

Theory for Solvent and Salt Transfer Accompanying Partial Redox Conversion of Electroactive Polymer Films under Permselective and Nonpermselective Conditions

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A comprehensive thermodynamic model for solvent and salt transfer accompanying a partial redox conversion, i.e., conversion between any two oxidation levels, of an electroactive polymer (EAP) film is presented. We discuss two possible cases, namely, one-phase and two-phase behavior of an EAP film. An expression describing the extent of solvent transfer in these situations is presented. Salt transfer is characterized by the difference in permselectivity indices ($\Delta R_{b,a}$) between two oxidation levels of the EAP film. $\Delta R_{b,a}$ represents the difference in co-ion (salt) exclusion properties of the EAP in the two different oxidation levels. $\Delta R_{b,a}$ is expressed in terms of the EAP's charge, number of electrons transferred in the redox reaction of an electroactive unit, concentration of the supporting electrolyte, salt partition coefficient between solvent and EAP phases, and salt activity coefficients in both phases. Plots of $\Delta R_{b,a}$ as a function of the electrolyte concentration allow determining the EAP's phase behavior, ratio of salt partition coefficients, and number of electrons exchanged in the redox process. $\Delta R_{b,a}$ is an experimentally accessible quantity; it can be obtained from electrochemical quartz crystal microbalance (EQCM) experiments. $\Delta R_{b,a}$ values can be used as a diagnostic tool to characterize an EAP film.

1. Introduction

Different thermodynamic and kinetic phenomena exhibited by electroactive polymer (EAP) films have been studied under a variety of experimental conditions and by many experimental techniques.^{1–3} Several approaches to understanding the thermodynamics of solvent and salt transfer which accompany the redox switching of such EAPs have been undertaken.^{4–7} Here, we focus on a thermodynamic interpretation of the electrochemical quartz crystal microbalance (EQCM) data under permselective (only counterion and solvent transfer) and nonpermselective (counterion, co-ion, and solvent transfer) conditions. Understanding partial redox switching phenomena is key to optimizing the technological applications of EAP films. It is also a prerequisite to understanding their kinetic behavior. Surprisingly, although accomplishment of complete redox conversion of an electroactive film requires one to pass through a continuum of partial redox conversion states, the associated data has generally failed to attract interpretation or comment. One possible reason for this is the absence of an interpretational framework, of which one significant ambiguity that arises here but not for fully converted states is whether the two redox states are homogeneously mixed in a single phase or form a two-phase system. The strategic goals of this work are to establish how one would make such a distinction and to encourage the acquisition and interpretation of such data.

Theoretical models predicting changes of mobile species populations during the redox process have been presented.^{8–10} These populations changes are available via a number of

techniques, including spectroscopy,¹¹ fluorescence,¹² ellipsometry,^{13,14} and neutron reflectivity.¹⁵ With no loss in generality, we express our results in terms of film mass changes obtained using the EQCM.¹⁶ Bruckenstein and Hillman describe in their paper⁸ a method to obtain film mass changes due to individual mobile species taking part in the redox switching process under permselective and nonpermselective conditions. However, that work was restricted to a one-electron, complete (“end-to-end”) redox process for a unipositive/uncharged (+1/0) redox couple, i.e., to interconversions between 0% oxidized (Ox) and 100% oxidized states occurring in 1:1 electrolytes. Salt was assumed to enter only the oxidized form of the EAP film, and the amount of solvent transferred was also assumed to be independent of electrolyte concentration in the bathing solution. These constraints were relaxed in our next model⁹ describing solvent and salt transfers, again under both permselective and nonpermselective conditions. There, *multi-electron transfers* between states with different arbitrary integer charges were considered. Even then, our treatment was still restricted to end-to-end redox processes. Here, we consider the general case of redox switching of an EAP film between two arbitrary charge levels, *a* and *b*, and include the change in film volume that accompanies this redox process. We treat the nonpermselective case, as it is easily converted to the permselective situation. The approach used here is completely parallel with the one used in our earlier, less general, treatment.⁹ The more general considerations presented here are more than an academic exercise. They can be used to describe a large number of situations encountered in applications including energy storage, sensing, artificial muscles, and membrane transport.

2. Theory

Chemical equations representing redox reactions of EAPs with various charge types, together with counterion, co-ion (salt),

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and solvent (H₂O) transfer, were given earlier.⁹ These are shown in the Appendix.

2.1. Solvent Transfer. Consider the situation where the EAP film is switched between any two fractional oxidation levels, a and b (where $b > a$, $0 \leq b \leq 1$). Solvent partitions between the bathing solution and the EAP film at either oxidation level are expressed as follows:

$$\text{solv}_s \rightleftharpoons \text{solv}_{p,j} \quad K_{\text{solv},p,j} = a_{\text{solv},p,j}/a_{\text{solv},s} \quad (1)$$

where solv designates solvent, p is for the EAP phase, s represents the solution phase, and $j = a$ or b . In the limiting case of a totally reduced EAP, $j = 0.0 = \text{Red}$, and for a totally oxidized EAP, $j = 1.0 = \text{Ox}$.

In our previous work⁹ dealing with the end-to-end process ($a = 0$ and $b = 1$), we obtained the following expression for the film mass change, Δm_{solv} , due to the solvent transfer:

$$\Delta m_{\text{solv}} = M_{\text{solv}} V c_{\text{solv},s} \gamma_{\text{solv},s} \left(\frac{K_{\text{solv},p,\text{Ox}}}{\gamma_{\text{solv},p,\text{Ox}}} - \frac{K_{\text{solv},p,\text{Red}}}{\gamma_{\text{solv},p,\text{Red}}} \right) \quad (2)$$

where M_{solv} is the molar mass of the solvent, V is the volume of the polymer in units consistent with those used for concentration, here dm³. $K_{\text{solv},p,j}$ is a partition coefficient of solvent between the solution and EAP film in its “ j ” state ($j = \text{Ox}$ or Red), $c_{\text{solv},s}$ is the solvent concentration in the bathing solution, and $\gamma_{\text{solv},s}$ and $\gamma_{\text{solv},p,j}$ are activity coefficients of solvent in solution (subscript s), and in an EAP phase (subscript p). Note that in the latter work we also assumed that there were no volume changes of the film on redox conversion. Here, we take these volume changes into account.

Proceeding analogously to our previous work, dealing with an end-to-end process,⁹ we derive the expression for the film mass change, Δm_{solv} , due to the solvent transfer accompanying partial redox switching:

$$\Delta m_{\text{solv}} = M_{\text{solv}} c_{\text{solv},s} \left(\frac{V_{p,b} K_{\text{solv},p,b} \gamma_{\text{solv},s}}{\gamma_{\text{solv},p,b}} - \frac{V_{p,a} K_{\text{solv},p,a} \gamma_{\text{solv},s}}{\gamma_{\text{solv},p,a}} \right) = M_{\text{solv}} c_{\text{solv},s} (K_{\text{solv},p,b}^* - K_{\text{solv},p,a}^*) \quad (3)$$

where $V_{p,j}$ is the volume of the EAP film and $K_{\text{solv},p,j}$ is the thermodynamic partition coefficient of the solvent between the solution and the EAP film in its “ j ” state ($j = b$ or a), while $\gamma_{\text{solv},s}$ and $\gamma_{\text{solv},p,j}$ are the activity coefficients of the solvent in solution (subscript s) and in an EAP phase (subscript p). $K_{\text{solv},p,j}^* = V_{p,j} K_{\text{solv},p,j} \gamma_{\text{solv},s} / \gamma_{\text{solv},p,j}$ is the concentration partition coefficient multiplied by the EAP film volume. The term Δm_{solv} may depend on the salt concentration in the solution at a fixed charge level j since the partition of mobile species into the film can cause $K_{\text{solv},p,j}^*$ ($= V_{p,j} K_{\text{solv},p,j} \gamma_{\text{solv},s} / \gamma_{\text{solv},p,j}$) to change, because either $V_{p,j}$ and/or $\gamma_{\text{solv},s} / \gamma_{\text{solv},p,j}$ changes. This is well-known for conventional ion exchangers¹⁷ that have no redox properties. Also, eq 3, which deals explicitly with the case of two different charge levels at the same electrolyte concentration in the bathing solution, makes it clear that it is not possible to separate the individual values of volume, partition coefficient, and activity coefficient from the value of Δm_{solv} . Equation 3 is the general expression that includes the previously described theoretical end-to-end case where $K_{\text{solv},p,j}^*$ was assumed, for simplicity, to be constant at all film charge levels.⁹

