\frac{f}{g} \right) (1 - f) \right] \right\}, \quad (5.49)$$

(g is the fraction of monomer units that are capable of binding protons, $B = gM$)

$$M_{el} = kT \left(\frac{z_{ad}^2 \phi_2^2 g^2 f^2}{2\nu_0 l} \right). \quad (5.50)$$

The sum of all these contributions will be the chemical potential of each type of polymer (i.e., $M_{pol,r}$ and $M_{pol,o}$ for the reduced and oxidized forms, respectively). When both types of polymers are present, a further conformational contribution should be considered, except in the case of the complete independence of the two types of polymers.

The description of the osmotic equilibrium is based on (5.2), and $\Delta\mu_1$ can be determined from $(\partial\Delta A_{pol}/\partial N_1)_{N,N_{ox},T} = 0$.

The electrode potential (E) can be derived from the potential of the cell reaction using an appropriate reference electrode:

$$FE = \left(\frac{\partial\Delta A}{\partial N_e} \right)_{N,N_{ox},T}, \quad (5.51)$$

where F is the Faraday constant, N_e is the number of electrons, N_{ox} and N_{red} are the number of redox centers ($N = N_{ox} + N_{red}$), and

$$dA = \tilde{\mu}_{ox} dN_{ox} + \tilde{\mu}_{red} dN_{red} + \tilde{\mu}_e dN_e + \mu_{pol,ox} dM_{pol,ox} + \mu_{pol,red} dM_{pol,red}, \quad (5.52)$$

where $\tilde{\mu}_{ox}$, $\tilde{\mu}_{red}$, and $\tilde{\mu}_e$ are the electrochemical potentials of the respective redox centers and the electrons.

The degree of advancement of the redox reaction ($d\xi$)

$$d\xi = dN_{ox} = -dN_{red} = dN_e, \quad (5.53)$$

and the number of redox centers are related to the number of units ($M_o = \alpha N_{ox}$ and $M_r = \alpha N_{red}$), thus

$$E = \left(\frac{1}{F} \right) \left[\mu_{ox} - \mu_{red} + \mu_e + \alpha (\mu_{pol,ox} - \mu_{pol,red}) \right], \quad (5.54)$$

where μ_{ox} , μ_{red} , and μ_e are the respective chemical potentials.

Fig. 5.4 Calculated change in the number of solvent molecules (ΔN_1) as a function of the potential [21] (Reproduced with the permission of the American Chemical Society.)

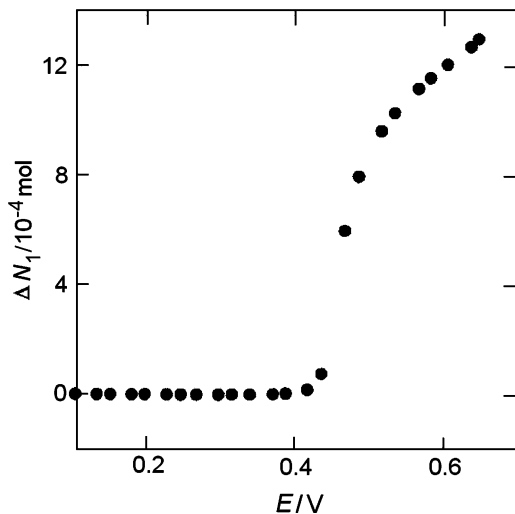
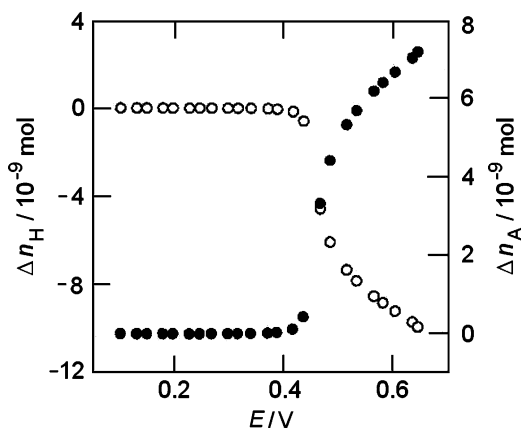


Fig. 5.5 Calculated change in (*open circles*) the number of expelled protons (Δn_H) and (*solid circles*) the number of injected anions (Δn_A) in the polymer as a function of the potential [21] (Reproduced with the permission of the American Chemical Society.)



