

## ARTICLES

## Mechanism of Actuation in Conducting Polymers: Osmotic Expansion

Lasse Bay,\* Torben Jacobsen, and Steen Skaarup

Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

Keld West

Danish Polymer Centre, Risø National Laboratory, DK-4000 Roskilde, Denmark

Received: October 20, 2000; In Final Form: April 13, 2001

Conducting polymers expand or contract when their redox state is changed. This expansion/contraction effect can be separated in an intrinsic part because of changes of the polymer backbone on reduction/oxidation and a part depending on the surrounding electrolyte phase, because of osmotic expansion of the polymer phase. The osmotic effect causes solvent molecules to move into the polymer in a number far in excess of those bound strongly in the solvation shell of the mobile ion, resulting in large volume changes. In this paper, a thermodynamic description of the osmotic expansion is worked out. The model is compared with measurements on PPy(DBS) films. The experiments show that the expansion decreases as the electrolyte concentration is increased. This means that a considerable part of the total expansion is due to the osmotic effect. The osmotic effect should be taken into account when interpreting and designing actuator experiments and when comparing experimental results from different sources.

## Introduction

The reversible oxidation and reduction, or “switching”, of conducting polymers can be associated with considerable changes in dimensions of the polymer.<sup>1–4</sup> This effect is being actively investigated as the basis for a new generation of soft actuators—“artificial muscles”.<sup>5,6</sup>

Different mechanisms have been proposed to account for the volume changes occurring during redox cycling of conducting polymers. Changes in the charge density on the backbone are known to change the length of the carbon–carbon bonds in the polymer backbone.<sup>7</sup> This effect has also been utilized in carbon nanotube actuators, where a capacitive charging of a sheet of single-walled nanotubes may change the linear dimensions of the sheet by up to 1% in aqueous electrolytes within a 1 V operation range and even more in nonaqueous electrolytes.<sup>8</sup> Changes in charge density may also lead to changes in the conformation of the polymer. These mechanisms are the intrinsic part of the volume change.

Although the ions that balance the charge on the polymer are believed to move in the “free volume” in the polymer matrix, these systems are fairly dense, and changes in the ion concentration will change the volume of the polymer. This effect may be augmented by solvent molecules moving in and out of the polymer matrix in response to changes in the ionic content. The force driving solvent movement is the change in water activity following changes in the ionic composition inside the polymer. This is analogous to the effect that generates an osmotic pressure difference between two solutions of different concentrations

separated by a semipermeable membrane. Because of this parallelism, the volume change associated with the movement of solvent is here coined *osmotic expansion*.

The total volume change of a conducting polymer during redox switching can be divided into a part stemming from osmotic expansion and an intrinsic part driven by the changes in bond lengths and conformation in the polymer backbone. The aim of the present paper is to examine the thermodynamics of the volume change of conducting polymers and to give experimental evidence for the existence of osmotic expansion as an important mechanism for a typical conducting polymer actuator system, polypyrrole (PPy) doped with dodecylbenzene sulfonate (DBS).

## Experimental Section

Free-standing PPy(DBS) films are made by constant current oxidative polymerization on a polished stainless steel electrode. The synthesis electrolyte is 0.05 M in both pyrrole and sodium dodecylbenzene sulfonate (NaDBS) and the current density is 1 mA cm<sup>-2</sup>. Experiments have shown that deposition of 0.16 C cm<sup>-2</sup> forms a layer thickness of 1 μm. The free-standing films studied here are all 10 μm thick (1.6 C cm<sup>-2</sup>). The linear length change and the elastic modulus of PPy(DBS) strips are determined in a force-displacement setup. This consists of a high precision micrometer translation stage from Physik Instrumente, a micro-balance, a potentiostat, and an electrochemical cell which is fixed to the moving parts of the translation stage. The setup is fully software automated. A feedback routine, based on the balance readings, allows for position control to maintain constant force on the film during length changes while it is redox cycled. Here, a constant load of 0.6 MPa is used. The force-

\* To whom correspondence should be addressed. E-mail: lb@kemi.dtu.dk. Fax +45 45883136.

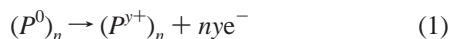
displacement setup is described elsewhere in more detail.<sup>9</sup> Typical dimensions of the polymer strips are 5 mm long and 3 mm wide. The film is immersed in the electrolyte, through which nitrogen is passed to remove dissolved oxygen. The potential is measured against a saturated calomel reference electrode (SCE).