Commonly, the lyophilicity characteristics of the two polymer redox states are very different, to the extent that phase segregation might be expected to occur. As an example, Daum and Murray¹⁸ reported “phaselike behavior” during the chro-

nopotentiometric oxidation of reduced poly(vinylferrocene) (PVF) films in water,¹⁸ while their immediately subsequent reduction data were characteristic of a homogeneous film. On short time standing after completion of the full chronopotentiometric cycle, the film was found to convert to one that behaved like the original reduced film. This change was attributed to solvent loss from the oxidized film. Our steady-state equilibrium studies of this system in water, obtained after waiting several hours after changing the oxidation level of PVF, were explained in terms of a single-phase model.¹⁹ These results are not inconsistent with those of Daum and Murray. Such observations trigger the need to be able to distinguish single-phase from two-phase behavior. In either case, one requires an appropriate set of relationships that describe the exchange of mobile species with the solution phase. We now proceed to explore these physically distinct cases.

2.1.1. Two-Phase Behavior (Noninteracting Phases). Here, we consider one of the possible situations and assume that the EAP in its intermediate oxidation state is a mixture of 0% oxidized and 100% oxidized EAP phases. We chose the simplest physical and algebraic situation, the case of a thermodynamically ideal mixture of two phases, which by definition do not interact. In this case, all film properties, including the solvent partition coefficients, are a linear combination of the properties of each component phase. This situation is approached by nonideal systems with small differences between b and a . Therefore, the equilibrium constant $K_{\text{solv},p,j}^*$, which appears in eq 3 can be written as

$$K_{\text{solv},p,j}^* = K_{\text{solv},p,\text{Red}}^* + j(K_{\text{solv},p,\text{Ox}}^* - K_{\text{solv},p,\text{Red}}^*) \quad 0.0 \leq j \leq 1.0 \quad (4)$$

Combining eq 4 written for $j = a$ and $j = b$ with eq 3 gives

$$\Delta m_{\text{solv}} = M_{\text{solv}} c_{\text{solv},s} (K_{\text{solv},p,\text{Ox}}^* - K_{\text{solv},p,\text{Red}}^*) (b - a) \quad (5)$$

Equation 5 is a variation of eq 3; it expresses Δm_{solv} through solvent partition coefficients into totally oxidized and totally reduced EAP rather than through solvent partition coefficients for intermediate oxidation levels. Equation 5 also contains the term $(b - a)$ that directly reflects the partial redox process of an EAP. The end-to-end case is the limiting case where $b = 1$, $a = 0$, and the film has a constant volume of magnitude V .

2.1.2. Homogeneous (One) Phase Behavior. Next, we consider the case where only one EAP phase exists. If the EAP exhibits ideal behavior, the solvent partition coefficients and volumes vary linearly over the entire range of charge levels and eq 5 also applies in the one-phase case. In the case of nonideal behavior, the solvent partition coefficients and volumes will vary approximately linearly only between small differences in a and b and deviations from eq 5 will exist. Hence, for ideal behavior, eq 5 cannot distinguish between one- and two-phase behavior. However, if eq 5 does not describe the experimental results, this is a diagnostic that identifies nonideal one-phase film behavior.

2.2. Salt Transfer. We define the term “permselectivity index”, R , to quantify the extent of co-ion content in a bulk phase that has the characteristics of an ion exchanger. It is a quantity accessible experimentally from EQCM data obtained during charge injection into the system. An EAP is ideally permselective if it contains no co-ion regardless of its charge level or concentration of salt in the bathing solution. We note that ideal permselectivity can never be achieved under equilibrium conditions. Here, we use the term “permselective” to

represent a situation where the amount of co-ion in the EAP film is negligible for experimental purposes.

Suppose, in a *partial* redox process, $n_{\text{salt},j}$ equivalents of a co-ion enter the EAP phase under nonpermselective conditions. Next, we define n_{total} as the number of equivalents of counterion that could enter the EAP phase under permselective conditions in the end-to-end switching process.

Hence, R is given by eq 6:

$$R_j = n_{\text{salt},j}/n_{\text{total}} = [\text{C}_{\text{p},j}^+]/[\text{M}] = [\text{co-ions}]_j/[\text{counterions}]_{\text{infinite dilution}, j=1} \quad (6)$$

In terms of an EAP with a positively charged backbone, immersed in a 1:1 electrolyte (C^+A^-), $[\text{C}_{\text{p},j}^+]$ represents the concentration of cations in the film and $[\text{M}]$ denotes the concentration of EAP backbone charges (the film's charge density); the latter concentration corresponds to the concentration of anions in the EAP phase under permselective conditions. The last equality relates the concentrations of co-ions and counterions that correspond to the equivalents of these species in the bulk of the EAP. This definition is purely phenomenological and makes no assumptions about the nature of the charge distribution over sites within the EAP. Thus, our results are independent whether charges are associated with fixed redox sites (as in poly(vinylferrocene)) or delocalized (as in polypyrrole).

We seek a general expression describing the difference in permselective indices, $\Delta R_{b,a} = (R_b - R_a)$, that occurs when an EAP is switched between two oxidation levels, a and b . Just as we did for solvent transfer, we examine two possibilities, namely, that the film exists (1) as a mixture of oxidized and reduced phases, whose ratio changes during oxidation, and (2) as a single identifiable phase whose oxidation state changes over the redox switching process.

In both these situations, it proved impossible to find variables, such as K^* in eq 5, that eliminated the *explicit* appearance of variable volume terms from the final results. Thus, the final result in which these variable volume expressions are imbedded becomes algebraically complicated. Consequently, we will proceed first to discuss the constant volume situation. Then, we will suggest how to proceed when volume changes become significant.

