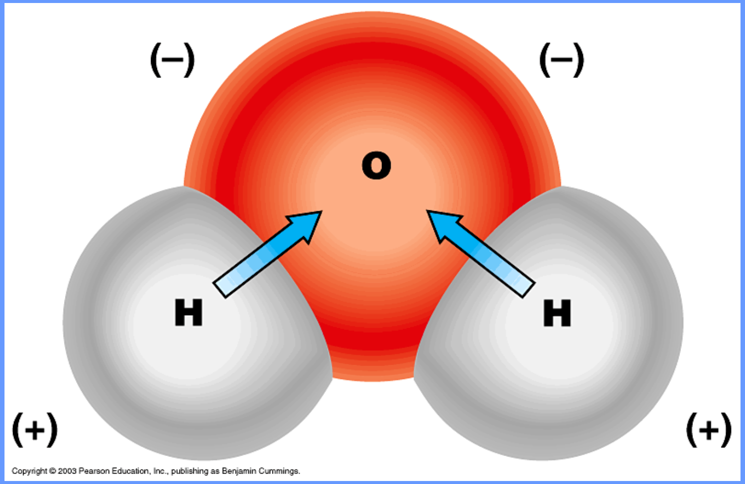
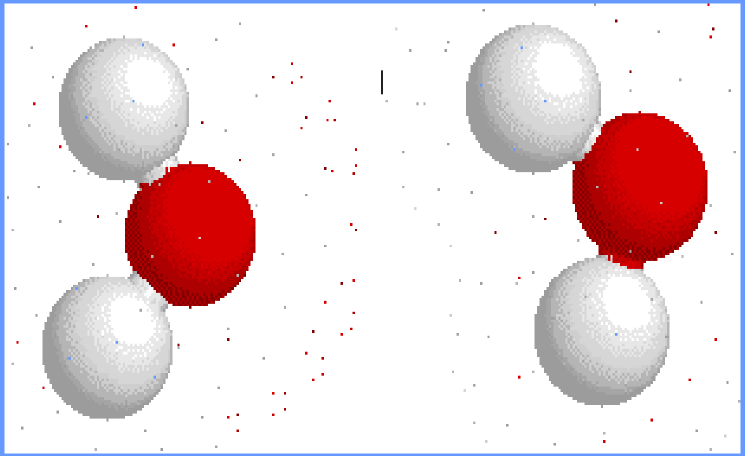
From Pure Water to Biomolecules in Non-Aqueous Solutions

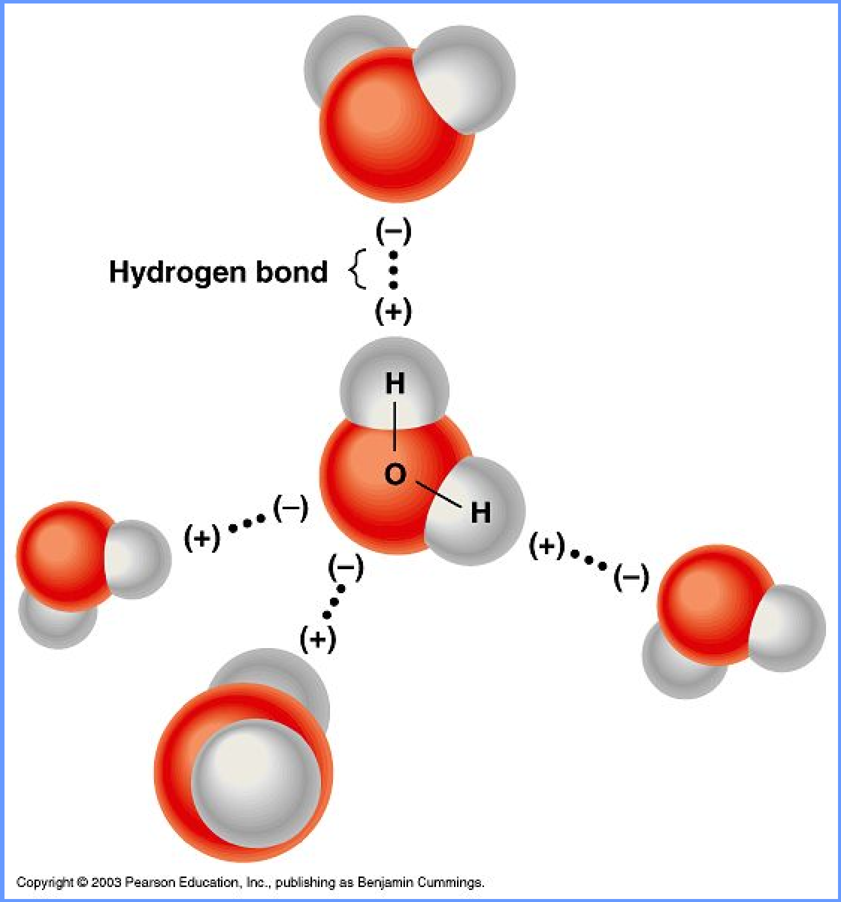
Babak Minofar


Hydrogen Bonds In Water

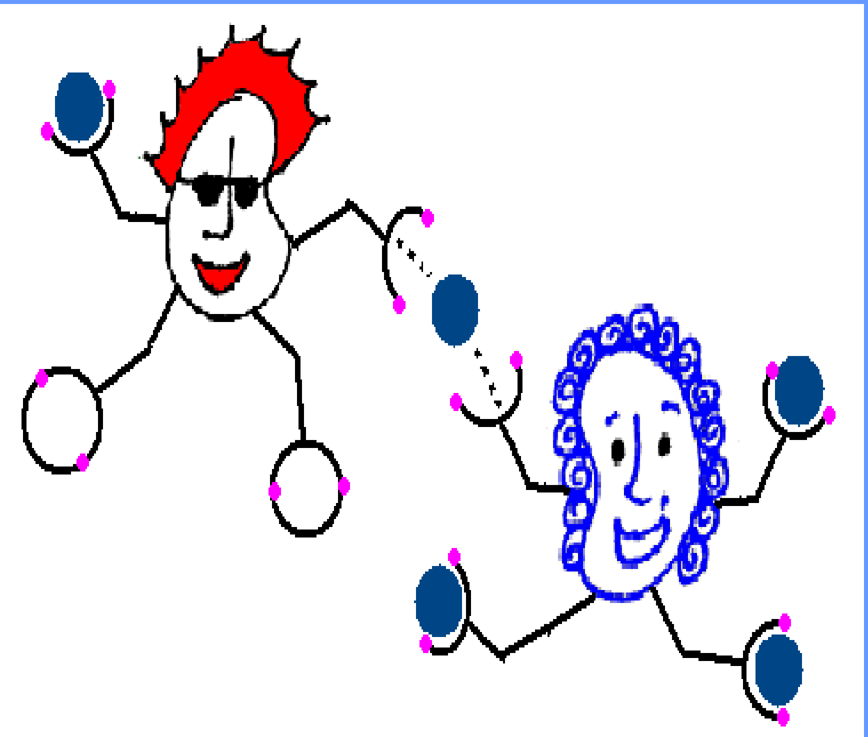
- Between a highly electronegative atom of a polar molecule and a hydrogen atom
- One hydrogen bond is weak but many hydrogen bonds are strong