An electrochemical quartz crystal microbalance (EQCM) using an ICM 10 MHz crystal with 0.2 cm<sup>2</sup> gold electrodes controlled by a Hewlett-Packard E4916A crystal analyzer in combination with a potentiostat (Autolab PGSTAT 30) were used to measure the change of mass during polymerization and cycling. With soft systems such as conducting polymers it is important to follow both the weight (via the oscillation frequency) and polymer viscosity (as indicated by the crystal impedance or damping). The Sauerbrey equation establishing the relationship between the oscillation frequency and the mass loading assumes that the oscillating mass is rigid.<sup>10</sup> An increase in the crystal impedance shows that the polymer has become softer. The quartz crystals were calibrated with Ag after the experiments, finding a proportionality constant of 0.96 ng Hz<sup>-1</sup>, close to the 0.904 ng Hz<sup>-1</sup> predicted by the Sauerbrey equation. For the EQCM experiments, a film thickness of approximately 0.2 μm (6.4 mC cm<sup>-3</sup>) was used.

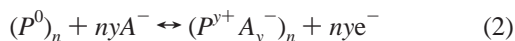
In this paper, the mass or length changes reported are differences between the fully reduced (long) state at -0.85 V vs SCE contra the oxidized (short) state at 0.3 V vs SCE. The potential is changed linearly between the two states with a sweep rate of 10 mVs<sup>-1</sup>.

## Theory

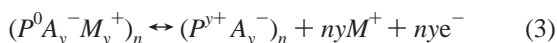
**Thermodynamic Description.** Redox active conducting polymers are characterized by the ability to undergo reversible redox reactions where the charge on the polymer backbone is changed, e.g.,



Here  $n$  is the degree of polymerization (the number of monomers,  $P$ , in the polymer backbone) and  $y$  is the degree of doping. These polymers have an appreciable electronic conductivity in the charged state, which is unusual for organic materials. The charge on the polymer backbone is balanced by counterions of opposite charge embedded in the polymer matrix, e.g., anions on polymer oxidation:



The charge balance scheme is more involved for hybrid materials containing immobile counterions. PPy prepared by electrochemical oxidation of pyrrole in the presence of DBS will be doped with DBS ions during the synthesis. These large anions are not mobile and will stay in the polymer matrix during redox cycling, even in electrolytes devoid of DBS. In PPy(DBS), mobile cations migrate into the polymer during reduction to compensate the unbalanced charge of the detergent anions where  $A^-$  represents the immobile DBS<sup>-</sup> anion and  $M^+$  the cation, e.g., Na<sup>+</sup>.<sup>11</sup>



Because of the associated changes in counterion composition, redox reactions such as eqs 2 and 3 are often described as *polymer doping*, in analogy with the control of conductivity by small composition changes in inorganic semiconductors. The differences between these processes are, however, larger than

their similarities: Polymer doping is in general a reversible process performed under mild, ambient conditions, whereas semiconductor dopants are a permanent part of the lattice. Furthermore, although semiconductor doping only requires minute changes in composition (typical in the ppb or ppm range), polymer doping involves much larger composition changes, typically one unit of charge per three to five monomer units.

For the charge compensation to obtain electroneutrality in the polymer phase, the following restraint on the concentration of the ionic species in the polymer is to be fulfilled:

$$\sum z_i c_i + \frac{q_p}{F} - c_A = 0 \quad (4)$$

$c_i$  is the concentration and  $z_i$  the charge number of the different mobile ions,  $q_p$  is the volume density of charge on the polymer backbone, and  $c_A$  is the concentration of immobile anions in the polymer. In addition to charge compensation, the requirement of constant electrochemical potentials for mobile species fixes the distribution of ions and solvent between electrolyte and polymer. Considering first the distribution of ions, equilibrium is obtained when

$$\bar{\mu}_i^p = \bar{\mu}_i^l \quad (5)$$

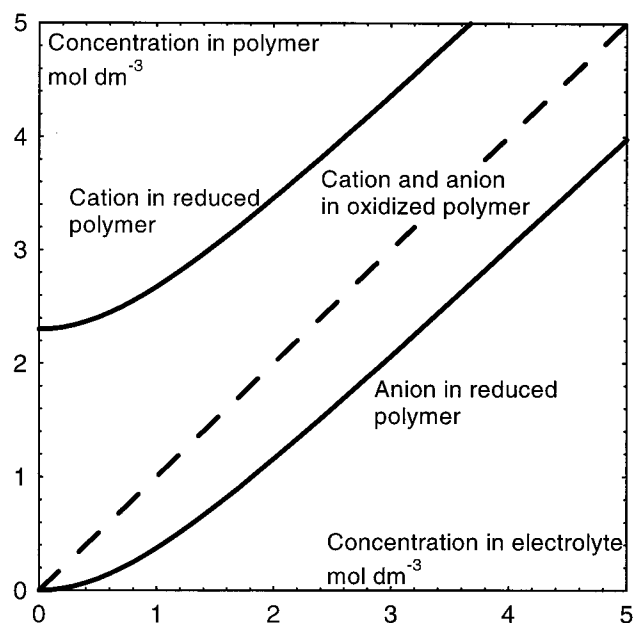
where the subscript  $i$  denotes the different ionic species in the system, and the superscripts p and l refer to the polymer phase and the electrolyte phase, respectively. This is an example of Donnan equilibrium.<sup>12</sup> The ionic activities,  $a_i$ , are then related as

$$a_i^p = a_i^l \exp\left(\frac{\Delta\mu_i^*}{RT}\right) \exp\left(\frac{z_i F}{RT} \Delta\varphi\right) \quad (6)$$

