Do we know what goes on at the surface of water?"

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Morkshop on Water at the Interface between Biology, Chemistry, Physics and Materials Sciences

Sometimes, it may be useful to examine water on the macro scale

To help explain what is happening on the nano scale





<u>Simple answer; given by most sources</u>

It is a colligative property like freezing point depression, boiling point elevation and vapour pressure lowering.

It depends on the concentration of the solute molecules or ions but does not depend on their size or structure.

The osmotic pressure of an aqueous solution is the pressure needed to stop the flow of water into the solution and across a semipermeable membrane







water drawn in, as though under pressure difference





Water molecules leaving the lower-water activity compartment will require more energy as they cause the formation of a localized even lower activity water in their wake. Therefore only higher energy water molecules can leave this compartment; necessarily a smaller amount than travel in the opposite direction



water drawn in until sufficient backpressure opposes it









The correction is due to approximations in the way that concentrations are calculated relative to the number of particles; They are only accurate at low concentrations



Fuller answer; in good physical chemistry textbooks

The colligative properties are caused by the increase in entropy of the solution on mixing solutes with the water



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It depends on the ratio of the solute molecules to the 'free' water molecules.

solution potential = water potential + RTLn(xw) solution potential = water potential + RTLn(aw)



Fuller answer

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Dissolving a solute in liquid water thus makes the liquid water more stable with lower activity







The tendency of a solution to take in water by osmosis.

It can be generated by a reduction in the water activity.

Any method that reduces the water activity will work.





The tendency of a solution to take in water by osmosis.

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Any method that reduces the water activity will work.

It does not require a membrane; just two phases





Rau et al, PNAS 81 (1984) 2621.

It can be produced on the nanoscale between molecules

e.g. DNA, hydroxypropylcellulose; ~10 MPa

Here it is a surface effect and not dependent on number of particles

Rau et al, PNAS 81 (1984) 2621 Parsegian and Zemb, *Curr. Opin. Colloid Interface Sci.* **16** (2011) 618.



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e.g. DNA, hydroxypropylcellulose; ~10 MPa

Here it is a surface effect and not dependent on number of particles

"Even at a huge pressure of 1000 atm, this work expressed as a perturbation of an individual water is only $\frac{3}{4}$ k_BT, comparable to the energy of a free water molecule driven by thermal energy. A small transfer (chemical) potential shows up as major physical work because the displacement of the surfaces incurs displacements of many water molecules."

Rau et al, PNAS 81 (1984) 2621 Parsegian and Zemb, *Curr. Opin. Colloid Interface Sci.* **16** (2011) 618.



Formation of osmotic pressure at water interfaces





Osmotic pressure without solutes?



The two phases could be a porous sheet and the bulk solution

If the water in the sheet has low activity and the sheet is strong and not too elastic



Osmotic pressure using particles? Forward osmosis



Solutes are not required to change the osmotic pressure of water



Draw solution contains poly(N-isopropylacrylamide) uncharged super hydrophilic nanoparticles

Ling and Chung,, Desalination 278 (2011) 194

What determines osmotic pressure?

PEG 20,000 has almost the same osmotic pressure as PEG 1000 with both at 40% weight

Does not depend on the number of entities

Cohen et al, J. Phys. Chem. B, 113 (2009) 3709



PEG 20,000 has almost the same osmotic pressure as PEG 1000 with both at 40% weight

Does not depend on the number of entities

Osmotic pressure of a poly sodium acrylate (PSA); 0.4 atm

Same PSA; attached to magnetic particles; 11.4 atm

To get 11.4 atm requires 200 x more free PSA

Does not depend on the number of counter charges



Dey and Izake, Desalination 373 (2015) 79.

Osmotic flux of a poly sodium acrylate on carbon particles is only three times that of uncharged N-isopropyl acrylamide on carbon particles

Osmotic pressure does not depend on any charges



Osmotic flux of a poly sodium acrylate on carbon particles is only three times that of uncharged N-isopropyl acrylamide on carbon particles

Osmotic pressure does not depend on any charges

Therefore the osmotic pressure does not depend on the charge of the particles

Also, the osmotic effect operates outside of the particles



Li, et al, Soft Matter 7 (2011) 10048.