2.2.1. Derivation of the Difference in Permselectivity Indices, $\Delta R_{b,a}$: Two-Phase Case. When two separate, fully oxidized and fully reduced phases exist within an EAP film, quite generally the concentrations of salt in these two phases may differ. These concentrations are determined by the salt partition equilibrium constants between each phase and the bathing solution and by the salt concentration of the solution. Consequently, the total amount of salt in the whole EAP film may change as the ratio of fully oxidized and fully reduced phases varies. Then, the number of moles of a salt in the EAP film in fractional oxidation state j (with j taking on values of either a or b) is

$$n_{\text{salt},j} = n_{\text{salt},\text{Ox},j} + n_{\text{salt},\text{Red},j} = [\text{X}_{\text{p},\text{Ox}}]V_{\text{p},\text{Ox},j} + [\text{X}_{\text{p},\text{Red}}]V_{\text{p},\text{Red},j} = (j[\text{X}_{\text{p},\text{Ox}}] + (1-j)[\text{X}_{\text{p},\text{Red}}])V_{\text{p},\text{T},j} \quad (7)$$

where "X" represents the co-ion (a cation, C^+ , for a positively charged EAP backbone or an anion, A^- , for a negatively charged EAP backbone), $V_{\text{p},\text{Ox},j}$ and $V_{\text{p},\text{Red},j}$ are volumes of the oxidized and reduced phases, and $V_{\text{p},\text{T},j}$ is the total volume of an EAP in the j oxidation level. Writing eq 7 for $j = b$ and $j = a$ and subtracting the two gives

$$\Delta n_{\text{salt}} = n_{\text{salt},b} - n_{\text{salt},a} = ([\text{X}_{\text{p},\text{Ox}}] - [\text{X}_{\text{p},\text{Red}}])(bV_{\text{p},\text{T},b} - aV_{\text{p},\text{T},a}) + [\text{X}_{\text{p},\text{Red}}](V_{\text{p},\text{T},b} - V_{\text{p},\text{T},a}) \quad (8)$$

The total volume of the EAP film at a given oxidation level, j , is a linear combination of the volumes of the oxidized and reduced phases:

$$V_{\text{p},\text{T},j} = V_{\text{p},\text{T},\text{Red}} + j(V_{\text{p},\text{T},\text{Ox}} - V_{\text{p},\text{T},\text{Red}}) \quad (9)$$

Combining the above with eq 8 gives the following expression for Δn_{salt} :

$$\Delta n_{\text{salt}} = (b-a)\{([\text{X}_{\text{p},\text{Ox}}] - [\text{X}_{\text{p},\text{Red}}])[V_{\text{p},\text{T},\text{Red}} + (b+a)(V_{\text{p},\text{T},\text{Ox}} - V_{\text{p},\text{T},\text{Red}})] + [\text{X}_{\text{p},\text{Red}}](V_{\text{p},\text{T},\text{Ox}} - V_{\text{p},\text{T},\text{Red}})\} \quad (10)$$

The simplest limiting case is the one of constant volume (independent of j) which yields eq 11 below. The second is the case when the EAP is switched in the redox process where b and a do not differ significantly and b is small. Other, algebraically complex, cases that yield the limiting equation exist. Consequently, we will, for convenience, consider only experiments that correspond to the limiting case of constant volume.

Now, assuming that the fully oxidized and reduced films have the same volume, V , then at the charge level j , we can write that $V_{\text{p},\text{Ox},j} = jV$ and $V_{\text{p},\text{Red},j} = (1-j)V$. Substituting the latter expressions into eq 10 yields

$$\Delta n_{\text{salt}} = n_{\text{salt},b} - n_{\text{salt},a} = (b-a)V([\text{X}_{\text{p},\text{Ox}}] - [\text{X}_{\text{p},\text{Red}}]) \quad (11)$$

Dividing eq 11 by V and counterion concentration, $[\text{M}]$, and combining with eq 6 yields

$$\Delta R_{b,a} = (b-a)\Delta R \quad (12)$$

ΔR (without subscripts) corresponds to the change of permselectivity properties of the film switched between fully oxidized (Ox, $b = 1.0$) and fully reduced (Red, $a = 0.0$) states, so $\Delta R = R_{\text{Ox}} - R_{\text{Red}} = \Delta R_{b=1.0;a=0.0} = \Delta R_{b,a}/(b-a)$.

The explicit expression for ΔR , given in eq 13, was derived previously⁹ using equilibrium constants for the salt partitioning processes and the electroneutrality rule for the EPA phase as the starting points.

$$\Delta R = R_{\text{Ox}} - R_{\text{Red}} = 0.5\{-|z| + |z - \nu| + (z^2 + 4S^2T_{\text{Ox}}^2)^{1/2} - [(z - \nu)^2 + 4\kappa S^2T_{\text{Ox}}^2]^{1/2}\} \quad (13)$$

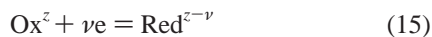
where z is the charge type of the EAP in its oxidized state, ν is the number of electrons exchanged in the redox process, and variables S and T_j are defined as follows: $S = c_{\text{salt}}/[\text{M}]$; $T_j = (K_{\text{salt},j})^{1/2}\gamma_{\pm,s}/\gamma_{\pm,p,j}$, where c_{salt} is the concentration of salt in the bathing solution and $K_{\text{salt},j}$ is a thermodynamic equilibrium constant for the partition of salt between solvent and an EAP film. The dimensionless variable κ is defined as follows:

$$\kappa = T_{\text{Red}}^2/T_{\text{Ox}}^2 = (K_{\text{salt},p,\text{Red}}/K_{\text{salt},p,\text{Ox}})(\gamma_{\pm,p,\text{Ox}}^2/\gamma_{\pm,p,\text{Red}}^2) = [\text{A}_{\text{p},\text{Red}}^-][\text{C}_{\text{p},\text{Red}}^+]/[\text{A}_{\text{p},\text{Ox}}^-][\text{C}_{\text{p},\text{Ox}}^+] \quad (14)$$

ΔR in eq 12 corresponds to the change in permselectivity properties of the EAP in the end-to-end redox process ($\Delta R_{\text{end-to-end}}$). Its value is always the same for a given EAP, at a given electrolyte concentration. Thus, plots of $\Delta R_{b,a}/(b-a)$

$= (R_{\text{Ox}} - R_{\text{Red}}) = \Delta R_{\text{end-to-end}}$ vs $\log(ST_{\text{Ox}})$ will all superimpose for every value of $(b - a)$. This behavior is diagnostic for the limiting two-phase cases with negligible volume changes and is illustrated by curves marked as $\bullet\text{---}\bullet$ in Figures 1–5 (compare with the one-phase behavior below).

2.2.2. Derivation of the Difference in Permselectivity Indices, $\Delta R_{b,a}$: One-Phase Case, EAP Film's Volume is Constant. The derivation for a one-phase case of partial charge transfer at a constant volume is analogous to the end-to-end case. The simplified form of the redox reaction can be represented by



where Ox and Red represent an oxidized and a reduced region in the EAP film, respectively, while z and $(z - \nu)$ denote their charges (including the sign). Equation 15 has been simplified by not showing counterions or solvent and salt in the film and in the bathing solution. Depending on the EAP, a region can consist of one or more monomer units, as for poly(vinylferrocene) or polypyrrole, respectively.

It is convenient to consider one kind of EAP and bathing solution system. Here, with no loss in generality, we choose an EAP whose “backbone” is cationic and a bathing solution that contains a salt C^+A^- . The electroneutrality rule for the partially reduced EAP has the following form

$$z[\text{M}_j^z] + (z - \nu)[\text{M}_j^{z-\nu}] + [\text{C}_{p,j}^+] = [\text{A}_{p,j}^-] \quad (16)$$

$[\text{M}_j^z]$ and $[\text{M}_j^{z-\nu}]$ are concentrations of oxidized and reduced sites (or regions), respectively. $[\text{M}_j^z] + [\text{M}_j^{z-\nu}] = [\text{M}]$, where $[\text{M}]$ is defined in eq 6. The following ratios between $[\text{M}_j^z]$, $[\text{M}_j^{z-\nu}]$, and $[\text{M}]$ exist:

$$[\text{M}_j^z]/[\text{M}] = j \quad \text{and} \quad [\text{M}_j^{z-\nu}]/[\text{M}] = 1 - j \quad (17)$$

The symbol j designates the oxidation level, thus $(1 - j)$ indicates the reduction level of the EAP.