$\Delta\varphi = \varphi^l - \varphi^p$  is known as the Donnan potential difference between electrolyte and polymer, and  $\Delta\mu_i^*$  is the difference in standard chemical potential. From eqs 4 and 6, the concentrations of the ions can be found by assuming that  $\Delta\mu_i^*$  is equal for all mobile ions, the concentrations in the electrolyte are constant, and activities are equal to concentrations,  $c_i$ . As the concentrations in the polymer may be rather high, here up to around 5 M, the last assumption may be questionable. Deviation from ideality will, however, not change the trends of the system properties. For a polymer polymerized with immobile anions, e.g., DBS, in equilibrium with a z-z electrolyte, e.g., NaCl, these assumptions lead to

$$c_i^p = c_{\text{NaCl}}^l \exp\left(\frac{\Delta\mu_i^*}{RT}\right) \left( \frac{c_A - \frac{q_p}{F}}{2c_{\text{NaCl}}^l \exp\left(\frac{\Delta\mu_i^*}{RT}\right)} + \sqrt{\left( \frac{c_A - \frac{q_p}{F}}{2c_{\text{NaCl}}^l \exp\left(\frac{\Delta\mu_i^*}{RT}\right)} \right)^2 + 1} \right)^{z_i} \quad (7)$$

The subscript  $i$  denotes either the cation or the anion, e.g., for NaCl  $z_+ = +1$  and  $z_- = -1$ . If the interactions between ions and surroundings are identical in the polymer and in the electrolyte,  $\Delta\mu_i^* = 0$ , then in the oxidized state the concentrations of Na<sup>+</sup> and Cl<sup>-</sup> in the polymer will be the same as in the electrolyte. When the polymer is reduced, the charge compensa-



**Figure 1.** Concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in the polymer as function of  $c_{\text{NaCl}}$  in the electrolyte according to eq 7.  $\Delta\mu_i^* = 0$  and  $c_A = 2.3 \text{ mol dm}^{-3}$ , obtained from a doping degree of 0.33 and the charge used for polymerization ( $1600 \text{ C cm}^{-3}$ ).<sup>9</sup> Redox states are indicated in the figure.

tion is shared between  $\text{Na}^+$  and  $\text{Cl}^-$  as shown in Figure 1. At low electrolyte concentration, mainly cations will move in and out of the polymer, whereas at higher concentration, both cations and anions will move. This concentration dependence of ionic insertion mechanism explains some of the discrepancies found in the literature data. In contrast, if the polymer repels ions,  $\Delta\mu_i^* \ll 0$ , no  $\text{Cl}^-$  enters the polymer regardless of the redox state. In this case, the amount of  $\text{Na}^+$  is that necessary for obtaining electroneutrality

$$c_{\text{Na}}^{\text{p}} = c_A - \frac{q_{\text{p}}}{F} \quad (8)$$

Hence, in the oxidized state ( $q_{\text{p}}/F = c_A$ ), no cations will be present in the polymer. The case  $\Delta\mu_i^* \gg 0$ , where the polymer is a far better solvent for ions than the electrolyte, is regarded as nonphysical.

In the same way as ions are distributed between the polymer matrix and the surrounding electrolyte, so is the solvent. In general, conducting polymers take up a certain amount of solvent during redox cycling. In the following, we will assume that the electrolyte is aqueous, but the arguments will be valid for any other electrolyte solvent that is mobile in the polymer phase.

Water is driven from the electrolyte into the polymer to counteract differences in water activity between the two phases. Equilibrium is reached when the following relation is fulfilled:

$$\mu_{\text{H}_2\text{O}}^{\text{p}} = \mu_{\text{H}_2\text{O}}^{\text{l}} \quad (9)$$