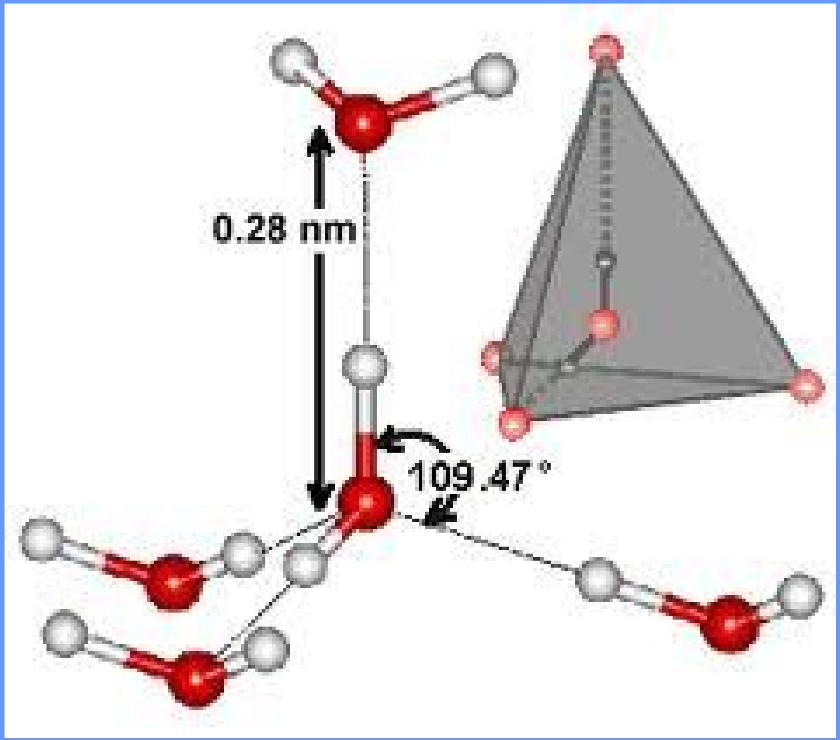


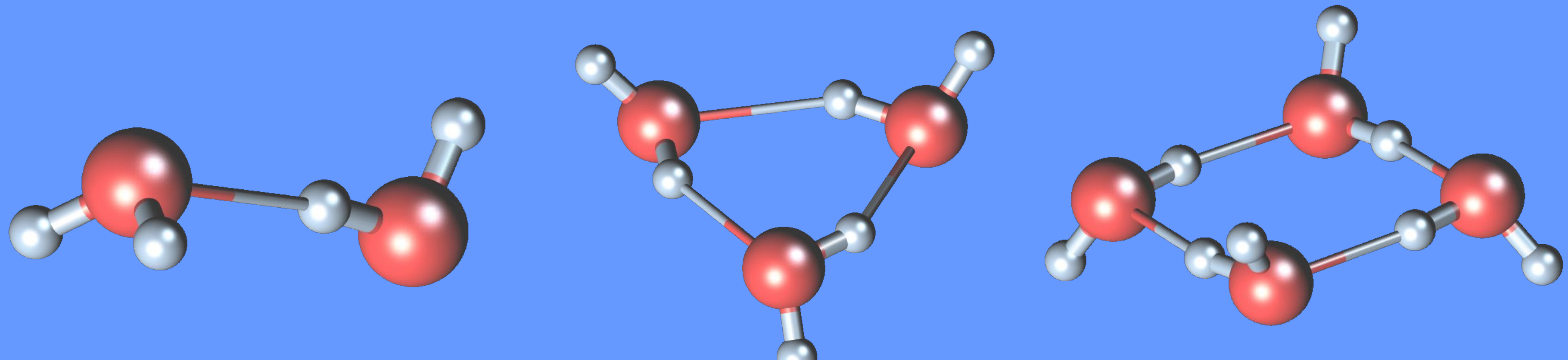




Water Clusters





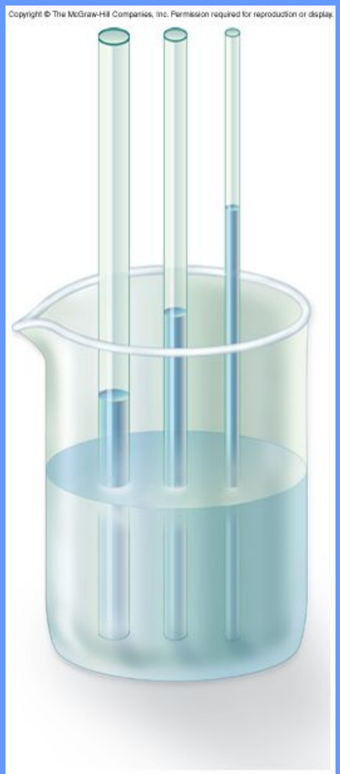


Cohesion

- Attraction between particles of the same substance.
- Hydrogen bonds make water cohesive and give water surface tension.
- Produces a surface film on water that allows insects to walk on the surface of water

