Chem. Engr. 06-607 Physical Chemistry of Colloids and Surfaces

Homework #3 **2-12-02**

Due: 2-19-02, beginning of class.

1. The following data were collected for a porosimetric analysis of a catalyst preparation; the cumulative pore volume *(V*)* occupied by mercury per gram of catalyst is given for the applied pressures indicated:

Pressure (psi)	**V* (cm^3/g)**	**Pressure (psi)**	**V* (cm^3/g)**
1,000	0.082	20,000	0.228
1,500	0.115	25,000	0.249
2,000	0.132	30,000	0.276
3,000	0.150	35,000	0.307
4,000	0.160	40,000	0.336
6,000	0.177	45,000	0.358
10,000	0.190	50,000	0.363
15,000	0.213		

Plot these data, and from the tangents to the curve estimate dV^*/dR at 2,000, 10,000, 30,000, and 45,000 psi. To what radii do these pressures correspond? Use g_L = 484 mN/m and q = 140 degrees for these calculations.

2. The Szyszkowsky equation is a semi-empirical equation describing the surface tension of dilute aqueous solutions of organic compounds:

$$\frac{g}{g_0} = 1 - b\ln\left(1+\frac{c}{a}\right)$$

where g_0 is the surface tension of pure water, c is the bulk concentration of organic solute, and a and b are empirical constants. Show that the adsorption of organic solutes to the air/water interface (described by the Szyszkowsky equation) fits the Langmuir adsorption model. How are the constants a and b are related to G_{max} and K' defined as follows?

$$G = \frac{G_{max}c}{K'+c}$$

3. The Temkin equation of state has the form $P_s = aG^2/G_{max}$ where a is a constant and G_{max} has the same meaning as in the context of the Langmuir adsorption isotherm. Derive an equation describing how the surface pressure will change upon increasing the bulk concentration from an initial value c_0 to a final value c.

4. Surface tensions of aqueous solutions of dodecyldimethylammonium chloride (DODA) at T = 20 C were measured with no added electrolyte and 0.20 M NaCl. The results are tabulated below.

No Salt		**0.2 M NaCl**	
***c* (M)**	***g* (mN/m)**	***c* (M)**	***g* (mN/m)**
1×10^{-5}	72	1×10^{-5}	72
8×10^{-5}	71.5	1.5×10^{-5}	70
3×10^{-4}	71	5×10^{-5}	66
1.0×10^{-3}	68	1.6×10^{-4}	58
2.0×10^{-3}	64	4.0×10^{-4}	52
3.5×10^{-3}	58	9.0×10^{-4}	46
5.6×10^{-3}	52	1.5×10^{-3}	40
9.5×10^{-3}	45	2.5×10^{-3}	35
1.1×10^{-2}	41	3.9×10^{-3}	34
1.4×10^{-2}	37.5	5.0×10^{-3}	34
2.0×10^{-2}	37.5	4.0×10^{-2}	34
4.0×10^{-2}	37.5		

a) Why does the surface tension go to a constant value at high concentrations?

b) Find the surface excess *(G)* and area/molecule (a_0) at $c = 1 \times 10^{-3}$ M and $c = 1.4 \times 10^{-2}$ M for the salt-free case.

c) Find the surface excess *(G)* and area/molecule (a_0) at $c = 1 \times 10^{-3}$ M and $c = 2 \times 10^{-2}$ M for the 0.2 M NaCl case.