Here  $\mu_{\text{H}_2\text{O}}$  is the chemical potential of water. Using conventional thermodynamics, the terms in eq 9 are expanded into standard terms, terms in water activity, and a term accounting for the volume work ( $PV$  work) required for moving water from the electrolyte into the polymer:

$$\mu_{\text{H}_2\text{O}}^* + \int_0^{\pi} V_{\text{H}_2\text{O}} d\pi + RT \ln(a_{\text{H}_2\text{O}}^{\text{p}}) = \mu_{\text{H}_2\text{O}}^* + RT \ln(a_{\text{H}_2\text{O}}^{\text{l}}) \quad (10)$$

$$\pi = \frac{RT}{V_{\text{H}_2\text{O}}} \ln\left(\frac{a_{\text{H}_2\text{O}}^{\text{l}}}{a_{\text{H}_2\text{O}}^{\text{p}}}\right) \quad (11)$$

where  $V_{\text{H}_2\text{O}}$  is the molar volume of water (the solvent). The elastic forces in the polymer counteract the difference in the osmotic pressure between polymer and electrolyte. It should be noted that as consequence of the water equilibrium not only the solvation shell of at most three to four water molecules will follow the ions, but as much water as it takes to establish the osmotic balance between the polymer and the surrounding electrolyte.

Applying the usual approximations for solvent activities in dilute solutions ( $\ln(a_{\text{H}_2\text{O}}) \approx -\phi \sum c_i$ ), the osmotic pressure difference is given by

$$\pi \approx RT\phi_{\text{p}}c_{\text{p}} - RT\phi_{\text{l}}\nu c_{\text{l}} \quad (12)$$

$c_{\text{l}}$  is the molar concentration,  $\nu$  is the number of ions formed from one unit of electrolyte salt, and  $\phi_{\text{p}}$  and  $\phi_{\text{l}}$  is the osmotic coefficient in the polymer and electrolyte, respectively; this has been tabulated for many electrolytes by Robinson and Stokes.<sup>13</sup>  $c_{\text{p}}$  is the total concentration of “free” particles in the polymer. For the PPy(DBS) system, the number of polymer chains is assumed to be small, and the DBS ions can be considered to be immobile and hence not “free”. Thus, only the mobile ions from the electrolyte, which balance the difference in the charge of the DBS anions and the net charge on the polymer backbone, will contribute to the osmotic pressure in the polymer phase. These ions are distributed according to eq 7. The number of independent particles will thus typically be large when the polymer is in its reduced state, where the polymer is neutral and the charge of the DBS ions associated with the polymer is balanced by ions extracted from the electrolyte.

**Osmotic Expansion.** In the following, an expression relating the dimension changes and the osmotic pressure is derived.  $\mathbf{L}$  is the vector describing the dimension of a conducting polymer strip, length, width, and thickness. We then introduce the relative change in dimension by the vector  $\mathbf{l} = (\mathbf{L} - \mathbf{L}_0)/\mathbf{L}_0$ , where  $\mathbf{L}_0$  is the dimension at a reference state, e.g., the polymer in the dry state. At constant temperature and constant hydrostatic pressure,  $\mathbf{l}$  will be a function of the three independent variables: the redox state of the polymer determined by the potential,  $E_{\text{p}}$ , the osmotic pressure,  $\pi$ , and the mechanical external forces,  $\mathbf{F}$ , applied to the polymer strip in each of the three dimensions. In stead of applied force, it is convenient to use the mechanical pressure on the strip  $\mathbf{P} = \mathbf{F}/\mathbf{A}_0$ . The sign is chosen so drag is positive.  $\mathbf{A}_0$  is the area of the strip perpendicular to each component of  $\mathbf{F}$  in the standard state, written as a diagonal tensor. The osmotic pressure will work on the actual cross sectional area,  $\mathbf{A}$ , of the strip. In general,  $\mathbf{A}$  will be a function of  $\mathbf{l}$ . Introducing the osmotic pressure normalized by the standard state area eliminates this difficulty:

$$\Pi = \frac{\mathbf{A}\pi}{\mathbf{A}_0} \quad (13)$$

Now both  $\mathbf{P}$  and  $\Pi$  will work on the area  $\mathbf{A}_0$  which by definition is constant. Using these variables the change in dimension can be written as

$$\mathbf{l} = f(\Pi, \mathbf{P}, E_{\text{p}}) \quad (14)$$

In differential form, this expression becomes

$$d\mathbf{l} = \left(\frac{\partial \mathbf{l}}{\partial \Pi}\right)_{\mathbf{P}, E_p} d\Pi + \left(\frac{\partial \mathbf{l}}{\partial \mathbf{P}}\right)_{\Pi, E_p} d\mathbf{P} + \left(\frac{\partial \mathbf{l}}{\partial E_p}\right)_{\Pi, \mathbf{P}} dE_p \quad (15)$$

To solve this, the partial derivatives of  $\mathbf{l}$  must be found. Assuming linear (Hookian) behavior of the polymer, force is related to elongation in the following way:

$$\Delta \mathbf{F} = \frac{E_Y A_0}{L_0} \Delta \mathbf{L} \leftrightarrow \frac{d\mathbf{F}}{d\mathbf{l}} = E_Y A_0 \quad (16)$$

