

## Ideal Mixing in Polyelectrolyte Complexes and Multilayers: Entropy Driven Assembly

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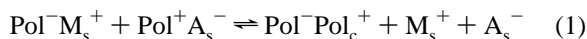
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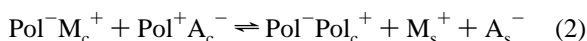
Mixing within blends of polymers is driven by a combination of entropic and enthalpic effects.<sup>1</sup> While entropy always provides a driving force for the mixing of pure components in polymer blends, specific (enthalpic) interactions often disfavor mixing at the molecular level. Thus, compatible polymer blends are the exception rather than the rule.<sup>1,2</sup>

Complexes between oppositely charged polyelectrolytes are amorphous and well mixed.<sup>3,4</sup> At first glance, oppositely charged polyelectrolyte segments would appear to be set up for strongly exothermic mixing, driven by multiple, cooperative, and specific (in the sense that positive attracts negative) “electrostatic” interactions. In reality, it is known that when polyelectrolytes are mixed to form complexes the process is athermal or ideal ( $\Delta H = 0$ ).<sup>5</sup> The entropic nature of polyelectrolyte association was recognized many decades ago. For example, Michaels and co-workers<sup>6</sup> ascribe the mixing to be driven by “the escaping tendency of microions.” However, most literature on polyelectrolyte complexation, particularly those works dealing with the more recent and widespread formation of ultrathin “polyelectrolyte multilayer” (PEMU) films,<sup>7</sup> continues to describe the driving force as “electrostatic.”

The association, or mixing, of polyelectrolytes from solution to form complex  $\text{Pol}^-\text{Pol}^+$ , PEC, is represented by



and the ion pairing when the complex is formed by

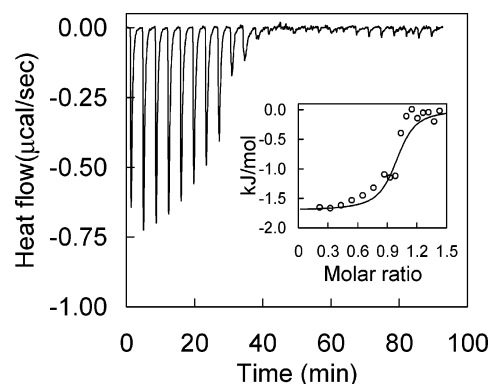


where  $\text{Pol}^-$  and  $\text{Pol}^+$  are respective polyanion and polycation repeat units and  $\text{M}^+$  and  $\text{A}^-$  are cation and anion (salt, usually NaCl). The subscripts “c” and “s” refer to material in the complexed and solution phase, respectively. Most complexes, including those in PEMUs, associate with 1:1 stoichiometry of charged repeating units.<sup>4–8</sup> For thermodynamic expressions, choice of the proper reference states is nontrivial. The association constant for complexes that have already formed and which are subjected to swelling (doping), the reverse of eq 2, is written as follows, using respective activities,  $a$ :<sup>9,10</sup>

$$K_a = \frac{(1-y)a_{\text{M}^+}a_{\text{A}^-}}{y^2} \approx \frac{a_{\text{MA}}}{y_{y \rightarrow 0}^2} \quad (3)$$

where  $y$  is the fraction of polyelectrolyte found in the counterion compensated (“extrinsic”) form, or the “doping level.” Reference states are  $y = 0$  for the completely dissociated complex,  $y = 1$  for the completely associated complex, and  $a_{\text{MA}} = 1.0$ .