Adhesion and Capilarry

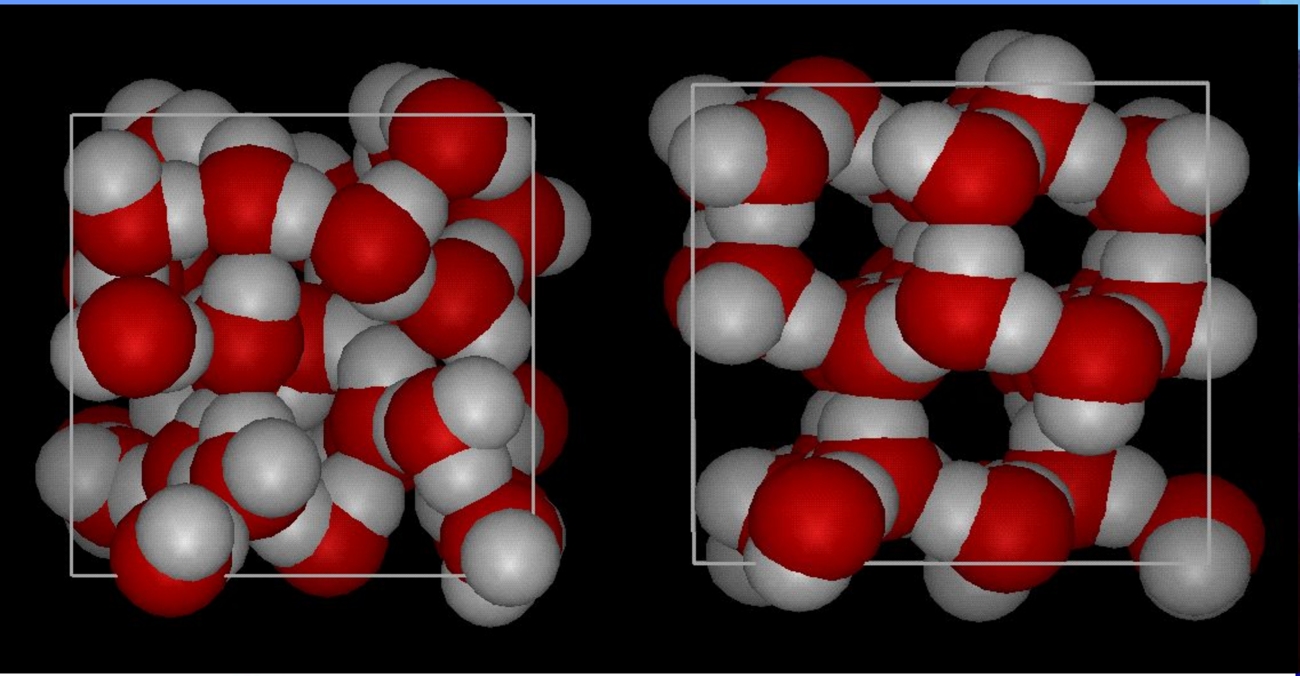
- Attraction between two different substances.
- Water makes hydrogen bonds with other surfaces such as glass, soil, plant tissues, and cotton.
- Because water has both adhesive and cohesive properties, capillary action is present. Capillary action is one of the major reasons that trees and other plants can grow very tall.