The Young's modulus tensor,  $E_Y$ , is a function of the redox state only. From eq 16, the two first differentials in eq 15 are seen to be equal to the reciprocal of the Young's modulus, because both involve pressure and length terms. The last term in eq 15 is the intrinsic part of the volume change. To calculate this, knowledge of the change in the bond length and conformation in the polymer backbone is required. Here only the osmotic part of the elongation is investigated. Therefore, the integration of the intrinsic term ( $dE_p$  term) will be omitted. However, it should be noted that this term is independent of the water activity and is written  $\mathbf{l}_{E_p}$ .  $\mathbf{l}$  is then calculated by integration of eq 15.

$$\mathbf{l} = \frac{\mathbf{P}}{E_Y} + \frac{A_0 \pi}{A_0 E_Y} + \mathbf{l}_{E_p} \quad (17)$$

At first, this is solved for elongation in one dimension only. This will be a good approximation for strips with small dimensional change, where the area and volume of the polymer strip can be considered to be constant. The dimensional change on going from the reduced to the oxidized state can be found directly from eq 17. By inserting eq 12 for the osmotic pressure, the following expression for the change of the strip length between reduced and oxidized state is found:

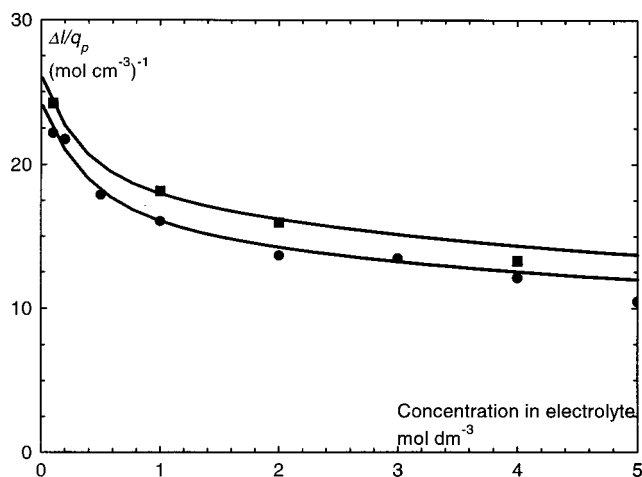
$$\Delta \mathbf{l} = RT \left( \frac{\phi_p c_p^{\text{red}}}{E_Y^{\text{red}}} - \frac{\phi_p c_p^{\text{ox}}}{E_Y^{\text{ox}}} \right) + \left( \frac{1}{E_Y^{\text{red}}} - \frac{1}{E_Y^{\text{ox}}} \right) (P - RT \phi_1 \nu c_1) + \Delta \mathbf{l}_{E_p} \quad (18)$$

The first term in eq 18 depends on the number of free ions in the polymer used to neutralize the combined charge on the backbone and immobile ions. In principle,  $c_p$  is not only the concentration of ions but the concentration of all (free) particles in the polymer. However, the number of independent polymer segments is considered to be small compared to the number of ions and is thus omitted here. The last term,  $\Delta \mathbf{l}_{E_p}$ , is the intrinsic part of the elongation. The second term is an elastic elongation because of change of the stiffness of the polymer when it is reduced and oxidized. The magnitude of the latter term depends on the difference in reciprocal values of  $E_Y$ , on the mechanical external force applied to the film,  $P$ , and on the concentration of the surrounding electrolyte. Thus, the length change decreases as the electrolyte concentration is increased. This finding is in accordance with the notion that this part of the expansion is due to an influx of water driven by the differences in water activity between the external electrolyte and the relatively high ionic strength in the polymer matrix. The more dilute the external electrolyte, the higher the driving force.

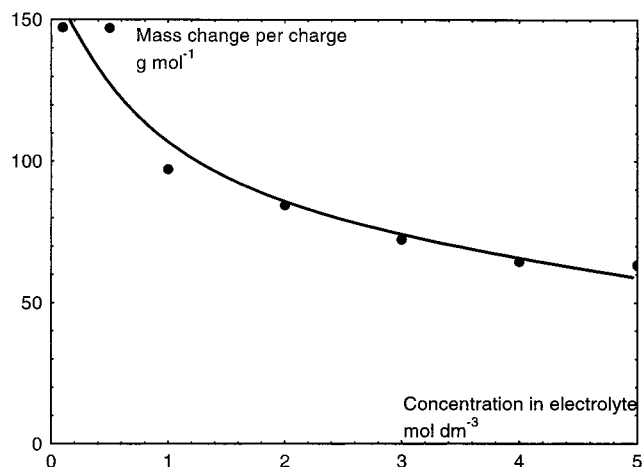
For larger expansions of the polymer, the volume change must be taken into account, because the concentration,  $c_p$ , in the osmotic pressure given by eq 12 depends on the volume of the polymer phase. Hence, eq 17 must be solved in three dimensions. In the present paper, this is done numerically only.