Does depend on lowered water activity within the particles

The hydrophilic particle surface holds on to the water:lowers water activity

Pore capillarity and confinement holds on to the water:lowers water activity



Does depend on lowered water activity within the particles

The hydrophilic particle surface holds on to the water:lowers water activity

Pore capillarity and confinement holds on to the water:lowers water activity

With polyelectrolytes, the high concentration of fixed binding sites prevent the counterions leaving the particles

With neutral hydrophiles, the high concentration of water binding sites holds the water tightly



Does depend on lowered water activity within the particles

The hydrophilic particle surface holds on to the water:lowers water activity

Pore capillarity and confinement holds on to the water:lowers water activity

The low potential water molecules must transfer their reduced entropy to their neighbours away from the surface until it can be balanced by the averaged energy of 'bulk' water.





Also excluded are low molecular weight dyes

Zheng et al, Adv. Colloid Interface Sci. 127 (2006) 19





Similar results with many other materials such as neutral cellophane and cellulose acetate; also with other polar solvents such as ethanol and DMSO

Sulbarán et al, *Cellulose* **21** (2014) 1143



Osmotic pressure without solutes?





Osmotic pressure without solutes?



 $1 \ \mu m$ beads

Zinc metal



Chai et al., Contemp Mater. 3 (2012) 1

Formation of osmotic pressure at water interfaces

- 1. Surface interacts with interfacial water
- 2. Greater proportion of strong clustering at interface
- 3. Lower proportion of 'free' water (x_w/x_B) at surface
- 4. Lower activity of water at interface $(a_w = x_w)$
- 5. Lower water potential at surface by $RTLn(x_w/x_B)$
- 6. Water drawn in until osmotic pressure in interfacial water opposes; $\Pi = -(RT/V_M).Ln(x_w/x_B)$
- 7. Solutes expelled from interfacial water to bulk or surface
- 8. Surface volume affected is the Nernst 'unstirred' layer



How deep is the Nernst 'unstirred' layer

Often underestimated

Far greater than can be found by any modelling; it depends on the radius of the surface

Generally thought to be difficult to estimate

Fortunately, unstirred layers are easily estimated from the kinetics of immobilised enzymes

Typically several microns in stirred particle solutions and greater on surfaces of enzyme biosensors



How deep is the exclusion zone?



As expected relationship to 'unstirred' layer

Nhan and Pollack, Int. J. Des. Nat. Ecodyn. 6 (2011) 139.



Osmotic pressure without solutes?



Osmotic pressure is proportional to -Ln(mole fraction of 'free' water). As the 'free' water reduces within the unstirred layer (~4-100 μ), so the osmotic pressure increases.



What goes on at the water/ice surface



Surface of liquid water on ice due to reduced water activity

Thickness (Å)





What goes on at the water/ice surface



Surface of liquid water on ice due to reduced water activity

Figures in red are the water activities

The layer thickness as a function of temperature depends only on the liquid water activity.



Henson et al, J. Chem. Phys. 123 (2005) 144707

What goes on at the water/ice surface



Surface of liquid water on ice due to reduced water activity

Figures in red are the water activities

Figures in blue are the freezing point depressions corresponding to the water activities.

Freezing point depression ^{10²} does not depend on solutes





Microsphere-free region in various [NaCI] solutions. All chambers contained suspensions with 2 μ m carboxylate-functionalized microspheres (0.025% v/v solids). Images are taken 4 hours after addition of microspheres to chambers.

Mork & Pollack, J. Undergrad. Res. Bioeng. (2008-2010) 105-113, U. Washington.





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Osmotic pressure is proportional to -Ln(mole fraction of 'free' water). As the 'free' water reduces within the unstirred layer, so the osmotic pressure increases. This will oppose the pressure generated by the surface tension.

Conclusions

Macro-scale phenomena can have effects on the nanoscale

Colligative properties do not 'require' solutes

Osmotic pressure has effects on all scales

Osmotic pressure causes exclusion zones



More on Water @

www.lsbu.ac.uk/water

Any questions?