If ideal behavior is assumed,

$$\mu_{\text{ox}} = \mu_{\text{ox}}^{\ominus} + kT \ln \theta, \quad (5.55)$$

$$\mu_{\text{red}} = \mu_{\text{red}}^{\ominus} + kT \ln (1 - \theta), \quad (5.56)$$

where $\theta = N_{\text{ox}}/N_t$.

The interactions between the oxidized and reduced sites have also been treated.

On the basis of this model, and by using the values of the different quantities determined experimentally (the protonation constants of the oxidized and reduced forms determined by titration, volume changes during the redox transformation, and the number of redox centers calculated from the charge consumed), the

calculations led to reasonable results which are in accordance with earlier findings. Figures 5.4 and 5.5 show the results of the calculation for the solvent and ion populations.

5.3 Dimerization, Disproportionation, and Ion Association Equilibria Within the Polymer Phase

On the basis of the results of simultaneous measurements of electron spin resonance and ultraviolet–visible spectroscopy, it was suggested by Dunsch et al. [26] that the electrochemical transformations of PANI take place via an EE mechanism that includes a disproportionation equilibrium:



where E_1^\ominus and E_2^\ominus are the respective standard potentials and $E_1^\ominus > E_2^\ominus$; K_{disp} is the disproportionation equilibrium constant, which can be expressed as

$$K_{\text{disp}} = \exp \left[- \left(\frac{F}{RT} \right) (E_2^\ominus - E_1^\ominus) \right]; \quad (5.60)$$

and A, P^+ , and B^{2+} are the symbols of the reduced state, the polaronic state, and the bipolaronic state, respectively. The single voltammetric wave that appears in the cyclic voltammograms may indicate that $E_1^\ominus > E_2^\ominus$; however, the theoretical calculations do not support this assumption. This apparent contradiction can be resolved by considering a reversible dimerization reaction; i.e.,



The dimerization reaction yields doubly charged segments on the polymer chain that are twice as big as a polaronic segment. For a bipolaronic state of this size, however, interchain bipolarons with a π - or σ -bond between the polymer chains can also be envisaged. This model can be extended by protonation equilibria [26]. There are several other hypotheses relating to the formation and interactions of polarons and bipolarons which also take into account the interactions between the charged sites in the polymer chains and counterions (C^-). Counterions may decrease the Coulomb repulsion between two polarons during the formation of a bipolaron.

Different complexes such as P^+C^- , $B^{2+}C^-$, and $B^{2+}C_2^-$ have been assumed by Paasch [27]. It was concluded that two processes are slow: the formation of bipolarons and the formation of $B^{2+}C_2^-$ complexes. The hysteresis effects were also explained by the bipolaron mechanism; i.e., due to the high formation energy of bipolarons, their decay into polarons is a slow process.

The effect of ion association has also been considered by Vorotyntsev et al. [28]. In order to explain the splitting of the voltammetric waves, it was assumed that ions inside the polymer film exist in two different forms: “free” and “bound”. The “bound” ions may be associated with neutral sites of the polymer matrix, resulting from the formation of a bond or ion binding by microcavities; or they may be due to the formation of P^+C^- , $B^{2+}C_2^-$ -type complexes. However, the results from cyclic voltammetric and EQCN experiments on PP and PANI cannot be explained by the hypothesis based on complex formation, while the “bound” ion theory is appropriate for interpreting the unusual behavior observed [28].

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