Tutorial on Molecular Interactions II

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Polymers

Problem 1 Elasticity (General)

Derive an expression for the force required to stretch a polymer chain and explain any assumptions you make.

Problem 2 Elasticity (DNA)

The two ends of a given DNA chain are attached to micro-beads which can then be manipulated with optical tweezers to stretch the chain. The DNA molecule may be considered as a random chain with $N = 1000$ and an effective freely-linked segment size $a = 50$ nm (this large segment size, taken equal the persistence length of the chain, is due to the very stiff backbone of the DNA).
a) Estimate the tension in the chains when the beads are held 6 μm apart under Θ-conditions (i.e., ideal random walk behaviour).
b) What is then the stored elastic energy in the stretched molecule ?
c) What would the tension and stored energy be if the DNA were in good solvent conditions ?

Problem 3 Osmotic pressure

Would you expect the osmotic pressure Π of a dilute ($c << c^*$) polymer solution in a Θ-solvent to be greater or smaller than its value in a good solvent, for a given c ? Give reasons.

Problem 4 M_n and M_w

A certain protein associates into dimers and tetramers in the molar proportions of monomers: dimers: tetramers in the ratio 4:2:1. Calculate the number average and weight average molecular weights of the mixture taking the molecular weight of the monomer to be 100k.

Problem 5 M_w and B

The following results were obtained for a globular protein:

Π / Pa	16.00	32.10	48.35	64.70	81.15
c/g cm^{-3}	1.0	2.0	3.0	4.0	5.0

Calculate the molecular weight of the protein and its second virial coefficient.

Amphiphilic Molecules

Problem 6 Surface tension and CMC

At 300 K measurements of the surface tension, γ, of solutions of the surfactant $C_{12}H_{25}(OC_2H_4)_3OH$ in water as a function of its concentration are given below.

c / 10^{-6} M	0.56	1.00	1.80	3.20	5.60	10.0	18.0	32.0	56.0	100	560
γ /mN m^{-1}	66.6	64.1	60.8	57.1	53.2	47.8	41.9	31.7	29.5	28.7	28.2

a) Plot a graph of γ against $\ln(c)$. Account qualitatively for the shape of this graph and estimate the critical micelle concentration (CMC).

b) The Gibbs equation ($d\gamma = -\Gamma RT d\ln(c)$) may be used to describe the variation of the surface excess Γ with concentration. Calculate Γ and γ at the concentrations 1.0×10^{-6}, 6.0×10^{-6}, 1.8×10^{-5}, and 3.0×10^{-5} M.

c) Given that the surface pressure π is given by $\pi = \gamma_0 - \gamma$ where γ_0 is the surface tension of pure water (72 mN m^{-1}) plot Γ against π. Comment on the shape of the curve and estimate the area, A, occupied by a single molecule when the monolayer is saturated.

d) A molecule in a saturated monolayer of the closely related surfactant $C_{12}H_{25}(OC_2H_4)_6OH$ occupies 0.52 nm^2. Comment on the reasons for the difference in this value for the two molecules.

e) How would you expect the variation of surface tension with concentration to differ for surfactants of different chain length but in the same series ? How might this behaviour be modified by changes in temperature ?

Methods

Problem 7 Scattering (General)

a) Explain how scattering can be used to address questions related to (i) the radius of gyration of polymers and (ii) the structure of surfactants.

b) What are the respective benefits of using (i) neutrons and (ii) X-rays ?

Problem 8 Scattering (Guinier's law)

The intensity of X-rays scattering by a 50 mg/cm protein solution falls by a factor of 10 then κ increases from 0.1 to 1.0 nm^{-1}. If the scattering obeys Guinier's law, what is the radius of gyration of the protein ?

Explain what is meant by the radius of gyration of a polymer. How is it related to the end-to-end distance for a single chain polymer and what is its significance?