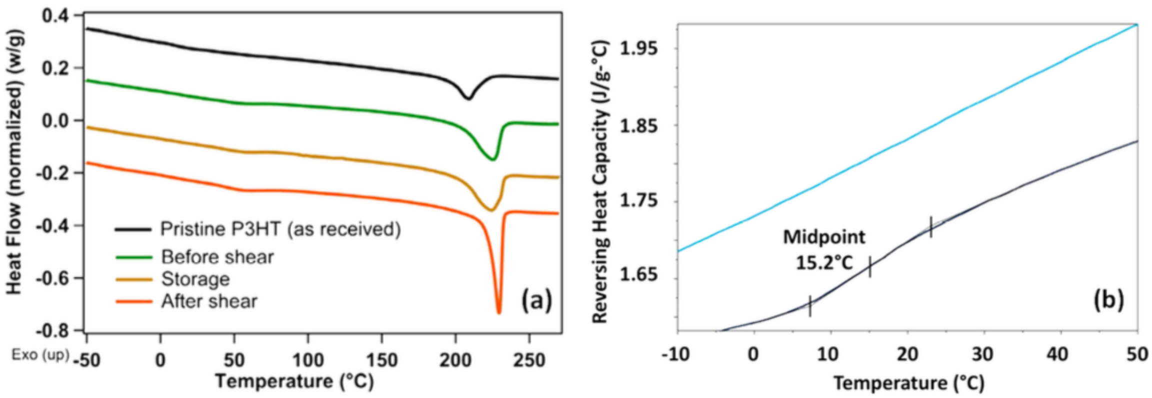
Thermodynamics Question 1

Nguyen NA, Remy RA, Mackay ME *Thermal Analysis of Semiconducting Polymer Crystals Free of a Mobile Amorphous Fraction* Macromolecules 2021 https://dx.doi.org/10.1021/acs.macromol.0c02509 grew crystals of poly(3-hexyl thiophene) (P3HT) that were microns in length and 6 by 21 nm in lateral dimension. They used the Gibbs-Thompson (GT) equation to describe the melting point depression for these nanocrystals. While the data agrees with the GT prediction for melting point, an analysis of the heat of melting didn't follow the GT expression. Nguyen was able to correct the GT expression for the enthalpy of melting using the heat capacity.



(a) (b)

Figure 1. Differential scanning calorimetry results for P3HT prepared under different conditions. (a) Standard DSC for P3HT as received (Pristine P3HT (as received)) and dissolved in 2-EN then prepared to make a DSC sample immediately after preparation (Before Shear), stored for 24 h (Storage), and sheared for 24 h at 100 s−1 (After Shear). (b) Reversing heat capacity as a function of temperature for the After Shear sample (upper curve) and the Pristine sample (lower curve).

a) Explain how figure 1 (a) was obtained by describing the differential scanning calorimeter. How is the reversing heat capacity in figure 1 (b) obtained?

b) From Figure 1(b) what can be said about the After Shear sample compared to the Pristine sample?

c) Nguyen gives the following GT equation for his parallelepiped samples,

$$T_m = T_m^{\infty}\left[1 - \frac{2\sigma_e}{L\rho_c \Delta\hat{H}_m^{\infty}} - \frac{2\sigma_s}{h\rho_c \Delta\hat{H}_m^{\infty}} - \frac{2\sigma_f}{w\rho_c \Delta\hat{H}_m^{\infty}}\right]$$

Derive the GT equation and explain Nguyen's modification for a parallelepiped. Why is the melting point depressed for nanocrystals? ρ_c is the crystalline mass density, *L, h, w* are the sizes of the parallelepiped, σ are the surface energies.

d) Nguyen gives the following expression for the melting enthalpy of a nanocrystalline parallelepiped,

$$\Delta\hat{H}_m = \chi_c\left\{\Delta\hat{H}_m^{\infty} - \frac{2\sigma_e}{L\rho_c} - \frac{2\sigma_s}{h\rho_c} - \frac{2\sigma_f}{w\rho_c}\right\}$$

Explain the origin of this equation. Why is the enthalpy of melting reduced for nanocrystals? χ_c is the degree of crystallinity which can be assumed to be 1.