### Experimental Results and Discussion

The length changes accompanying the change in the redox state of PPy(DBS) strips are measured in NaCl solutions of



**Figure 2.** Relative length per charge density of PPy(DBS) during a potential sweep between  $-0.85$  and  $0.3$  V vs SCE in a NaCl solution of different concentration. ● and ■ are measured on two similar films. Curves are fitted to the model in the text eq 18.



**Figure 3.** Mass change as measured by EQCM during a potential sweep between  $-0.85$  and  $0.3$  V vs SCE in NaCl solutions of different concentrations. The curve is fitted to the model in eq 18.

concentration between  $0.1$  and  $5.0$  M at a load of  $0.6$  MPa. The results are shown in Figure 2 as the relative length change per change in charge density. The charge density is the charge found from the simultaneously obtained voltammograms per volume of the strip. The length change decreases with increasing salt concentration from around  $25$  down to  $12$  ( $\text{mol electrons cm}^{-3}$ ) $^{-1}$ . At high electrolyte concentration, the decrease levels out. To compare with the EQCM measurements, the corresponding volume change can be initially estimated as 3 times the length change if isotropic expansion of the polymer is assumed. Then the expansion would decrease with increasing salt concentration from around  $80$  down to  $40$   $\text{cm}^3 \text{mol}^{-1}$  electrons. Although the expansion will be shown not to be isotropic, this will not affect the results of the measurements of the length change.

The EQCM measurements, Figure 3, gave results with the same trend for increasing electrolyte concentration as for the measurements of linear elongation described above. The mass change decreases from  $150$   $\text{g mol}^{-1}$  electrons at low concentrations and levels off at approximately  $60$   $\text{g mol}^{-1}$  at high concentrations. The correspondence is especially remarkable considering the difference in conditions between these experiments: The elongation experiments are on  $10$   $\mu\text{m}$  thick free-standing polymer films, whereas the EQCM experiments are

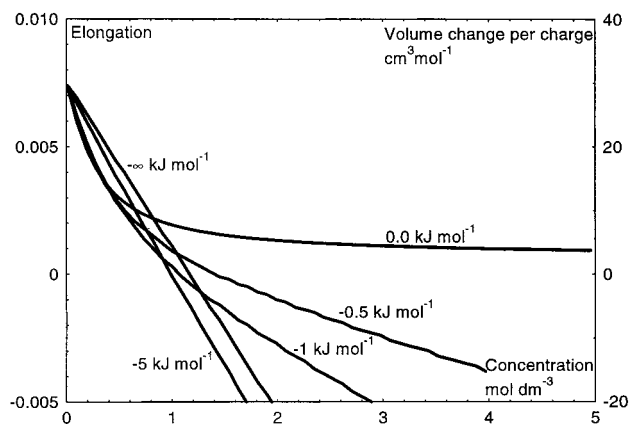


performed on 0.2  $\mu\text{m}$  surface confined films. The parameter linking these two types of experiments is the specific density associated with the volume expansion. The measured density of the as prepared PPy(DBS) is 1.2–1.4  $\text{g cm}^{-3}$ , and the density of the electrolyte is between 1.0 and 1.2  $\text{g cm}^{-3}$  depending on salt concentration. This gives a volume expansion decreasing from around 120 to 50  $\text{cm}^3\text{mol}^{-1}$  for the EQCM experiments. These higher values compared with the linear elongation indicate that the PPy film is anisotropic: it is softer perpendicular to the film than along the film. Therefore the thickness expansion is higher than the expansion along the film observed for free-standing films. This conclusion agrees with the observation by Smela et al.<sup>14,15</sup> A large expansion of the film thickness is reported with values up to 35% strain for films with thicknesses of 1–2  $\mu\text{m}$ . Diminishing, however, for thicker films.

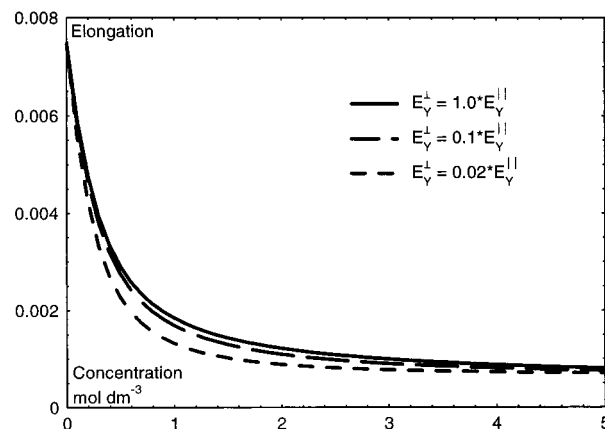
From both the linear length change and the EQCM measurements, it is clear that the concentration of the surrounding electrolyte is an important parameter influencing the expansion of conducting polymers, between 0.1 and 1.0 M the expansion is reduced by 30%. It is thus important to take this effect into consideration when comparing different results on conducting polymer expansion, and ignoring it has probably led to unexplained discrepancies between experimental results.

