Problem 2

There is a multitude of applications where PDMS (polydimethylsiloxane) membranes are used to extract or deliver an analyte from/to an aqueous medium (e.g. Kwon et al. 2007 Journal link Download paper); Kwon and Escher 2008 Journal link Download paper); Mayer et al. 1999 Journal link Download paper)). The transfer kinetics are governed by molecular diffusion through the aqueous boundary layer and the PDMS membrane itself. While the diffusion coefficients for any compound will be much larger in water than in PDMS this does not necessarily mean that diffusion in PDMS is the rate limiting step because the capacity of PDMS for non-polar compounds is orders of magnitude higher than that of water (i.e. the movement in PDMS is slower but there are much more molecules moving at any time).

Calculate for which partition coefficient $K_{PDMS/water}$ (m^3/m^3) the diffusive transfer resistance through both layers is equal. Use PDMS thicknesses of 30, 100, and 500 μm, aqueous boundary layer thicknesses of 15 μm (achievable by strong stirring) and 100 μm, a D_{PDMS} of about 10^{-7} cm^2/sec (Kwon et al. 2007) and a D_{water} of about 10^{-4} cm^2/sec.

Help:

The transfer resistancies can be expressed analogously to those for air/water exchange.

Answer:

$K_{PDMS/water}$ (m^3/m^3)-values for which the diffusive transfer resistances through PDMS and water layer are equal:

thickness of aqueous boundary layer/ μm	**thickness of PDMS layer/ μm**		
	30	**100**	**500**
15	$2 \cdot 10^3$	$6.7 \cdot 10^3$	$3.3 \cdot 10^4$
100	$3 \cdot 10^2$	$1 \cdot 10^3$	$5 \cdot 10^3$

For your orientation: non-polar chemicals have $K_{PDMS/water}$ (m^3/m^3)-values in the order of 10^3 to 10^6. Polar organic chemicals such as many pesticides will have $K_{PDMS/water}$ (m^3/m^3)-values smaller than 10^3. Hence, we can conclude from the above results that for 15 μm aqueous boundary layer the transfer kinetics of polar compounds ($K_{PDMS/water}$

(m^3/m^3) < $2 \cdot 10^3$) will be dominated by the PDMS layer if this is thicker than 30 μm. Of course, there is a gradual transition between polar and non-polar chemicals and not a clear border line. Watch out for DOM facilitated transport through the water laminar layer though (ter Laak et al. 2009 Journal link Download paper).