Combining eqs 16 and 17 gives

$$(z - \nu(1 - j))[\text{M}] + [\text{C}_{p,j}^+] = [\text{A}_{p,j}^-] \quad (18)$$

Equation 19 was obtained by combining eq 18 with the expression for the salt partition coefficient to eliminate the counterion concentration, dividing the resulting expression by $[\text{M}]^2$, and introducing variables S and T_j (already defined after eq 13). An analogous procedure was used previously⁹ to obtain the expressions for R_{Ox} and R_{Red} in the end-to-end case.

$$R_j = 0.5\{-j|z| - (1 - j)|z - \nu| + [(j|z| + (1 - j)|z - \nu|)^2 + 4S^2T_j^2]^{1/2}\} \quad (19)$$

This relation describes the permselectivity index R_j of an EAP in any oxidation level j . The difference in permselectivity indices for the EAP in two different oxidation levels a and b is given by

$$\Delta R_{b,a} = R_b - R_a = 0.5\{\pm\nu(b - a) + [(z - \nu(1 - b))^2 + 4S^2T_b^2]^{1/2} - [(z - \nu(1 - a))^2 + 4S^2T_a^2]^{1/2}\} \quad (20)$$

The sign in front of the term “ $\pm\nu(b - a)$ ” depends on the charge type of the EAP. It is “+” for anionic cases ($\text{Ox}^{[z]-}/\text{Red}^{([z]-\nu)-}$, where $|z| \geq 0$) and “−” for cationic cases ($\text{Ox}^{[z]+}/\text{Red}^{([z]-\nu)+}$, where $|z| > 0$ and $\nu \leq |z|$). $\Delta R_{b,a}$ is a function of six variables,

i.e., ν , a , b , z , ST_a , and ST_b , of which a and b are controlled experimentally, while z and ν are determined by the system. Also, because ST_a and ST_b depend on both the volume of the EAP film and the salt partition coefficients for the a or b oxidation level, we use a graphical presentation to illustrate the effect of each of the variables (section 3).

We note that for the two-phase case the partition coefficient of a salt between the solvent and the EAP film is a linear combination of thermodynamic partition coefficients of the oxidized and reduced forms of the EAP. Consequently, the thermodynamic quantity that describes the partition of salt, $K_{\text{salt},p,j}$, changes exactly linearly with the oxidation level, j , eq 21:

$$K_{\text{salt},p,j} = K_{\text{salt},p,\text{Red}} + j(K_{\text{salt},p,\text{Ox}} - K_{\text{salt},p,\text{Red}}) \quad \text{where } j = a \text{ or } b \quad (21)$$

We also assume that this expression holds for the one-phase case. This assumption is equivalent to postulating that a mean activity coefficient of salt in the EAP film is a linear function of j . As a consequence, a similar expression for T_j^2 , which is proportional to $K_{\text{salt},p,j}$, can be written (see explanation of terms in eq 13)

$$T_j^2 = T_{\text{Red}}^2 + j(T_{\text{Ox}}^2 - T_{\text{Red}}^2) \quad (22)$$

Combining eqs 22 and 14 (definition of κ) with expression 20 yields $\Delta R_{b,a}$ as a function of dimensionless variables a , b , κ , ν , z , and ST_{Ox} (eq 23).

$$\Delta R_{b,a} = R_b - R_a = 0.5\{\pm\nu(b - a) + [(z - \nu(1 - b))^2 + 4S^2T_{\text{Ox}}^2(\kappa + b(1 - \kappa))]^{1/2} - [(z - \nu(1 - a))^2 + 4S^2T_{\text{Ox}}^2(\kappa + a(1 - \kappa))]^{1/2}\} \quad (23)$$

Equation 23 provides a novel way to extract quantitative data relevant to a variety of physicochemical applications. The ability to better characterize materials used in these applications can lead to their improved and wider utility. Among characteristics accessible via eq 23 are phase behavior of an EAP, the concentration salt partition coefficient as a function of charge level, and the number of electrons transferred in the redox process. Equation 13 discussed earlier is a limiting case of eq 23 and can be obtained from eq 23 by setting $a = 0.0$ and $b = 1.0$, $R_{b=1} = R_{\text{Ox}}$ and $R_{a=0} = R_{\text{Red}}$.

3. Discussion

3.1. Characterization of $\Delta R_{b,a}/(b - a)$ vs $\log(ST_{\text{Ox}})$ Plots for an $\text{Ox}^+/\text{Red}^\circ$ Type EAP. Plotting $\Delta R_{b,a}/(b - a)$ provides a convenient way to compare and distinguish one- and two-phase case behaviors of an EAP. Relationship 23 written for the $\text{Ox}^+/\text{Red}^\circ$ type EAP ($z = 1$; $\nu = 1$) and divided by $(b - a)$ takes the following form:

$$\Delta R_{b,a}/(b - a) = 0.5/(b - a) \times \{- (b - a) + [b^2 + 4S^2T_{\text{Ox}}^2(\kappa + b(1 - \kappa))]^{1/2} - [a^2 + 4S^2T_{\text{Ox}}^2(\kappa + a(1 - \kappa))]^{1/2}\} \quad (24)$$

where κ represents the ratio of the concentration partition coefficient of the electrolyte species from solution to the totally oxidized and totally reduced EAP films (see eq 14).

Plots of $\Delta R_{b,a}/(b - a)$ vs $\log(ST_{\text{Ox}})$ derived from eq 24 are shown in Figures 1–4 for various representative values of κ and $(b - a)$. They illustrate the characteristic features of $\Delta R_{b,a}$

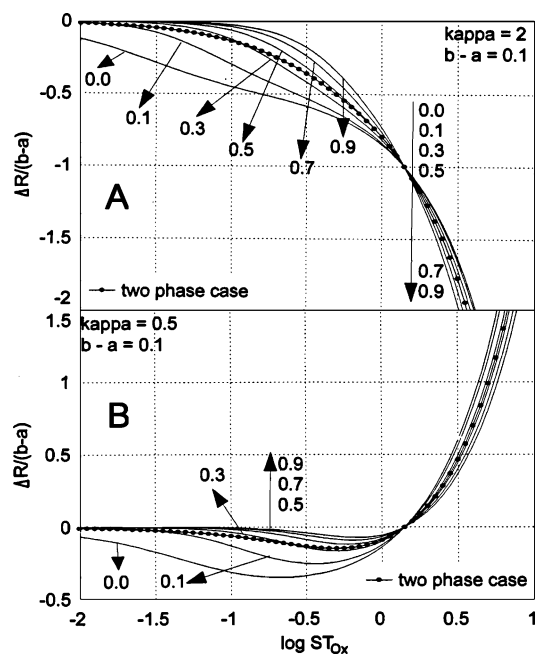


Figure 1. $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ in a partial redox switching of an Ox^+/Red^0 type EAP at constant $(b-a) = 0.1$ for κ values = 2.0 (A) and 0.5 (B). The numbers adjacent to smooth curves, representing one-phase behavior, indicate the starting oxidation level (a value). The line marked as $-\bullet-\bullet-$ illustrates two-phase case behavior (for all values of $(b-a)$) and also the end-to-end case for both one- and two-phase behavior.

