approaches. We use a combined approach that calculates free energies at the energy minima with adiabatic charging (AC) and the activation barriers with potentials of mean force (PMF). This approach is a good compromise between the absolute and the relative energy scale method, AC and PMF, which gives accurate energy profiles and the consistency of these methods. Other free energy methods such as the weighted histogram analysis method and the 2-dimensional method that combines EVB and PMF are examined as well. The comparison of these microscopic simulation methods give a good idea of their strong and weak points and help us to know how to apply them properly.

486.
FLUORESCENT METHOD FOR EVALUATION OF BINDING AFFINITY OF ETHIDIUM HOMODIMER-III TO DNA. ***Nikolay N. Barashkov**, Fei Mao, and Debra Carr, Biotium, Inc, Investment Blvd., Suite 8, Hayward, CA 94545, Fax: 510-265-1352, nbarashk@hotmail.com*

Various polycationic homodimeric and heterodimeric dyes form fluorescent complexes with double-straned DNA (dsDNA). Well known 4,4-diazadecyl-5,5'-bis(3,8-diamino-6-phenylphenanthridium) dichloride dihydrochloride (ethidium homodimer-1, EthH-1) strongly binds to dsDNA with a large fluorescence enhancement (>30-fold). Its intristic dsNDA binding affinity is at least three orders of magnitude greater than the intristic dsDNA binding affinity of ethidium bromide. In order to further improve the binding affinity of homodimeric dyes the new ethidium homodimer -III (EthH-III) with a larger amount of cations compared to EthH-1 has been developed. The absorbance and fluorescence spectra of EthH-III in 0.2M aqueous Na acetate solution in absence and presence of dsDNA have been investigated and compared with the spectral data of EthH-1 and its complexes with dsDNA. The fluorescence intensity of homodimers before and after an addition of dsDNA have been measured. The Scatchard's equation has been used for determination of the binding constants. It was found that due to the presence of the additional cations in its structure EthH-III has the higher value of the binding intristic constant ($K=12.5\times10^{6}\ M^{-1}$) compared to EthH-1 ($K=9\times10^{6}\ M^{-1}$).

487.
INTERACTION OF BE WITH CARBOXYLATES IN PROTEINS AND INFLUENCE OF THE DIELECTRIC ENVIRONMENT. ***James A. Snyder**, Analytical Services Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, 1095 Willowdale Rd., Morgantown, WV 26505, Fax: 304-285-6041, nyu4@cdc.gov*

To gain insight into the interaction of Be^{2+} ions with negatively charged protein residues, the free energy changes associated with the replacement of water molecules in the first hydration shell of with one and two formate anions were computed for the gas phase reactions using ab initio methods at the MP2 and DFT-B3LYP computational level. Both unidentate and bidentate modes of coordination of the carboxylate group with the Be^{2+} ion are considered. Continuum dielectric calculations were then performed to estimate the corresponding free energy changes in several environments of varying dielectric strength. Environments with dielectric constants of 2 and 4 to represent a protein interior, and 78, which corresponds to water, were used. It is found that the free energy changes for the substitution reactions decrease in magnitude with increasing dielectric strength, in agreement with similar results reported for Mg^{2+}, Ca^{2+} and Zn^{2+} (Dudev, T.; Lim C. J. Phys. Chem. B 2000, 104, 3692). However, unlike Mg^{2+}, Ca^{2+} and Zn^{2+}, the free energy change for the substitution reactions with Be^{2+} remain negative and indicate the reactions are still favorable in the high dielectric aqueous environment. It is also found that the unidentate mode of binding is favored over the bidentate mode, and this is attributed, in part, to introduction of hydrogen bonds between one carboxylate oxygen and a water molecule within the cluster when unidentate binding with Be^{2+} is involved.

488.
INTERACTION OF TRANSITION METALS WITH OVERLAPPING HISTIDINE RESIDUES IN MODEL PEPTIDES. ***Zhigang Liu**, Kang Chen, and Neville R. Kallenbach, Department of Chemistry, New York University, 31 Washington Place,Room 1001,Mailbox 16, new york, NY 10003, Fax: 212-995-4475, al264@nyu.edu*

Pairs of His residues at appropriate spacing have been used to stabilize the helical structure in peptides upon binding transition metals. In addition to histidines spaced at positions i and i+4 in a peptide that stabilizes alpha helix, transition metals interact with histidines at positions (i, i+3) and (i, i+5). Here we use a model peptide AcSAAEHHHRHHHRGGYNH2 containing multiple overlapping histidines, to investigate the binding of divalent transition metals, Zn2+, Ni2+, Cu2+, and Pd2+. Experiments were carried out in aqueous solution or water/TFE and UV CD was used to characterize the structure present. The results show that Ni2+and Cu2+ can introduce intrinsic turn conformations in both aqueous solution and TFE while Zn2+ introduces an apparent á-helical conformation. Binding 3 equivalents of palladium (II) (ethylenediamine) Pd (en) stabilizes alpha helix in the presence of TFE. Thus transition metal binding to the overlapping histidine residues in our model is selective and specific.