e) Nguyen corrects the equation in question "d" with the expression,

$$\Delta\hat{H}_m = \chi_c \left\{ \Delta\hat{H}_m^{\infty} - \frac{2\sigma}{d\rho_c}\left[1 + \frac{C_{pl} T_m^{\infty}}{\Delta\hat{H}_m^{\infty}}\right] \right\} \quad \text{where} \quad \frac{2\sigma}{d\rho_c} \equiv \frac{2\sigma_e}{L\rho_c} + \frac{2\sigma_s}{h\rho_c} + \frac{2\sigma_f}{w\rho_c}.$$

Explain the reasoning for the difference between this expression and that in question "d".

Thermodynamics Question 2

a) The Langmuir absorption equation gives the fraction of surface sites bound with an adsorbent (A), θ_A, as a function of the partial pressure or concentration of the adsorbent in a solution or gas in contact with the surface, p_A,

$$\theta_A = \frac{K_{eq}^A p_A}{1 + K_{eq}^A p_A}$$

Where K^A_{eq} is the thermodynamic equilibrium constant. Derive the Langmuir equation using a thermodynamic approach. List the assumptions.

b) 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 TiO2 films for dye-sensitized solar cells* Phys. Chem. Chem. Phys DOI: 10.1039/d0cp05403h (2020) use a kinetic equation to describe adsorption of a dye onto titania,

$$\frac{d\theta}{dt} = k_a(1-\theta)c - k_d\theta \qquad (2)$$

where k_a and k_d are the adsorption and desorption rate constants. How is this equation related to the equilibrium Langmuir equation given above?

c) Figure 3 of Mao is shown below. What is the purpose of this plot and what assumptions are involved? Are these assumptions appropriate for adsorption of dye from a solution on a titania surface?

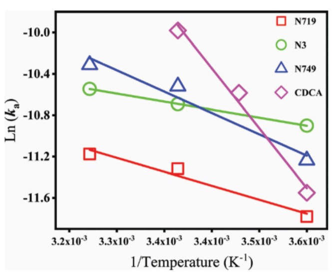
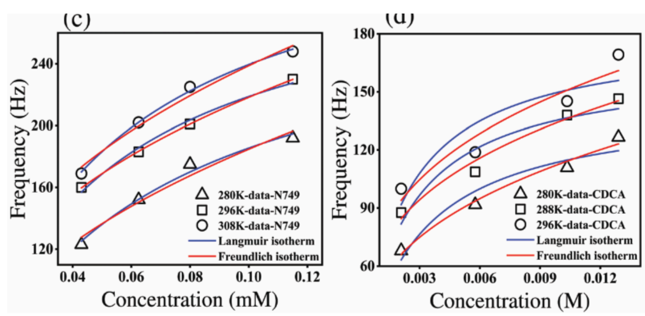


Fig. 3 Arrhenius plots for the adsorption of N719, N3, N749 and CDCA onto TiO_2 surfaces.



d) CDCA (chenodeoxycholic acid) in Figure 3 is a bile acid used to improve adsorption of the dyes ("cheno" is Greek for goose and CDCA is found in goose bile). CDCA forms micelles. In the two graphs to the right, (c) is for adsorption of a dye N749 and (d) is for adsorption of CDCA. The dye follows the Langmuir equation while CDCA does not. Explain why CDCA might not follow the Langmuir equation.

e) Mao uses the van't Hoff equation to determine if the adsorption is exothermic, $\frac{d(\ln K_{eq})}{dT} = \frac{\Delta H}{RT^2}$. Explain how this equation is used in figure 5, below, to make this determination. Is the adsorption endothermic or exothermic?

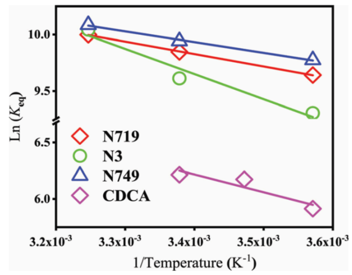


Fig. 5 Van't Hoff plots for the adsorption of N719, N3, N749 and CDCA onto the TiO_2 surfaces.