

**Homework 14a Advanced Thermodynamics**  
**Due Tuesday December 7, 2020**

Dye-sensitized solar cells were originally produced using titania nano-aggregates (Evonik P25 used in white paint and paper), and electrolyte ( $I^-/I_3^-$  redox pair), and an organic dye (berry juice). Sunlight is absorbed by the dye which is adsorbed to the titania nanoparticles, the solar energy oxidizes the dye releasing electrons to the titania which conducts them to the anode through a particle network. The dye is reduced by the electrolyte and  $I^-$  ions diffuse to the cathode to be reduced. This Graetzel cell performs best with a monolayer of dye and a co-adsorbent, chenodeoxycholic acid (CDCA), is used to prevent agglomeration of the dye. The mechanism of action for this co-adsorbent is not known. Mao Z; Liu W; Cai H; Shi J; Wu Z; Yang Y; Duan J *A kinetic/thermodynamic study of transparent co-adsorbents and colored dye molecules in visible light based on microgravimetric quartz-crystal microbalance on porous TiO<sub>2</sub> films for dye-sensitized solar cells* Phys. Chem. Chem. Phys DOI: 10.1039/d0cp05403h (2020) used a quartz-crystal microbalance and the Langmuir model to determine the adsorption rate and thermodynamics for three ruthenium/organic dyes and CDCA. In the microbalance the change in a quartz crystal oscillator's vibrational frequency,  $\Delta f$ , is proportional to the change in mass on the crystal,  $\Delta m$ , a larger mass has a lower frequency, Mao Fig. 1. The kinetics of absorption can be measured in this way.

- a) Derive the Langmuir model for adsorption using a thermodynamic approach. List the assumptions you need for this model.
- b) Compare your derivation with equations 2 of Mao at equilibrium where  $d\theta/dt$  reaches 0. How do his assumptions differ?
- c) Figure 3 shows an Arrhenius plot to determine the activation energy,  $E_a$ . Explain the assumptions involved in the Arrhenius equation and their reasonableness for this experiment. Do you think that the data presented is sufficient for this type analysis?
- d) CDCA is a bile acid ("cheno" is Greek for goose and it is found in goose bile) that forms micelles. In Fig. 4 the dyes follow Langmuir equation while CDCA does not. Explain why CDCA might not follow the Langmuir equation.
- e) Derive the van't Hoff equation, equation 8. Explain how Fig. 5 shows that the adsorption is endothermic. Mechanistically, how could entropy increase on adsorption (intercept is positive, adsorption occurs in ethanol).