When separate component polyelectrolytes are mixed from the aqueous phase, ion pairing of the first monomer units on each chain is represented by eq 1, but each of the vastly more numerous



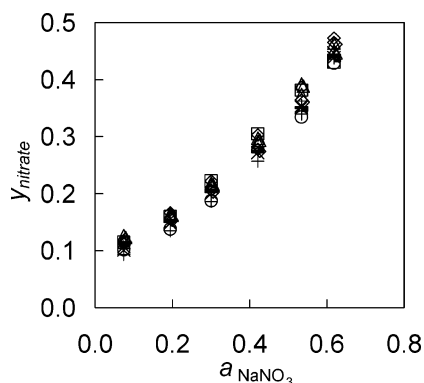
**Figure 1.** Heat flow per injection versus time for the isothermal injection of PDADMA (11.36 mM) into a cell containing PSS (0.44 mM) to form a complex. Inset depicts the molar enthalpy versus the mole ratio of PDADMA to PSS with a fit for  $K_a = 3$ . All solutions contain 0.3 M NaCl and were maintained at 25 °C. A 1:1 stoichiometry was observed.

subsequent ion pairings is represented by eq 2. In other words, the first ion pairing removes the complex from bulk solution, and it is therefore incorrect to refer to a “concentration” of the remainder of the polymer. The difference in association energy between  $\text{Pol}_s$  and  $\text{Pol}_c$  complexation is small—a polymer segment loses about 0.25 kT ( $\sim 0.6$  kJ) in configurational entropy on adsorption.<sup>11</sup>

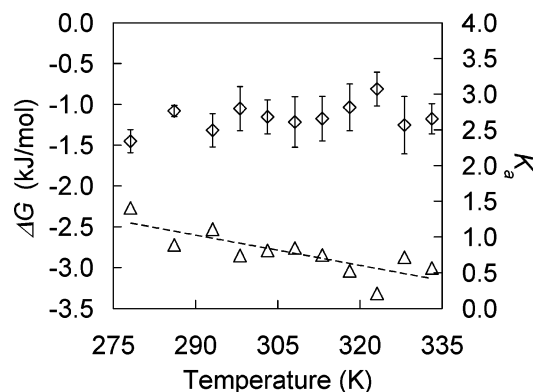
Obtaining crucial thermodynamic data for polyelectrolyte complexation by calorimetry is problematic because of the lack of heat evolved. While no data for PECs was provided in the earlier studies, modern ultrasensitive calorimetric techniques are capable of shedding some quantitative insight.<sup>12</sup> For example, Figure 1 shows the isothermal calorimetry titration (ITC, a technique commonly used to study the interaction of biological molecules<sup>13</sup>) of poly(styrene sulfonate) (PSS) by poly(diallyldimethylammonium) (PDADMA). The inset depicts the  $\Delta H$  determined from the individual aliquots of PDADMA added. Although the data are somewhat noisy because of the small exothermicity, a  $\Delta H$  of ca.  $-1.7$  kJ mol<sup>-1</sup> is evident, independent of mixing order and polymer concentration. The quality of the data makes it very difficult, however, to perform the standard procedure of fitting a curve to the  $\Delta H$  data to obtain a  $K_a$  and therefore a  $\Delta G_{\text{mixing}}$  (from  $\Delta G_m = -RT \ln K_a$ ). The fit in Figure 1, for example, described in detail in Supporting Information, is for a  $K_a$  of 3 (for 0.3 M NaCl) and  $\Delta G_m$  of  $-2.7$  kJ mol<sup>-1</sup>, but a range of  $\Delta G_m$  from about  $-1$  to  $-10$  kJ would also have given reasonable fits.

We recently employed attenuated internal reflectance FTIR (ATR-FTIR) methods on polyelectrolyte multilayers to measure, in situ, doping of these ultrathin films of complex (the reverse of eq 1).<sup>14,15</sup> The techniques were adapted from earlier ATR-FTIR work<sup>16,17</sup> used to evaluate PEMUs.

If infrared-active counterions are employed they may be observed as they enter the multilayer.<sup>9,15</sup> Comparison with specific polymer



**Figure 2.** Doping level versus  $\text{NaNO}_3$  activity at various temperatures for a 30-layer PDADMA/PSS multilayer: ( $\diamond$ ) 5 °C; ( $\square$ ) 13 °C; ( $\triangle$ ) 20 °C; ( $\circ$ ) 25 °C; ( $\times$ ) 30 °C; (+) 35 °C; (\*) 40 °C; (-) 45 °C; (-) 50 °C; double diamonds, 55 °C; and double triangles, 60 °C.