as a function of $\log(ST_{Ox})$. We note that in all our figures the abscissa covers a 1000-fold concentration range of salt in the bathing solution; this will broadly span the range from a few millimolar to a few molar. The absolute value of salt concentration depends on the salt partition coefficient, activity coefficients of salt between solvent and polymer phases, and $[M]$ as defined above in section 2.2. In all figures, a curve representing the two-phase case behavior is denoted as $-\bullet-\bullet-$. This curve also represents the end-to-end case. It depends only on κ and, thus, serves as a convenient guide/reference line for all plots made for the same κ . The fact that only the two-phase plots superimpose for all values of $(b-a)$ at fixed κ immediately distinguishes between the one- and two-phase cases. When the EAP film has a volume that is independent of charge level and salt content, these curves provide a simple diagnostic tool to identify the various equilibrium parameters. We note that all the curves shown in Figures 1, 3, and 4 intersect with each other at one common point; however, the curves shown in Figure 2 do not intersect anywhere with each other. The presence of common intersection points is shown below using (24) and also in the appendix by means of another approach. After the distinction between one- and two-phase behavior has been established, a nonlinear least-squares approach could be used to estimate volume changes when our experimental conditions no longer permit the constant volume approximation.

3.1.1. Effect of κ at $(b-a) = \text{Constant}$. Figures 1 and 2 illustrate the behavior of an Ox^+/Red^0 type EAP film at a constant $(b-a) = 0.1$ for κ values = 2.0 (Figure 1A), 0.5 (Figure 1B), 1.0 (Figure 2A), and 0.0 (Figure 2B). Each panel contains plots of $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ for the same set of values of the initial oxidation level, a (0.0, 0.1, 0.3, 0.5, 0.7, and 0.9, as indicated next to each curve).

$\Delta R_{b,a}/(b-a)$ curves plotted for $\kappa \geq 1.0$ (Figures 1A and 2A) are decreasing functions of ST_{Ox} . They exhibit a minimum when $0.0 < \kappa < 1$ (Figure 1B) and are increasing functions of ST_{Ox} when $\kappa = 0.0$ (Figure 2B).

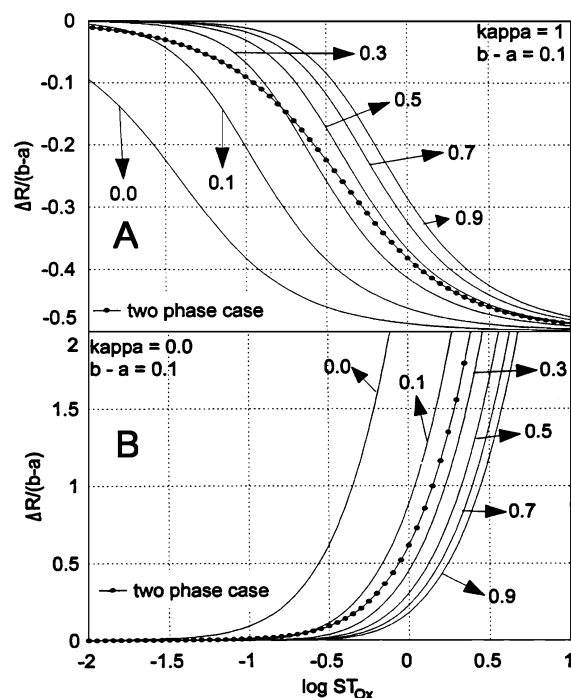


Figure 2. $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ in a partial redox switching of an Ox^+/Red^0 type EAP at constant $(b-a) = 0.1$ for κ values = 1.0 (A) and 0.0 (B). The numbers adjacent to smooth curves, representing one-phase behavior, indicate the starting oxidation level (a value). The line marked as $-\bullet-\bullet-$ illustrates two-phase case behavior (for all values of $(b-a)$) and also the end-to-end case for both one- and two-phase behavior. The y-axis scale in part A is different than that in part B.

A characteristic feature of all plots with a constant κ ($\kappa \neq 1.0$ and $\kappa \neq 0.0$) is the existence of a common intersection point for all the curves, including the “two-phase case” curve. After an intersection point in plots with constant $(b-a)$, the curves are closer to each other than before it. The latter feature in these plots shows that the higher the salt concentration, the smaller the difference between permselectivity indices of the more oxidized (R_b) and less oxidized (R_a) forms of the EAP. This feature is more obvious as the κ value approaches 1 (not shown for brevity).

The origin of the intersection point and relations between $\Delta R_{b,a}/(b-a)$ values, κ values, and ion concentrations at intersection points for all cationic and anionic EAPs are discussed in the Appendix (section A-2)

The ordinate at the intersection point for a “+1/0” charge type EAP can have only the following values, either -1.0 (for $\kappa > 1.0$, e.g., $\kappa = 2.0$, Figure 1A) or 0.0 (for $0.0 < \kappa < 1.0$, e.g., $\kappa = 0.5$, Figure 1B). Although not shown, the abscissa of the intersection point changes with κ ; for $\kappa > 1.0$, it increases when κ decreases, and for $0.0 < \kappa < 1.0$, it decreases with a decrease of κ . It is noteworthy that the ST_{Ox} value at the intersection point is the same for pairs of κ 's which are the reciprocal of each other (compare Figure 1A and B for $\kappa = 2$ and $\kappa = 0.5$, respectively). This property emerges from eq 24, which can be manipulated, after setting the value of $\Delta R_{b,a}/(b-a) = 0.0$ or -1 , to yield

$$ST_{Ox} = \kappa^{1/2}/(1-\kappa) \equiv \kappa^{-1/2}/(\kappa^{-1}-1) \quad (25)$$

Equation 25 is independent of $(b-a)$ and only positive values of ST_{Ox} have a physical meaning. One can see that, for instance, by comparing intersection point coordinates in Figure 3A and B ($\kappa = 2$, $(b-a) = 0.1$ and $\kappa = 2$, $(b-a) = 0.7$, respectively)

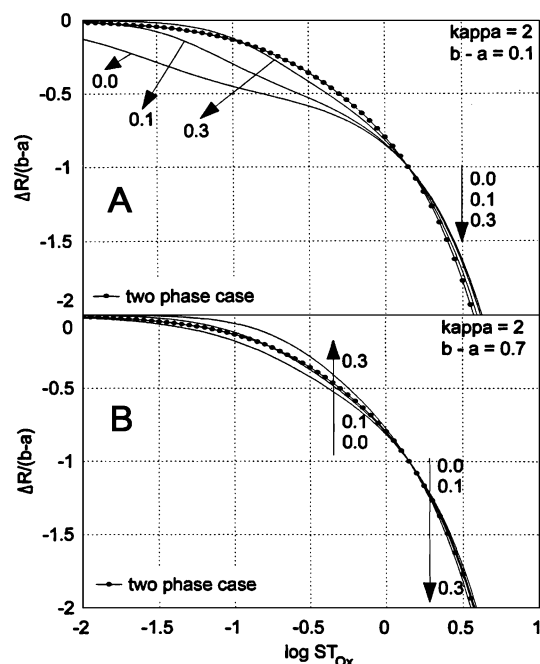


Figure 3. $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ in a partial redox switching of an Ox^+/Red° type EAP for $\kappa = 2.0$ and $(b-a)$ values equal to 0.1 (A) and 0.7 (B). The numbers adjacent to smooth curves, representing one-phase behavior, indicate the starting oxidation level (a value). The line marked as $-\bullet-\bullet-$ illustrates two-phase case behavior (for all values of $(b-a)$) and also the end-to-end case.

where $\log(ST_{Ox})$ at the intersection point is the same and equal to 0.15. Similar observations hold for other values of κ , not shown here. The abscissa's value at the intersection point in an experimental set of curves can serve as a useful tool to estimate a κ value.

