Calculation of the free polymer fraction

The used approach[1s] for calculating the fraction of free polymer in solution assumes that the laponite RD is composed of a certain number of sites of binding each one interacting with one polymer molecule.

$$S_t = z\, m_{RD} \qquad (1s)$$

where S_t is the total number of interaction sites per kg of water, z is the number of moles of sites per moles of laponite RD formula unit and m_{RD} is the laponite molality calculated using the molecular weight of the laponite RD unitary cell. This model allowed[1s] to determine the thermodynamics of adsorption of polymers on the solid substrate. The equilibrium constant (K_1) and the polymer mass balance are given by

$$K_1 = x_1/[m_{P,w}\,(1-x_1)] \qquad m_P = m_{P,w} + z\, x_1\, m_{RD} \qquad (2s)$$

where x_1 is the fraction of the laponite RD site occupied by one macromolecule, m_P and $m_{P,w}$ are the stoichiometric and the unbound polymer molalities, respectively.

By combining K_1 and the polymer mass balance one may write

$$x_1 = \frac{K_1 m_{RD} z + K_1 m_P + 1 - \sqrt{(K_1 m_{RD} z)^2 + 2K_1 m_{RD} z(1-K_1 m_P) + (K_1 m_P)^2 + 2K_1 m_P + 1}}{2K_1 m_{RD} z} \qquad (3s)$$

Once that K_1 and z values are known,[1s] x_1 and $m_{P,w}$ can be computed by means of eqs 3s and 2s, respectively. From those values the fraction of unbound polymer (x_p) and its volume fraction ($\phi_{p,free}$) are given by

$$x_p = m_{P,w}/m_P \qquad \phi_{p,free} = x_p \phi_p \qquad (4s)$$

where ϕ_p is the stoichiometric polymer volume fraction.

Reference

1s. De Lisi, R.; Lazzara, G.; Lombardo, R.; Milioto S.; Muratore, N.; Turco Liveri M.L. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3994.