**Figure 3.**  $K_a$  of the PEMU from Figure 2 for each temperature (5–60 °C) ( $\diamond$ ); corresponding  $\Delta G$ 's in  $\text{kJ mol}^{-1}$  ( $\triangle$ ).

**Table 1.** Thermodynamic Parameters of Select PECs

complex	$\Delta H^\circ$ , kJ	$\Delta S^\circ$ , J	$\Delta G_m^\circ$ , kJ
PDADMA/PSS	-1.7	3.5	-3
PAH <sup>a</sup> /PSS	-1.45	33.5	-11
PDADMA/SPEEK <sup>b</sup>	+2.2	34	-8

<sup>a</sup> PAH = poly(allylamine). <sup>b</sup> SPEEK = sulfonated poly(etheretherketone).

bands and the use of standards permits precise determination of  $\gamma$ . In Figure 2 we present doping as a function of concentration for sodium nitrate, which, in our experience,<sup>10</sup> swells PDADMA/PSS multilayers in a manner similar to NaCl. The doping is performed over a range of temperatures. Association constants are obtained in a straightforward step by inserting the slopes from Figure 2 into eq 3.

Association constants, along with corresponding free energies of mixing, as a function of temperature are summarized in Figure 3. From  $\Delta G = \Delta H - T\Delta S$ , an ideally mixing system should have  $\Delta H \rightarrow 0$  (in Figure 3 the appropriate intercept is  $1.0 \pm 1$  kJ), or put another way,  $K_a$  should be independent of temperature.

ITC data for two other common pairs of polyelectrolytes are presented in Table 1. The thermodynamic data obtained here show that mixing for popular pairs of polyelectrolytes is driven largely by entropy, that is, by the release of counterions and waters of hydration from the dissolved polyelectrolyte chains. Interestingly, the free energy of association is not large, as might be expected from electrostatic arguments. Polyelectrolyte association is fundamentally an ion exchange process, where polymer-counterion associations are replaced by polymer-polymer ion pairs. Because of the underlying requirement for polyelectrolyte charge neutralization, whether by counterions or by oppositely charged polymer,

the mechanism for polyelectrolyte complexation would be more appropriately termed "electronneutralization."

Several attributes of stoichiometric polyelectrolyte complexes make them amenable to classical thermodynamic analysis. From an electrostatics perspective, the charge density is such that long-range interactions are screened and the chains behave as though they were neutral. Quantitative estimates for interaction energies in these interesting condensed phases are possible without recourse to daunting electrostatics descriptions. Indeed, for ideal mixing, the chains in a polyelectrolyte complex should maintain their unperturbed dimensions ( $\theta$ -condition). In addition, because they are highly condensed systems, they are not susceptible to the breakdown of mean field assumptions that plague thermodynamic treatments of polymer solutions.

In conclusion, a complete and accurate picture for the thermodynamics of polyelectrolyte complexation may be garnered from a combination of techniques. Isothermal calorimetry provides accurate  $\Delta H$  while direct measurement of doping equilibria gives reliable  $\Delta G$ . The association constant for complex formation shows little temperature dependence, confirming the ideal nature of complexation. As such, polyelectrolytes are intriguing building blocks for entropy-driven assembly.

**Acknowledgment.** This work was supported by the National Science Foundation (via Grant DMR 0309441).

**Note Added after ASAP Publication.** After this paper was published ASAP on October 4, 2006, a typographical error in the acronym introduced for  $\text{Pol}^-\text{Pol}^+$  in the third paragraph was corrected. The corrected version was published ASAP on October 4, 2006.

**Supporting Information Available:** Experimental details and raw data for ATR-FTIR and ITC experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA064532C