489.
INTERACTIONS OF N-ALKYL-2-PYRROLIDINONE SURFACTANTS WITH LIPID BILAYERS. ***Yasemin Kopkalli**[1], Milton J. Rosen[2], and Lesley Davenport[1]. (1) Department of Chemistry, The Graduate Center & Brooklyn College of the City University of New York, 2900 Bedford Ave, Brooklyn, NY 11210, Fax: 718-951-4607, ytkopkalli@aol.com, (2) Surfactant Research Institute, Brooklyn College of the City University of New York*

We are studying the interactions of the non-ionic surfactants, N-octyl-2-pyrrolidinone (C8P) and N-(2-ethylhexyl)-2-pyrrolidinone (C2,6P), on the physical structure of DMPC lipid bilayers using both fluorescence emission anisotropy (EA) and isothermal titration calorimetry (ITC) methodologies. While the physical properties of these surfactants are well studied, their impact on bilayer and integral membrane protein solubilization, and membrane permeability, has not been investigated. Since the CMC values for C8P and C2,6P are greater than their water solubilization limits, they may constitute good candidates for membrane-protein solubilization and reconstitution applications. Fluorescence emission anisotropy (EA) studies of DMPC bilayers labeled with either DPH or TMA-DPH, suggest that C8P exhibits a greater effect on the lipid ordering both within the acyl chain and head group regions on the bilayer compared with the C2,6P analogue. Several key thermodynamic quantities on binding of these surfactants to DMPC bilayers have been determined using ITC studies.

490.
INVESTIGATING THE EFFECT OF THE ZWITTERION/LACTONE EQUILIBRIUM OF RHODAMINE B ON THE CYBOTACTIC REGION OF THE ACETONITRILE/$SCCO_2$ CO-SOLVENT. ***Steven G. Mayer**, Andreas Gahlmann, and Kimberly D. Kester, Department of Chemistry, University of Portland, 5000 N. Willamette Blvd., Portland, OR 97203, mayer@up.edu*

We investigated the effect of adding acetonitrile to supercritical carbon dioxide ($scCO_2$) in the presence of rhodamine B. This spectroscopic investigation of the $scCO_2$/acetonitrile, rhodamine B/$scCO_2$ and rhodamine B/acetonitrile interactions revealed that rhodamine B, which possesses a temperature dependent equilibrium between a zwitterionic form and a neutral form, had a strong affect on the cybotactic region. To confirm that this effect was only dependent upon the rhodamine B/acetonitrile interactions and not merely due to the bulk-phase behavior of the $scCO_2$, we measured the compressibility of the $scCO_2$/acetonitrile mixture and found it to be independent of the acetonitrile concentration to less than ~0.047 mole fraction. We fit the compressibility data using the Peng-Robinson equation of state because it is most appropriate for fluids in the region between 1.72 MPa and 12.45 MPa and between 313 K and 333 K.

491.
KINETICS AND MECHANISM OF ß-SHEET ALIGNMENT AND FIBRIL NUCLEATION BY A PRION PEPTIDE. ***Sarah A. Petty** and Sean M. Decatur, Department of Chemistry, Mount Holyoke College, Carr Lab, 50 College Street, South Hadley, MA 01075, Fax: 413-538-2327, spetty@mtholyoke.edu*

Syrian hamster PrP(109-122) (H1) forms ß-sheets in vitro. Isotope-edited infrared spectroscopy has shown that the initial antiparallel ß-sheet formed is disordered, with no regular register across the strands; however, time or heat can induce the realignment of H1 until the hydrophobic core of the strands pack together and residue 117 is aligned across the sheet. The realignment kinetics have been monitored for wild-type and mutated H1 (A117I, A117L and A117Abu) at varying concentrations. At low concentration the H1 realignment mechanism involves detachment and reannealing of ß-strands whereas at higher concentrations a reptation mechanism is observed. Once ordered and aligned

General Search Results--Full Record

Article 1 of 1

MARK

Interaction of be with carboxylates in proteins and influence of the dielectric environment.

Snyder JA

ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY
229: 487-PHYS Part 2 MAR 13 2005

Document type: Meeting Abstract **Language:** English **Cited References:** 0 **Times Cited:** 0

Addresses:
NIOSH, Analyt Serv Branch, Hlth Effects Lab Div, Morgantown, WV 26505 USA

Publisher:
AMER CHEMICAL SOC, 1155 16TH ST, NW, WASHINGTON, DC 20036 USA

IDS Number:
008UQ

ISSN:
0065-7727

Article 1 of 1