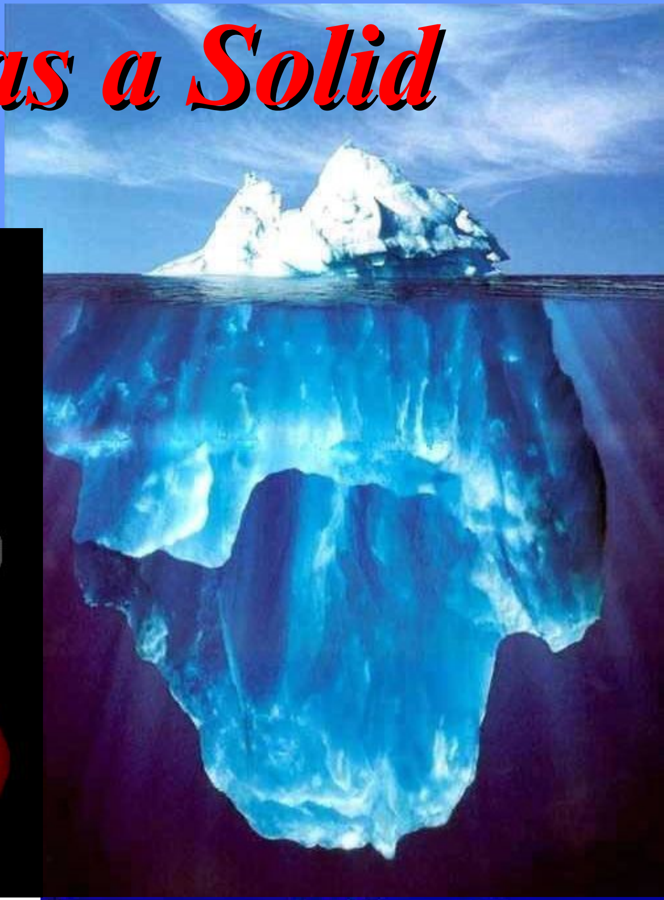


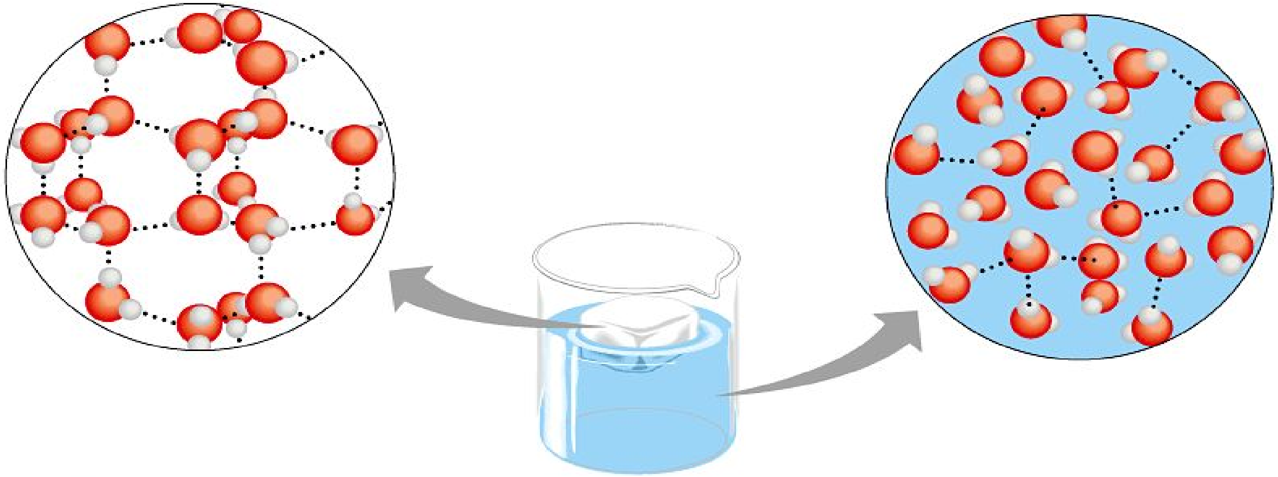
Color of Water

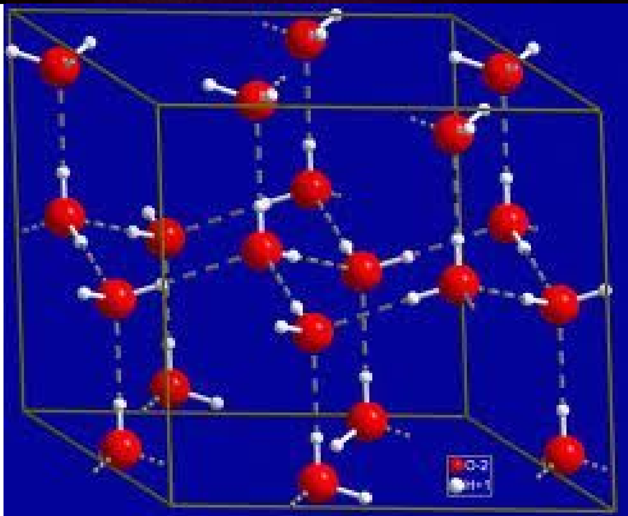
The blueness of the water is neither due to light scattering nor dissolved impurities. In water color is caused by the absorption of both red and yellow light. The absorption spectrum of ice is similar to that of water, except that hydrogen bonding causes all peaks to shift to lower energy - making the color greener.

Water is Less Dense as a Solid









The Snowflake Man

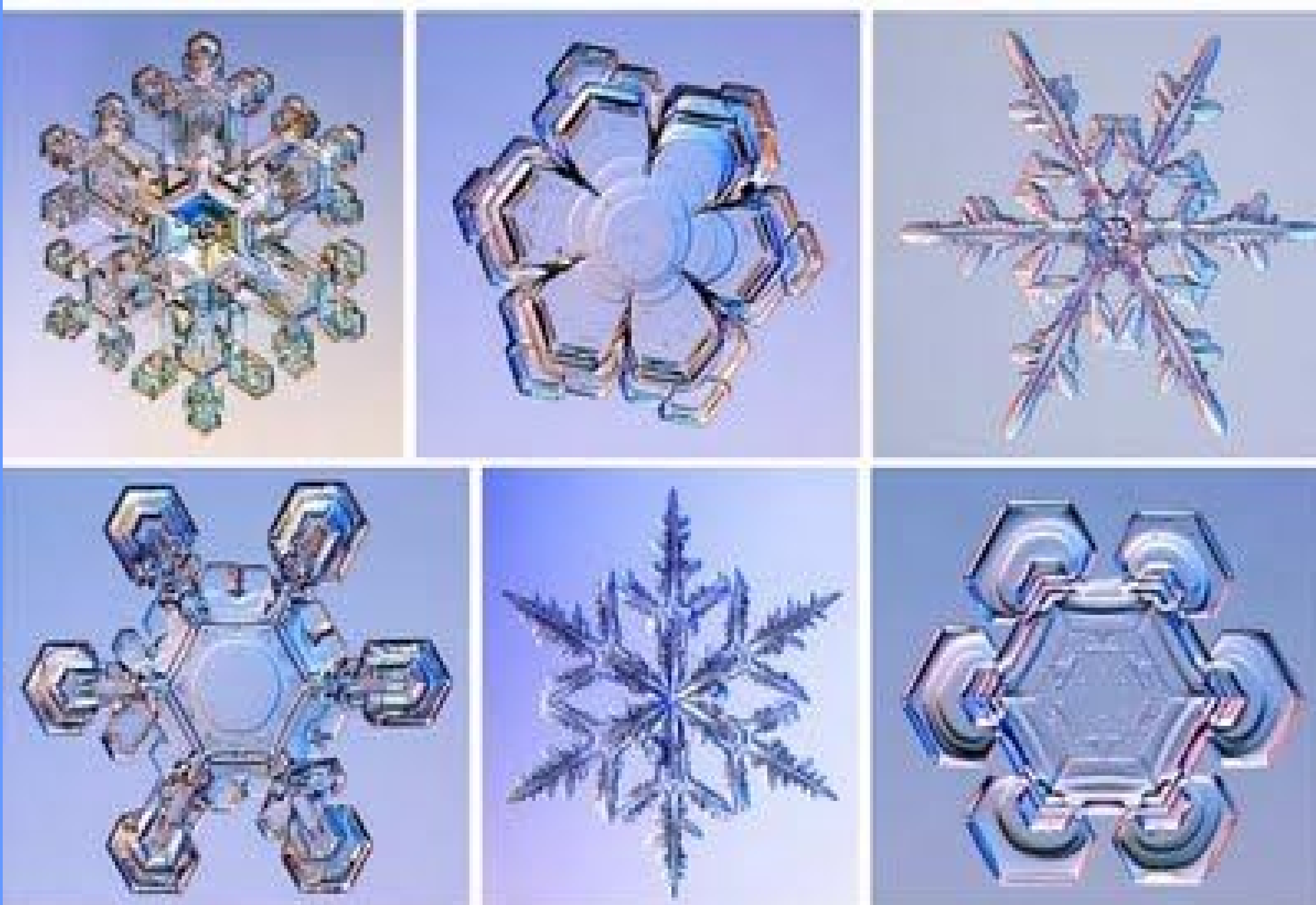
Wilson Bentley (1865 -1931)







