

[*J. Photopolym. Sci. Technol.*, **13**, 79-82 (2000)]

[Lab. of Pharm. Physical Chemistry]

**Effect of Plasma-Irradiation on Reduction of Drug Adsorption onto the Surface of Plastic Infusion Bag.**

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In this study, we obtained the data concerning the effect of plasma treatment on the reduction of adsorption of insulin on the surface of polyethylene-vinylacetate (EVA) bag. It was shown that the adsorbed amount of insulin on EVA film decreased with increasing the duration of plasma irradiation. The observed ESR spectra of EVA are similar in pattern to those of LDPE. EVA contains an acetoxy group,  $\text{CH}_3\text{COO}-$ , which is easily decomposed by the plasma-irradiation. Thus, the elimination of acetoxy group by plasma irradiation to EVA produces the mid-chain alkyl radical, which is also formed by plasma irradiation to PE. From the present study on the effect of plasma-irradiation on reduction of the drug adsorption onto the surface of plastic infusion bag, it can be concluded that the plasma treatment of EVA is effective on the reduction of insulin adsorption. The plasma treatment can make the surface modification possible without a significant change of polymer morphology, so that this method seems applicable for enhancing the surface functionalization in a wide variety of polymers for medical use.

[*J. Org. Chem.*, **65**, 1448-1455 (2000)]

[Lab. of Pharm. Anal. Chemistry]

 **$n-\sigma$  Charge-Transfer Interaction and Molecular and Electronic Structural Properties in the Hydrogen-Bonding Systems Consisting of *p*-Quinone Dianions and Methyl Alcohol.**

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Molecular and electronic structural properties of the hydrogen-bonded complexes of *para*-quinone dianions ( $\text{PQ}^{2-}$ ) were investigated by electrochemistry and spectroelectrochemistry of PQ in MeCN combined with *ab initio* MO calculations. Detailed analyses of the cyclic voltammetric and spectral behaviors for the hydrogen-bonding systems reveal that  $\text{PQ}^{2-}$  forms the 1:2 complexes at low concentrations of MeOH and the 1:4 complexes at high concentrations by the hydrogen bonding involving strong  $n-\sigma$  type CT interaction. The HF/6-31G(d) calculation results show that the structure of  $\text{PQ}^{2-}$  is characterized by a lengthening of the C=O bonds and a benzenoid ring. In conclusion, the differing functions and properties of biological quinones are conferred by the  $n-\sigma$  CT interaction through hydrogen bonding of the dianions with their protein environment.

[*J. Phys. Chem. A*, **104**, 3064-3072 (2000)]

[Lab. of Pharm. Anal. Chemistry]

**Bistable Charge-Transfer Complex Formation of Redox-Active Organic Molecules Based on Intermolecular HOMO–LUMO Interaction Controlled by the Redox Reactions.**

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The bistable complex formation systems consisting of biphenylene (BP) and redox-active organic molecules such as chloranil (CL) and TCNE have been experimentally and theoretically investigated, based on an intermolecular interaction which characteristically occurs in the electrogenerated dianions forming a  $\pi-\pi$  type charge-transfer complex. It has been found that BP forms the redox-mediated bistable complexes with TCNE and CL, characterized by the geometrical alteration and the chromatic change. The interconversion in the systems is modulated through redox control of the intermolecular HOMO–LUMO interaction, with trichromic change arising from the neutral complex formation, the anion radical generation, and the dianion complex formation. This is an original approach to the redox-mediated bistable complex formation in terms of use of the properties of organic dianions.

[*Chem. Pharm. Bull.*, **48**, 537-541 (2000)]

[Lab. of Pharm. Anal. Chemistry]

**Structural and Spectral Characteristics of the Electrogenerated Tetracyanoethylene Dianion.**

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Structural and spectral characteristics of the electrogenerated tetracyanoethylene dianion ( $\text{TCNE}^{2-}$ ) were experimentally and theoretically examined. The bands in  $\text{CH}_3\text{CN}$  and in  $\text{CH}_2\text{Cl}_2$  are assigned to the degenerate  ${}^1\text{E} \leftarrow {}^1\text{A}_1$  transition at the  $D_{2d}$  structure and the  ${}^1\text{B}_{2u} \leftarrow {}^1\text{A}_g$  transition at the  $D_{2h}$  structure, respectively. The rotation barrier of the C=C bond in  $\text{TCNE}^{2-}$  is estimated by HF, MP2 and MP4 calculations with 6-31G(d), 6-31+G(d) and 6-311+G(d) basis sets as 42–51  $\text{kJ mol}^{-1}$ . The  $D_{2d}$  structure is most stable, and the  $D_{2h}$  structure represents the transition state of the internal rotation. The calculations reveal that the two-electron addition to the antibonding LUMO of TCNE causes an easy rotation around the C=C bond of  $\text{TCNE}^{2-}$  characterized by the formal single bond. These results show that  $\text{TCNE}^{2-}$  preferentially adopts  $D_{2d}$  and  $D_{2h}$  structures in solvents depending upon the solvent nature by virtue of the easy rotation around the C=C bond.