In two limiting cases, there is no intersection point. These are (1) $\kappa = 1.0$, i.e., equal salt partition constants exist in the reduced and oxidized EAP form (Figure 2A), or (2) $\kappa = 0.0$, i.e., no salt exists in the reduced EAP form (Figure 2B). These plots originate from the same common point, $\log(ST_{Ox}) = -\infty$ and $\Delta R_{b,a}/(b-a) = 0.0$. These two cases are easily distinguishable from the shapes of the plots.

3.1.2. Effect of $(b-a)$: $\kappa = \text{Constant}$. We discuss now various characteristics of the plots in Figures 3 and 4, of $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ that are diagnostic of one- and two-phase behavior. Figure 3 illustrates how changing $(b-a)$ alters plots generated for the same value of κ . In other words, how $\Delta R_{b,a}/(b-a)$ depends on the difference in oxidation levels of the two EAP states assuming that the ratio of salt partition coefficients between the bathing solution and these two states remains constant. We chose $\kappa = 2$ with values of $(b-a) = 0.1$ and 0.7 as examples (Figure 3A and B). Since values of a must lie in the range $0 \leq a \leq (1-b)$, we decided to make plots for $a = 0.0, 0.1$, and 0.3.

The intersection point separates the abscissa in Figure 3A and B into two regions where $\Delta R_{b,a}/(b-a)$ curves behave differently. As $(b-a)$ changes from 0.1 in Figure 3A to 0.7 in Figure 3B, curves corresponding to different a values shift differently with respect to each other and to the "two-phase case curve". The visible result is that curves plotted for the larger $(b-a)$ value are closer to each other and to the end-to-end curve; thus, it is more difficult to distinguish the curves with different a values from each other. This is intuitively understandable since for an end-to-end process $(b-a) = 1$, so the

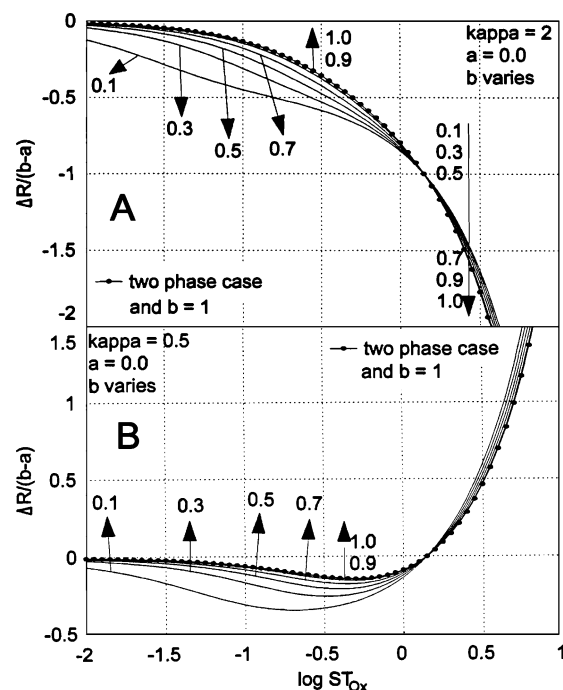


Figure 4. $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ in a partial redox switching of an Ox^+/Red° type EAP for $a = 0.0$ and κ values equal to 2.0 (A) and 0.5 (B). The numbers adjacent to smooth curves, representing one-phase behavior, indicate the final oxidation level (b value). The line marked as $-\bullet-\bullet-$ illustrates two-phase case behavior (for all values of $(b-a)$) and also the end-to-end case ($b = 1.0$).

closer a given $(b-a)$ is to 1, the more the system will resemble an end-to-end process. Thus, using smaller values of $(b-a)$ will be more informative.

Analogous observations can be made for plots with other κ values. Curves with various a values fall on both sides of the end-to-end curve, and the bigger $(b-a)$ value, the closer the curves lie to each other.

Figure 4A and B show $\Delta R_{b,a}/(b-a)$ as a function of $\log(ST_{Ox})$ during partial redox switching of an Ox^+/Red° type of EAP with $\kappa = 2$ and $\kappa = 0.5$, respectively. Both graphs are plotted for a totally reduced EAP as the starting level, i.e., $a = 0.0$. We show curves for varying $(b-a)$ (effectively b varies, since $a = 0.0$). Before the intersection point, all curves lie below the "two-phase case line", and after the intersection point, they are above it.

For $a > 0.0$ (i.e., partially oxidized starting states), with reference to the intersection point (see Figures 1 and 3), the curves fall on both sides of the two-phase curve. Similar behavior is observed for all values of κ other than 0 or 1. However, a family of curves, not shown, for $\kappa = 1.0$, $a = 0.0$, and various $(b-a)$ values falls to the right of the two-phase case line, while if $\kappa = 0.0$, they fall to the left of it. These two curve families have no intersection points.

3.2. Characterization of $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ Plots for Cationic and Anionic Types of EAPs. Table 1 lists examples of EAPs with several anionic and cationic charge types whose behavior we have chosen to examine. As seen in Figure 5A and B, plots of $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ for these EAPs exhibit similar general features to the ones observed for the Ox^+/Red° type of EAP, discussed in detail in section 3.1. In these plots, an intersection point exists as it does in other cases listed, but not shown, in Table 1. The intersection point coordinates are given in columns five and six of Table 1. These results demonstrate a correlation between the parameters of the

TABLE 1: Relationships between Various Properties for Anionic and Cationic Types of EAPs

EAP type	z	n	κ	$\log(ST_{Ox})^a$	$\Delta R_{b,a}/(b-a)^b$	ordinate values for EAPs of various types
Ox ⁺ /Red ^o (cationic)	1	1	0.5	0.150	0.0	cationic EAPs $\Delta R_{b,a}/(b-a) = 0.0$ for $\kappa < 1.0$ $\Delta R_{b,a}/(b-a) = -\nu$ for $\kappa > 1.0$
Ox ²⁺ /Red ^o (cationic)	2	2	0.5	0.451	0.0	
Ox ³⁺ /Red ⁺ (cationic)	3	2	0.5	0.301	0.0	
			2.0	0.500	-2.0	
Ox ^o /Red ⁻ (anionic)	0	1	0.5	0.301	1.0	anionic EAPs $\Delta R_{b,a}/(b-a) = 0.0$ for $\kappa > 1.0$ $\Delta R_{b,a}/(b-a) = +\nu$ for $\kappa < 1.0$
Ox ¹⁻ /Red ³⁻ (anionic)	-1	2	0.5	0.650	2.0	
			2.0	0.150	0.0	

^a Values of $\log(ST_{Ox})$ according to eq 26 at the common intersection point of the curves defined by the content in columns 1–4. ^b Values of $\Delta R_{b,a}/(b-a)$ at intersection points corresponding to the value of κ appearing in eq 26.