**Parameters Derived from Model.** The measured elongation of a PPy(DBS) strip cycled in aqueous NaCl solutions of different concentrations is compared with the expansion calculated from eq 18. This is reasonable even if the film is anisotropic, as the Young's modulus perpendicular to the strain direction only has minor influence on the elongation, see later in Figure 5. In the present case, the polymer is doped with large immobile anions. The concentration of ions in the polymer is then found from eq 7 as  $c_p = c_{\text{Cl}} + c_{\text{Na}}$ . As the osmotic coefficient for the polymer,  $\phi_p$ , is unknown, the osmotic coefficients are omitted here and the concentrations used to describe the activities in the osmotic pressure. It is not supposed to change the trends of the predicted effects as only the deviation from ideality is omitted. This was also checked by using the known osmotic coefficient for the solvent for both solvent and polymer. The changes in the parameters were insignificant. The values for stiffness, charge, and external force used in the model are those measured on the strip ( $E_Y^{\text{ox}} = 0.42$  GPa,  $E_Y^{\text{red}} = 0.27$  GPa,  $q_p = 73.4$  C  $\text{cm}^{-3}$ , and  $P = 0.6$  MPa). The only parameters in the model not measured are  $\Delta\mu_i^*$  used for the calculation of the concentrations in the polymer according to eq 7 and the constant contribution from the intrinsic expansion,  $\Delta E_p$ . Fitting these two parameters to the two series of measurements in Figure 2, gives a small negative value for  $\Delta\mu_i^*$  of  $-0.2$  and  $-0.34$   $\text{kJ mol}^{-1}$  and a constant contribution of 13 and 17 (mol electrons  $\text{cm}^{-3}$ ) $^{-1}$  from the intrinsic contribution per charge density. For an isotropic film, the intrinsic expansion corresponds to 40 and 50  $\text{cm}^3\text{mol}^{-1}$ .

For the EQCM measurements, Figure 3, the film is thin and confined to the surface of the Au electrode. Therefore, the film can only expand in thickness. The charge  $q_p$  is 175 C  $\text{cm}^{-3}$ , and the external force,  $P$ , is zero, but the Young's modulus in this direction is not known because it is very difficult to measure. From earlier experience and the large expansion of PPy(DBS) found by Smela, it is assumed that the stiffness is 1 order of magnitude less than that measured along the film and that the density of the expansion (solvent) is 1  $\text{g cm}^{-3}$ , the values  $\Delta\mu_i^* = -0.34$   $\text{kJ mol}^{-1}$ , and an intrinsic contribution of 73  $\text{cm}^3\text{mol}^{-1}$  are found. The value found for the intrinsic expansion is very uncertain as it depends strongly on the Young's modulus.



**Figure 4.** Osmotic part of expansion of PPy(DBS) film in a 1–1 electrolyte calculated from eqs 18 and 7. Isotropic expansion assumed. Different values of the difference in ionic standard chemical potential between electrolyte and polymer are used. Measured parameters used in the equation are  $E_Y^{\text{ox}} = 0.42$  GPa,  $E_Y^{\text{red}} = 0.27$  GPa,  $q_p = 73.4$  C  $\text{cm}^{-3}$ , and  $P = 0.6$  MPa.

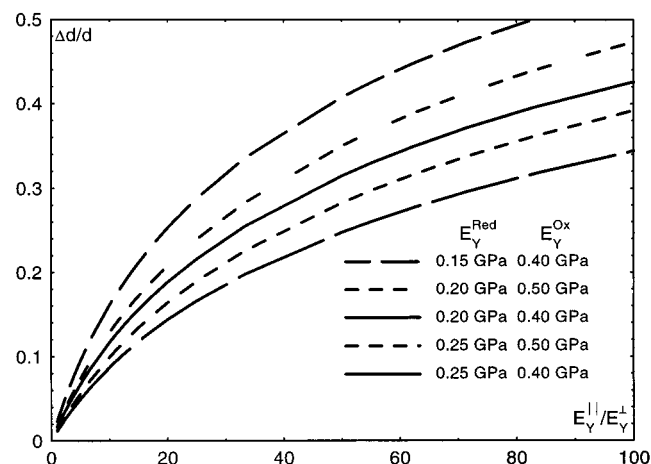


**Figure 5.** Similar to Figure 4 for  $\Delta\mu_i^* = 0$   $\text{kJ mol}^{-1}$ , but the stiffness of the film is allowed to be different perpendicular ( $E_Y^{\text{T}}$ ) and parallel ( $E_Y^{\text{L}}$ ) to the film.  $E_Y^{\text{L}}$  is  $E_Y^{\text{ox}} = 0.42$  GPa and  $E_Y^{\text{red}} = 0.27$  GPa depending on redox state. Even a high degree of anisotropy is seen to have little effect on the elongation.