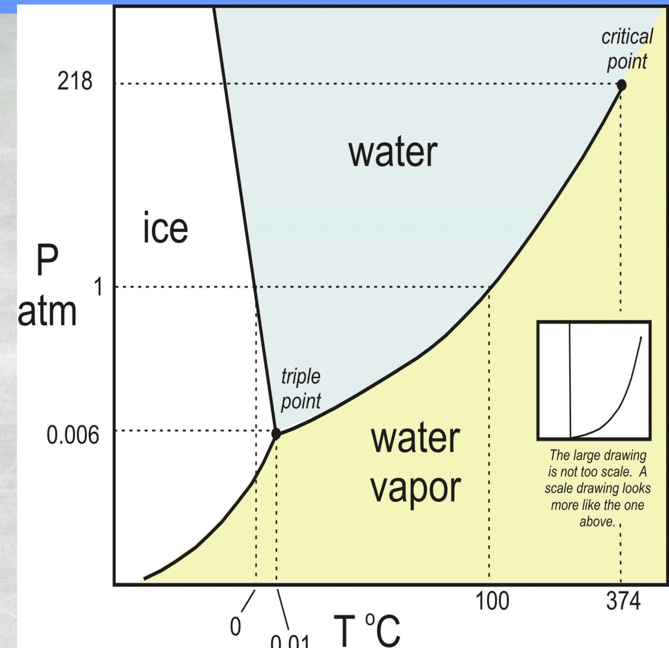

The Snowflake

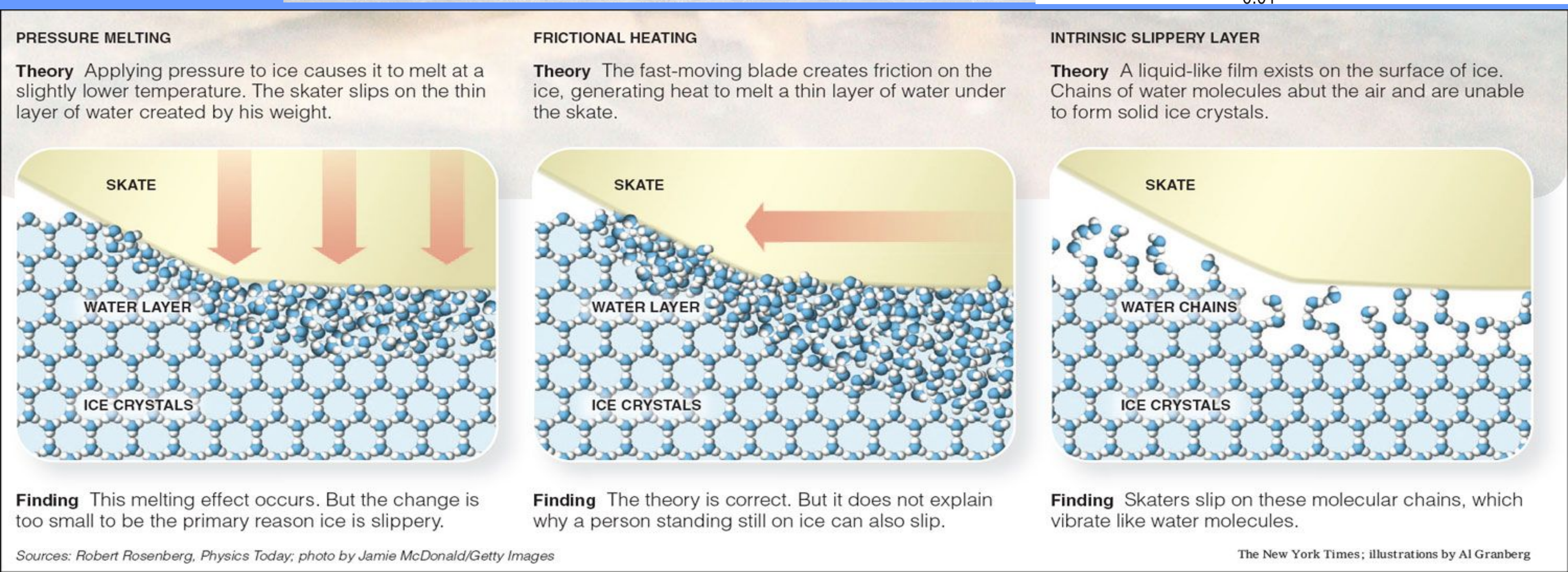


The Snowflake

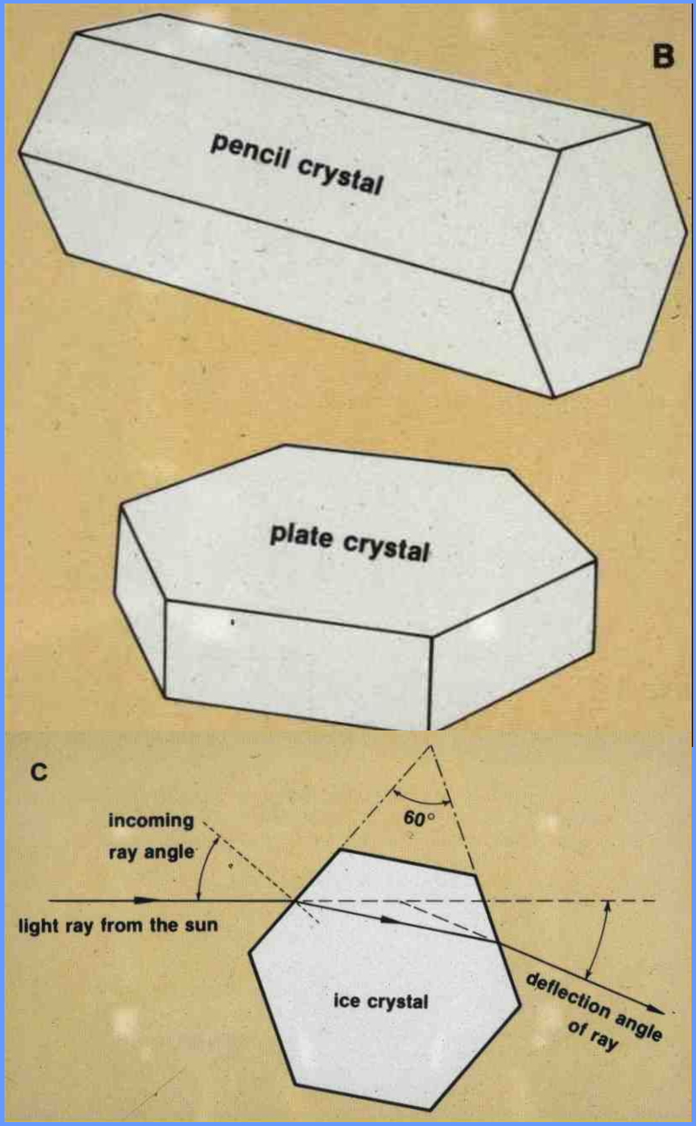
Ice Surface

Thin film of liquid on ice surface lets skate blades glide





Ice Crystals and Fire Rainbow



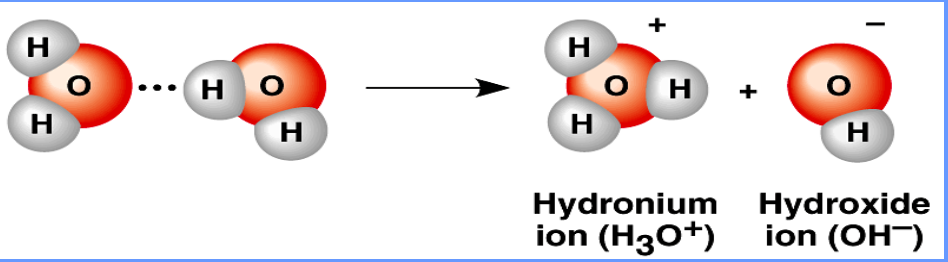
Sunlight enters the hexagonal plate crystals' vertical side faces and