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13. ABSTRACT *(Maximum 200 words)*

ARO supported research of electrochemical studies in four related areas is summarized. The research involved electron transfer reactions to reactants bound electrostatically to soluble polyelectrolytes; application of a scanning electrochemical microscope to electrode surfaces coated with polyelectrolytes; kinetic measurements on thermodynamically disfavored electron-transfer reactions at polyelectrolyte-coated electrodes and the synthesis and electrochemical testing of polyelectrolytes containing electroactive labels permanently attached to the polyelectrolyte chains. The nine publications that have thus far resulted from the research are listed.

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The research carried out with ARO support during the period between 1991 and 1995 was focused on four inter-related topics: i) Experimental studies of the interactions between soluble polyelectrolytes and electroactive counterions or complexes that are bound to the polyelectrolytes by coordination or electrostatic attractions; ii) The application of the technique of scanning electrochemical microscopy to monitor ion fluxes at the interface between polymer coatings on electrodes and the supporting electrolyte solutions in which they are utilized; iii) Analysis of the behavior of thermodynamically unfavorable electron transfer reactions between reactants in solution and co-reactants confined in polyelectrolyte coatings on electrodes; iv) The synthesis and electrochemical testing of new, soluble polyelectrolytes containing a few electroactive labeling groups per polymeric chain.

i. Electrochemistry of Electroactive Reactants Bound to Soluble Polyelectrolytes.

Electrochemical experiments involving relatively simple measurement techniques (cyclic and especially rotating disk voltammetry, spectroelectrochemistry, equilibrium dialysis) were conducted to gain insight into the equilibria governing the interactions between polyelectrolytes and electroactive counterions with which they associate [1-2]. The mobilities of the species formed from the reaction between macromolecules and small, electroactive probes were estimated from the electrochemical measurements. Information was obtained about kinetics of the formation and dissociation of polyelectrolyte-counterion complexes [2]. Electron-transfer between counterions that are bound to polyelectrolytes, and therefore diffuse at correspondingly low rates, and counterions or other co-reactants in the solution that are unbound and therefore diffuse more rapidly, can produce very significant effects on the electrochemical responses obtained. A quantitative treatment of these effects, based on an analysis of Andrieux et al. [3], was presented for the case of chronoamperometry and a new equation appropriate for the analysis of data obtained with rotating disk electrodes was derived [4] and tested [2].

Experimental systems investigated during the current support period included mixtures of electroactive cationic counterions with polystyrene sulfonates or polyacrylates and polyelectrolytes produced by the coordinative binding of $Ru(edta)^{2-/-}$ (edta = ethylenediamminetetraacetate) to partially protonated poly(4-vinylpyridine) [2].

ii. Scanning Electrochemical Microscopy of Polyelectrolyte Coated Electrodes.

A scanning electrochemical microscope, based on the design that originated in the group of Prof. A. J. Bard [5],was constructed in our laboratory. The instrument was applied to monitor the fluxes of electroactive ions that were ejected from coatings of protonated poly(4-vinylpyridine) [6] and Nafion [7]. In addition, images of Nafion coatings were obtained with features that could be traced to the rate of electron propagation through the coatings [8]. One of the more interesting phenomena observed during these experiments occurred when Nafion coatings on electrodes were loaded to saturation with $Os(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) and stepped to potentials where the $Os(bpy)_3^{2+}$ was oxidized to $Os(bpy)_3^{3+}$. In order to maintain electroneutrality within the highly permselective coatings, cations had to be ejected from them. The unexpected feature was that the ejected ions consisted almost entirely of $Os(bpy)_3^{3+}$. The preferential ejection of $Os(bpy)_3^{3+}$ occurs before most of the cations incorporated in the coatings have had time to be oxidized to $Os(bpy)_3^{3+}$ and it indicates that migration of the counterions in the electric field present in the coating may result in a high discrimination for ejection of more highly charged counterions.

iii) Thermodynamically Disfavored Electron Transfer at the Interface between Redox Polymer Coatings and Solutions

This topic was explored to try to understand the possible effects of Donnan potentials on the kinetics of electron transfer at polyelectrolyte/solution interfaces [9]. It was demonstrated that the (now widely practiced) analysis of rotating disk plateau currents by means of Koutecky-Levich plots of $(\text{current})^{-1}$ vs. $(\text{rotation rate})^{-1/2}$ can lead to serious errors in the evaluation of the rate constants for electron transfer if thermodynamically disfavored reactions are involved [10]. The appropriate theoretical relations have been provided by Andrieux and Saveant [11] but they are more cumbersome to employ than the appealingly simple Koutecky-Levich plots. However, failure to utilize the full Andrieux-Saveant equations when disfavored reactions are being examined can produce rate constants that are in error by orders of magnitude [10].

A second feature that cannot be ignored when disfavored reactions are under study is the frequently encountered non-ideal shapes of current-potential characteristics for redox groups confined within polymer/polyelectrolyte coatings on electrodes. One way of (empirically) accounting for the non-Nernstian wave widths and peak currents exhibited by such systems is to regard the coating as containing an array (usually Gaussian) of redox couples with a range of formal potentials centered at the peak potential. One result of such a model is that substrates in solution (with a single formal potential) encounter an array of co-reactants during oxidation or reduction at the redox polymer coatings. There is no single equilibrium constant (or driving force) for the electron transfer but rather an array of constants. This situation can usually be safely neglected when thermodynamically favored electron transfer reactions are involved because only a small portion of the redox couples in the array participate significantly in the reaction. However, with disfavored reactions it is usually obligatory to consider the full set of redox couples in the array in analyzing the rotating disk current data to obtain reasonable rate constants. A quantitative treatment of the model and corresponding data analysis were presented and applied to several experimental systems [12]. A satisfying aspect of the treatment was its ability to bring otherwise discordant results into reasonable agreement with expectations based on Marcus theory for outer-sphere electron-transfer reactions [13].

iv) Preparation and Testing of Polyelectrolytes Labeled with Electroactive Functional Groups

When soluble polyelectrolytes having molecular weights of 10 KDa or greater are added to solutions of small, rapidly diffusing counterions, the rate of diffusion of the counterions is diminished because of their association with the large, slowly diffusing macroions. With sufficiently high concentrations of the polyelectrolyte, essentially all of the counterions are bound to the polyelectrolyte molecules and the diffusion-limited current for the counterions reaches a constant value which has been assumed to reflect the diffusion coefficient of the polyelectrolyte molecules themselves [1, 2]. An independent test of this assumption becomes possible if the polyelectrolyte molecules are intrinsically electroactive even before they bind electroactive counterions. With this possibility as an objective, we prepared polyelectrolytes labeled with ferrocene groups by carrying out copolymerizations of vinyl ferrocene with vinylpyridine or acrylic acid [14]. Entry to a second class of labeled polyelectrolytes was obtained by copolymerization of acrylic acid and acrylonitrile followed by coordination of complexes of Ru(II) to a few of the nitrile groups in the resulting copolymers [15]. The first electrochemical experiments with these labeled materials have supported the assumption that counterions exhibit the same diffusion coefficients as the polyelectrolytes when the latter are present in sufficient excess.

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