$\Delta\mu_i^*$ , in contrast, is better determined as it depends on the shape of the curve and is rather independent of the Young's modulus.

As the model fits the measurements well and reasonable parameters are found, it yields evidence that a substantial part of the expansion is due to osmotic expansion with diffusion of ions and solvent in and out of the polymer. That part of the expansion which is independent of the surrounding electrolyte concentration we have called the *intrinsic expansion* of the polymer as it is due to changes in bond lengths and conformation in the polymer backbone. The intrinsic expansion is expected to be strongly dependent on the type of polymer in question.

**Parameter Sensitivity.** It is of interest to analyze the consequences of changing some of the parameters in the model. Unless otherwise indicated, the measured values given above are used. Equation 18 is plotted for different values of  $\Delta\mu_i^*$  in Figure 4. For the present parameters, the numerically calculated three-dimensional solution of eq 17 only differs insignificantly, less than 1  $\text{cm}^3\text{mol}^{-1}$ , from the analytical one-dimensional solution. In all cases, the expansion decreases as the electrolyte concentration increases. For  $\Delta\mu_i^* = -\infty$  (ions are excluded from the polymer), the change in expansion is linear in the concentration. When  $\Delta\mu_i^* = 0$ , the expansion only depends on



**Figure 6.** Relative expansion of the film thickness between the oxidized and reduced state as function of the ratio of the stiffnesses parallel and perpendicular to the polymerization electrode. Values of Young's modulus parallel to the polymerization electrode are as given in the figure. External load,  $P$ , is 0.6 MPa, and the electrolyte concentration is 0.5 M.

the electrolyte concentration at lower molarities ( $\sim 1$  M). At higher concentrations, the change in ionic concentrations in the polymer is identical to that in the electrolyte and the charge compensation is shared between cations and anions. The limiting expansion as the electrolyte concentration approaches zero will be finite in the model, hence, changing the concentration from 0.1 M to, e.g., 0.01 M will only make little difference. In reality, the measured expansion may decrease if equilibrium is not reached because of longer diffusion times of ions in the electrolyte.

As the polymer is polymerized on a planar electrode, Young's modulus,  $E_Y^||$ , is identical for the length and width of the strip. However, in the perpendicular direction, the Young's modulus,  $E_Y^⊥$ , may as well be different. Assuming that the tensor  $E_Y$  contains no cross-terms, the expansion is shown in Figure 5 as function of the electrolyte concentration and for different values of  $E_Y^⊥$ . Softening in the direction of the thickness of the film will only have a minor influence on the elongation perpendicular to the thickness. The opposite is true, of course, for the expansion of the film thickness, see Figure 6. The softer the film, the larger the expansion. If  $E_Y^⊥$  is 40–80 times softer than  $E_Y^||$ , this gives values comparable to what Smela<sup>14</sup> has observed for thin films.

## Conclusion

The volume change of a conducting polymer during redox switching can be divided into a part stemming from osmotic

expansion and an intrinsic part from the changes in bond length and conformation in the polymer backbone. The osmotic expansion is due to changes in the number of free particles (ions) in the polymer. The number of ions in the polymer is determined according to a Donnan equilibrium and changes with the oxidation/reduction of the polymer backbone. Measurements of elongation and EQCM on PPy(DBS) show that the expansion decreases with increasing electrolyte concentration, the decrease is around 30% between 0.1 and 1.0 M. A model of the osmotic part of the expansion can explain the observed change of expansion with electrolyte concentration. Fitting the model to measurements on the PPy(DBS) system gives values between  $-0.2$  and  $-0.34$  kJ mol<sup>-1</sup> for the difference in standard chemical potential for the mobile ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) between the electrolyte and the polymer. For the measurements on linear elongation, an intrinsic expansion per change in charge density of 13 and 17 (mol electrons cm<sup>-3</sup>)<sup>-1</sup> is found. If the film is isotropic, this correspond to 40–50 cm<sup>3</sup> mol<sup>-1</sup> electrons.

The osmotic expansion is a significant effect, which can make a large contribution to the total volume expansion of a polymer actuator. The effect should be taken into account when interpreting and designing actuator experiments and when comparing experimental results from different sources.

**Acknowledgment.** The work is part of the ARTMUS project (artificial muscles) sponsored by the Danish Research Councils as part of the THOR program.

## References and Notes

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