leaves through their bottom faces, is refracted (as through a prism) and separated into an array of visible colors.

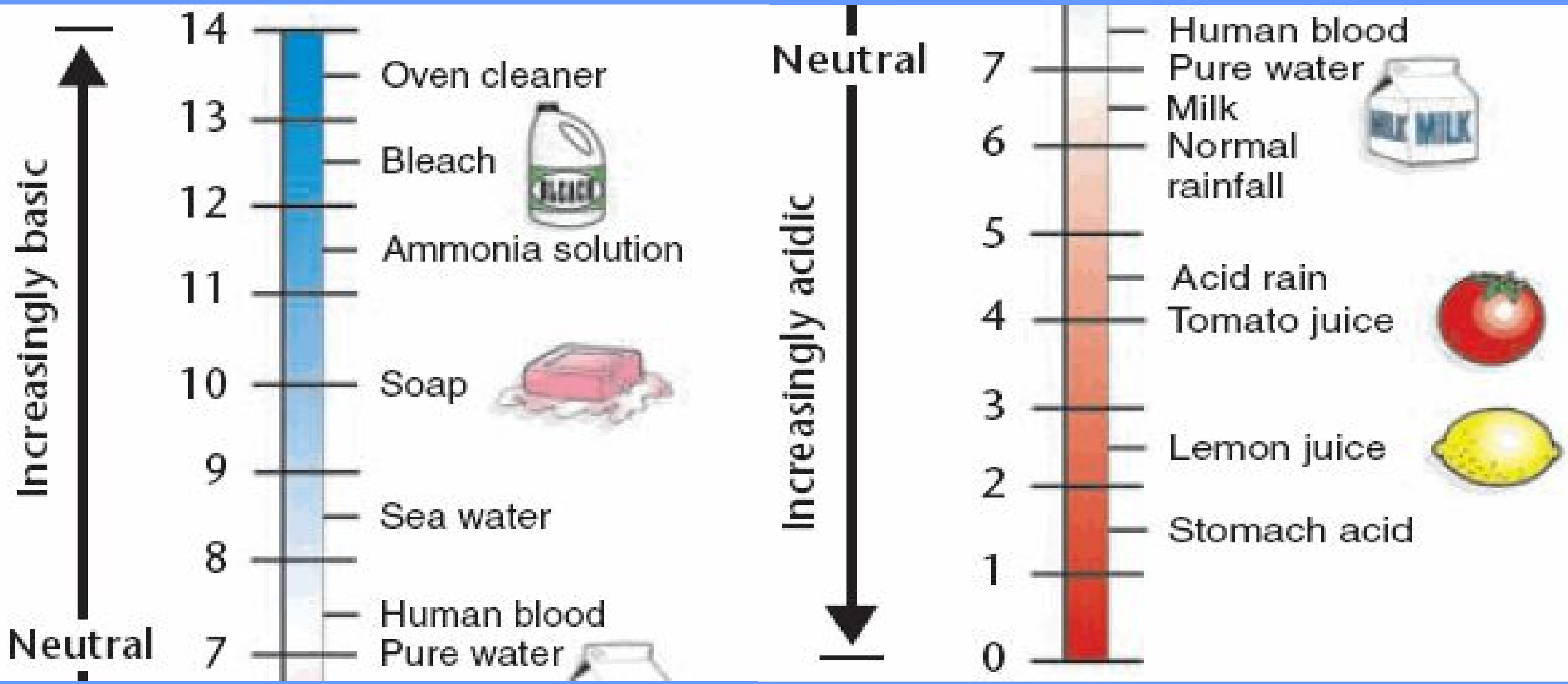
Dispersion by Hexagonal Crystal

Dissociation of Water Acids and Bases

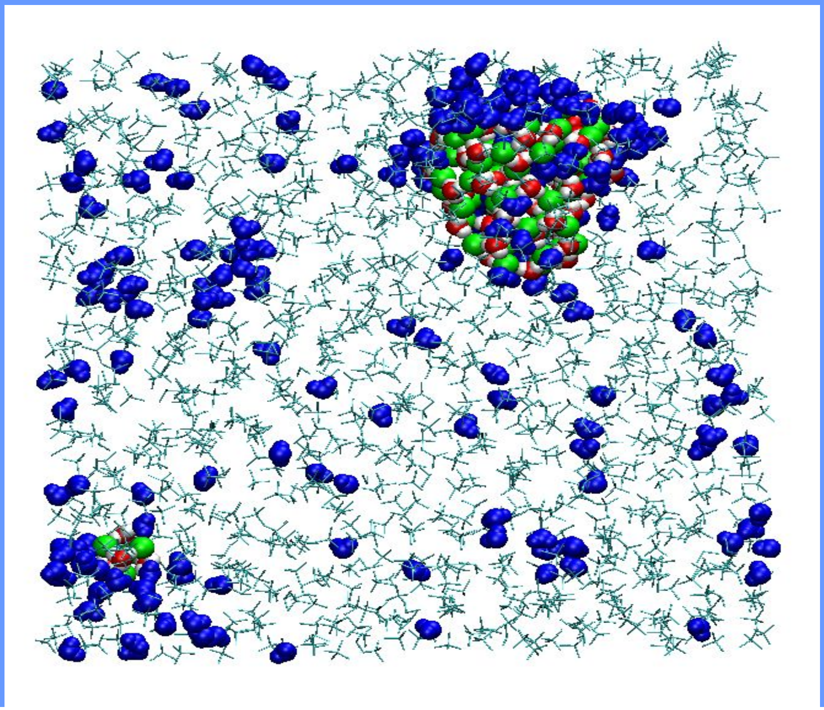
One water molecule in 550 million naturally dissociates into a hydrogen ion (H^+) and a hydroxide Ion (OH^-)