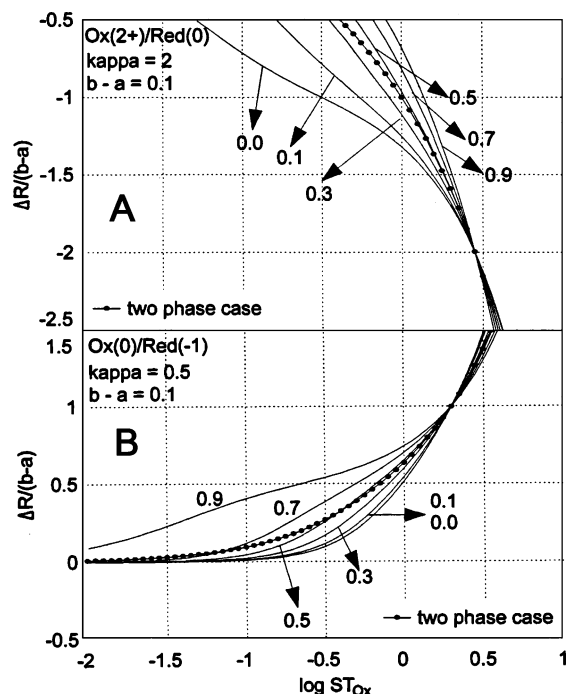


Figure 5. $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ in a partial redox switching of an Ox²⁺/Red^o type EAP with $\kappa = 2.0$ (A) and an Ox^o/Red⁻¹ type EAP with $\kappa = 0.5$ (B) for $(b-a) = 0.1$. The numbers adjacent to smooth curves, representing one-phase behavior, indicate the starting oxidation level (a value). The line marked as $-\bullet-\bullet-$ illustrates two-phase case behavior (for all values of $(b-a)$) and also the end-to-end case.

intersection point and the number of electrons transferred in the redox reaction of the EAP.

Inserting $\Delta R_{b,a}/(b-a) = 0.0$ or $\pm\nu$ into eq 23 yields values of ST_{Ox} at the intersection point. The significance of these results in terms of co-ion and counterion concentrations is given in the Appendix (section A-2).

Associated with the intersection point values of $\Delta R_{b,a}/(b-a)$ is the following expression for the corresponding abscissa:

$$(ST_{Ox})^2 = [z\nu(\kappa - 1) + \nu^2]/(1 - \kappa)^2 \quad (26)$$

This expression was used to calculate $\log(ST_{Ox})$ values at the intersection points listed in Table 1.

In the specific cases where $z = \nu$, eq 26 takes the following form:

$$(ST_{Ox})^2 = \nu^2\kappa/(1 - \kappa)^2 = \nu^2\kappa^{-1}(\kappa^{-1} - 1)^2 \quad (27)$$

Equation 27 shows that the same (ST_{Ox}) value is obtained for κ

and for its reciprocal, κ^{-1} , as seen in Table 1 for cases where $z = \nu$ (first two lines in Table 1). This property was discussed above (section 3.1.1) for the Ox⁺/Red^o type of EAP, where $z = \nu = 1$.

Relationships between the number of electrons involved in the redox process, charge type of the EAP, κ value, and coordinates of the intersection point for EAPs with specific charge types are given in columns 1–6 in Table 1. The last column in Table 1 gives the pattern for intersection point values of $\Delta R_{b,a}/(b-a)$ for EAPs with anionic and cationic charge types.

4. Diagnostic Features of $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ Plots

In the following discussion of diagnostics, it is important to recognize that equilibrium is required but EAP systems may be slow to reach it. To establish that equilibrium has been reached, in addition to waiting until the system no longer changes with time, the technique of approaching equilibrium from more than one direction should be used. For example, one may switch the charge level by going from level b to a and, then, from a to b and reach a chosen electrolyte concentration in the bathing solution by changing it from above and also from below.

The results of our approach are concentration equilibrium constants at particular concentrations of electrolyte in the bathing solution. True thermodynamic constants could be obtained by the extrapolation of the appropriate activity coefficient functions to zero electrolyte concentration.

4.1. Phase Behavior. The theoretical behavior discussed above may serve as a novel diagnostic tool allowing one to distinguish between one- and two-phase behavior of the EAP. Few other techniques can do this under dynamic conditions; the chronopotentiometric study of PVF films by Murray is one example.¹⁸

According to our model, in the charge regions where two distinct phases exist, experimental $\Delta R_{b,a}/(b-a)$ vs $\log(ST_{Ox})$ results obtained for various $(b-a)$ values will give just one curve. On the other hand, in the charge regions where only one phase exists, a whole family of curves will be seen.

4.2. Values of κ and ν . The parameter κ is an important constant characteristic for a given EAP–electrolyte couple. Upon changing electrolyte, quite generally, κ may change as well.

Previously, we discussed the diagnostic properties obtained from the theoretical curves for the end-to-end switching of a redox EAP. There, on the basis of the comparison of experimental data with the shape of the theoretical curve, only qualitative information about κ could be obtained. For example, a decreasing ΔR vs $\log(ST_{Ox})$ dependence indicated that $\kappa \geq$

1.0. Finer distinctions based on the effect of κ on ΔR vs $\log(ST_{\text{Ox}})$ plots were problematic. However, experiments involving partial redox switching produce an intersection point that characterizes κ and ν .

Theoretical results presented in Figures 1, 3, 4, and 5 suggest experiments that could be used to optimize the estimation of the numerical value of κ . We note that, in order to utilize our theoretical results, accurate and precise frequency QCM measurements are needed and are feasible under well-controlled experimental conditions. Two types of experiments are possible. The first corresponds to varying the a value while holding the value of $(b - a)$ constant, i.e., starting with different initial oxidation levels of an EAP and then oxidizing the film with the same amount of charge (Figures 1, 3, and 5). In the other type of experiment, one would start with the same initial oxidation level (e.g., fully reduced, $a = 0.0$) and inject different amounts of charge. This experiment corresponds to the same, constant value of $a = 0.0$ and varying $(b - a)$ (Figure 4). Visual comparison between experimental data and theoretical curves will allow estimation of various parameters characterizing the EAP, such as ν (from the ordinate at the intersection point), κ (from the abscissa at the intersection point), and T_{Red} . Then, these values would be used as a starting values in the nonlinear least-squares procedure for conditions where the constant volume approximation does not apply.

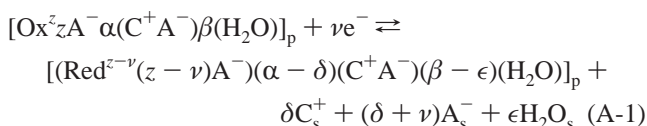
5. Conclusions

Theoretical analysis of the equilibrium model quantitatively characterizes the behavior of electroactive polymer (EAP) films during partial redox processes under permselective and nonpermselective conditions. The model relates amounts of mobile species (solvent, counterion, and salt) transferred during the redox process with thermodynamic properties of the system and considers volume changes associated with the oxidation level and the nonpermselective behavior of the EAP. The calculated changes in population of mobile species may be correlated with the response of any appropriately sensitive and selective population probe including but not restricted to gravimetric, spectroscopic, and optical techniques. The results give a powerful diagnostic tool to distinguish between one- and two-phase behavior of the EAP. They also allow one to estimate parameters characterizing the EAP–electrolyte system, such as the ratio of the partition coefficients of salt between the bathing electrolyte solution and EAP phase and the number of electrons transferred in the redox reaction. Quite generally, these parameters are important to a large number of fundamental and practical chemical situations.