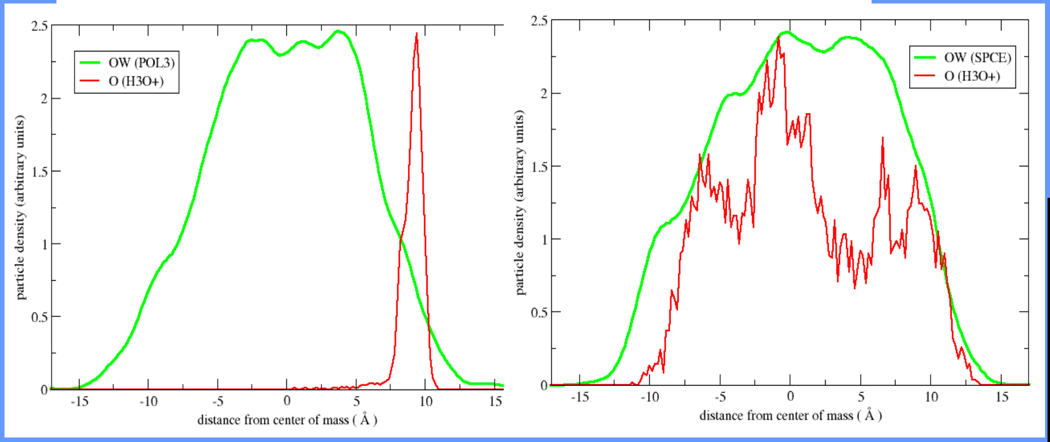
$$H_2O \leftrightarrows H^+ + OH^-$$



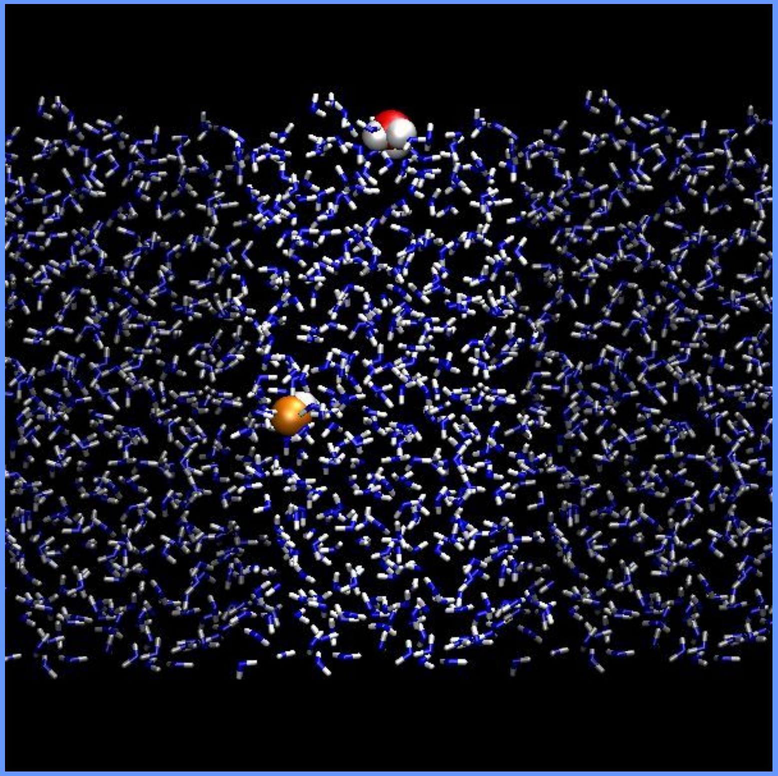


Solvation of H_3O^+

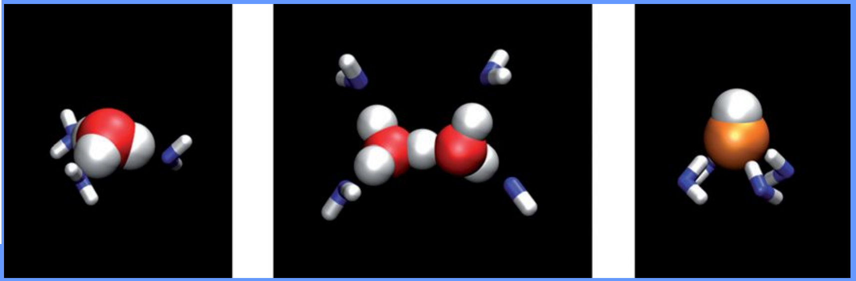




6M solution of HCl in CCl_4

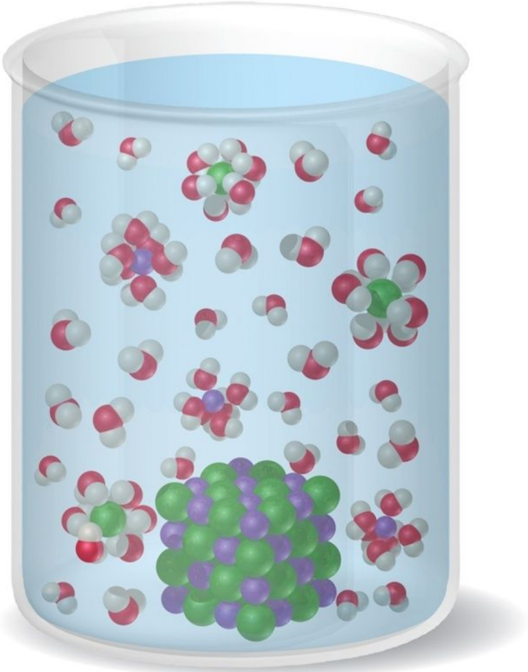


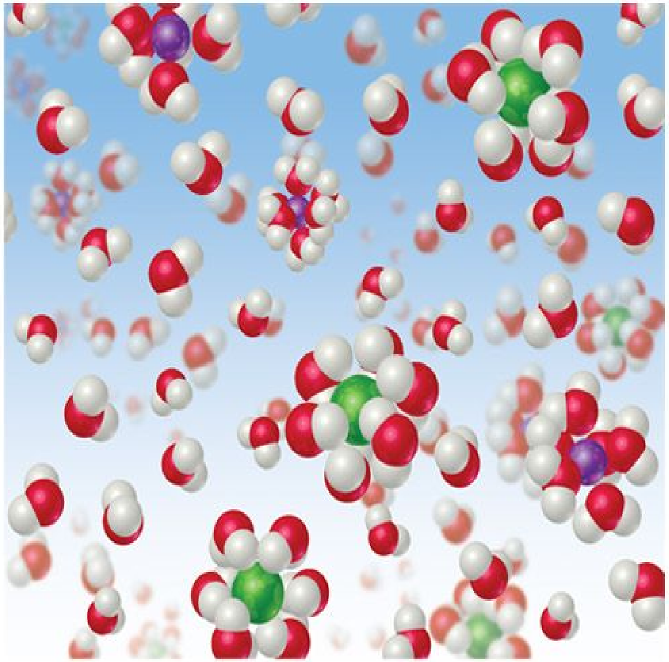
Surface monolayer is acidic with pH below 4.8