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Appendix

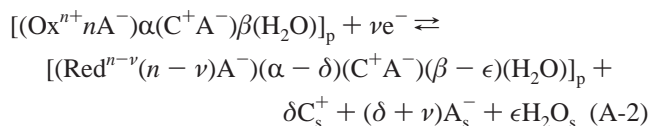
A-1. General Redox Reactions. The switching of an electroactive polymer immersed in a bathing solution containing a 1:1 electrolyte (C^+A^-) can be represented by the following equation:



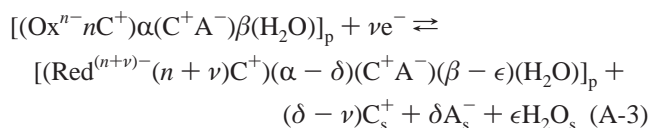
Equation A-1 describes five possible cases involving: (1) two

cationic polymer species, (2) two anionic species, (3) one cationic and one uncharged species, (4) one anionic and one uncharged species, and finally (5) one cationic and one anionic species. These five processes are encompassed by the following three redox equations:

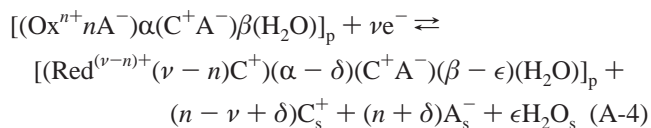
(1) cationic oxidized (Ox) \rightarrow cationic ($\nu < n$) or uncharged ($\nu = n$) reduced (Red):



(2) anionic or uncharged ($n = 0$) oxidized (Ox) \rightarrow anionic reduced (Red):



(3) cationic oxidized (Ox) \rightarrow anionic reduced (Red), ($\nu > n$):



In eqs A-1 to A-4, the subscripts designate the polymer (p) and solution (s) phases. The coefficients α , β , δ , and ϵ can be of either sign or equal to 0 and are not necessarily integer numbers.¹⁰ Equations A-1 to A-4 represent the overall redox process. Many possible paths exist by which the final state is reached. These equations do not attempt to describe these paths, i.e., they are not mechanisms; they describe the starting and finishing global equilibrium states.

Solvent and salt can enter the oxidized (Ox) or reduced (Red) forms of the polymer or both. We seek a solution to the equilibrium problem in a form that relates the experimentally accessible values (mass and charge changes) with thermodynamic quantities (equilibrium constants and salt activities).

A-2. Interrelations between $\Delta R_{b,a}/(b-a)$ Values, κ Values, and Ion Concentrations at Intersection Points. We show below that the existence of the intersection points is a property emerging from the rule of electroneutrality. Furthermore, intersection points occur at unique salt concentrations where the difference in equilibrium concentrations of co-ions or counterions is independent of charge level. If the concentration of co-ions does not vary with charge level, $\Delta R_{b,a}/(b-a) = 0$, while if the concentration of counterions does not vary with charge level, $\Delta R_{b,a}/(b-a) = \pm\nu$. This holds for EAPs of all charge types where $+\nu$ applies to anionic EAPs and $-\nu$ to cationic EAPs. The values of $\Delta R_{b,a}/(b-a)$ at the intersection point depend on ranges of κ that are characteristic for the EAP charge type and are given in the last column of Table 1.

A-2.1. Cationic EAP. The electroneutrality rule for an EAP with a positively charged backbone is given in eq 18. Using eq 18 to obtain $\Delta R_{b,a}/(b-a)$ when $j = b$ or $j = a$ yields

$$\Delta R_{b,a}/(b-a) = ([\text{C}_{p,b}^+] - [\text{C}_{p,a}^+])/[\text{M}](b-a) = ([\text{A}_{p,b}^-] - [\text{A}_{p,a}^-])/[\text{M}](b-a) - \nu \quad (\text{A-5})$$

The characteristic property of the plots in Figures 1, 3, 4, and 5 is that all curves generated by changing a and b at constant

κ intersect at a common abscissa corresponding to the particular salt concentration. Note that the abscissa in Figures 1–5, $\log(ST_{\text{Ox}})$, consists of salt concentration (c_{salt}) divided by $[M]$ and multiplied by the partition coefficient and ratio of activity coefficients (see eq 13).

We see in section 3.2 that, associated with a $\log(ST_{\text{Ox}})$ value at the intersection point, there are two values of $\Delta R_{b,a}/(b-a)$. The formulation A-5 gives the chemical significance of the intersection points. When (1) $\Delta R_{b,a}/(b-a) = 0$, the difference in co-ion concentration is zero, and when (2) $\Delta R_{b,a}/(b-a) = -\nu$, the difference in counterion concentration is zero. The values of κ (eq 14) determine the values of $\Delta R_{b,a}/(b-a)$ at the intersection point.

A-2.1.1. Determining the Range of κ Values That Yield $\Delta R_{b,a}/(b-a) = 0$. The EAP with charge levels b and a have corresponding “apparent” salt partition coefficients, $K_{p,b}$ and $K_{p,a}$. Elimination of $[A_{p,b}^-]$ and $[A_{p,a}^-]$ from eq A-5 by making use of the salt partition concentration constant and taking into account that for $\Delta R_{b,a}/(b-a) = 0$, by definition, $[C_{p,b}^+] = [C_{p,a}^+] = [C_p^+]$ gives

$$T_b^2 - T_a^2 = \nu[M](b-a)[C_p^+]/c_{\text{salt}}^2 \quad (\text{A-6})$$

Using eq 21 and the definition of κ (eq 14) with eq A-6 yields

$$1 - \kappa = \nu[M][C_p^+]/K_{\text{Ox}}c_{\text{salt}}^2 \quad (\text{A-7})$$

Since the right-hand side (rhs) of eq A-7 is always greater than zero, thus, $\kappa < 1$. Consequently, at the intersection point, for a positively charged EAP, when $\kappa < 1$, the ordinate value, $\Delta R_{b,a}/(b-a) = 0$.

A-2.1.2. Determining the Range of κ Values That Yield $\Delta R_{b,a}/(b-a) = -\nu$. The starting point in this derivation is given in eq A-5. If we assume that $\Delta R_{b,a}/(b-a) = -\nu$, then from eq A-5

$$([A_{p,b}^-] - [A_{p,a}^-])/[M](b-a) = 0 \quad (\text{A-8})$$

Next, we eliminate $[C_{p,b}^+]$ and $[C_{p,a}^+]$ present in eq A-5 by making use of the salt partition constant, take into account that $[A_{p,b}^-] = [A_{p,a}^-] = [A_p^-]$, and combine with eq 21 and the definition of κ (eq 14) to obtain

$$1 - \kappa = -\nu[M][A_p^-]/K_{\text{Ox}}c_{\text{salt}}^2 \quad (\text{A-9})$$

Since the rhs of eq A-9 is always smaller than zero, $\kappa > 1$. Consequently, for a positively charged EAP, when $\kappa > 1$, the ordinate value $\Delta R_{b,a}/(b-a) = -\nu$.

A-2.2. Anionic EAP. Analogous to the approach used for cationic EAPs, considerations for anionic EAP lead to the following expression for $\Delta R_{b,a}/(b-a)$,

$$\Delta R_{b,a}/(b-a) = ([A_{p,b}^-] - [A_{p,a}^-])/[M](b-a) = ([C_{p,b}^+] - [C_{p,a}^+])/[M](b-a) + \nu \quad (\text{A-10})$$

and to the values of $\Delta R_{b,a}/(b-a)$ at the intersection point, depending on the range of κ . When the co-ion concentration is constant, $\kappa > 1$ and $\Delta R_{b,a}/(b-a) \equiv 0$, and when the counterion concentration is constant, $\kappa < 1$ and $\Delta R_{b,a}/(b-a) = +\nu$.

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