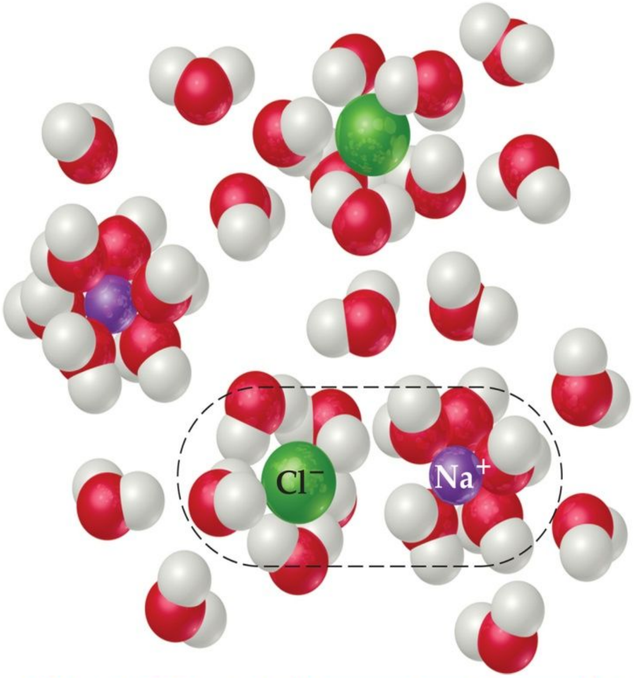


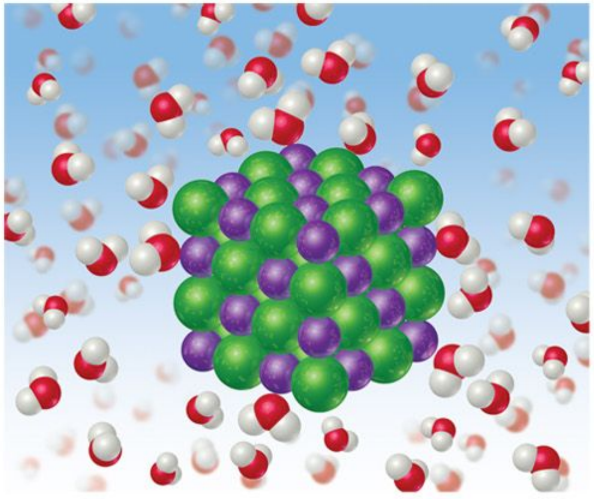
V. Buch, A. Milet, R. Vacha, P. Jungwirth and J. P. Devlin, Water surface is acidic, Proc.Natl. Acad. Sci. U. S. A., 2007, 104(18), 7342–7347.

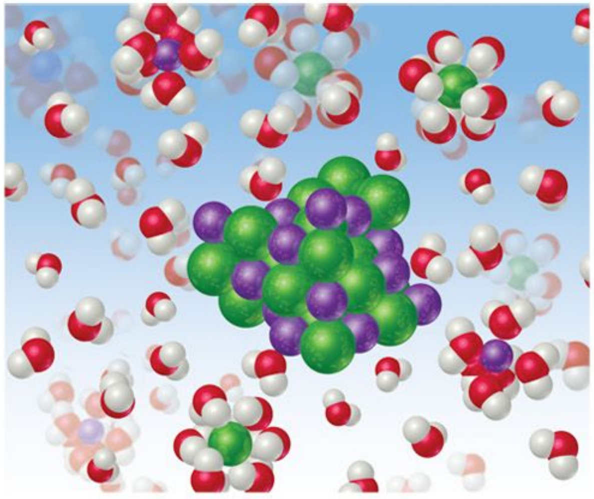
How Does a Solution Form?

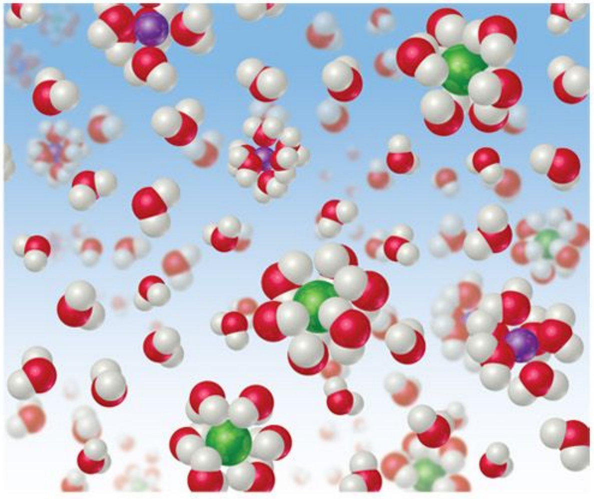




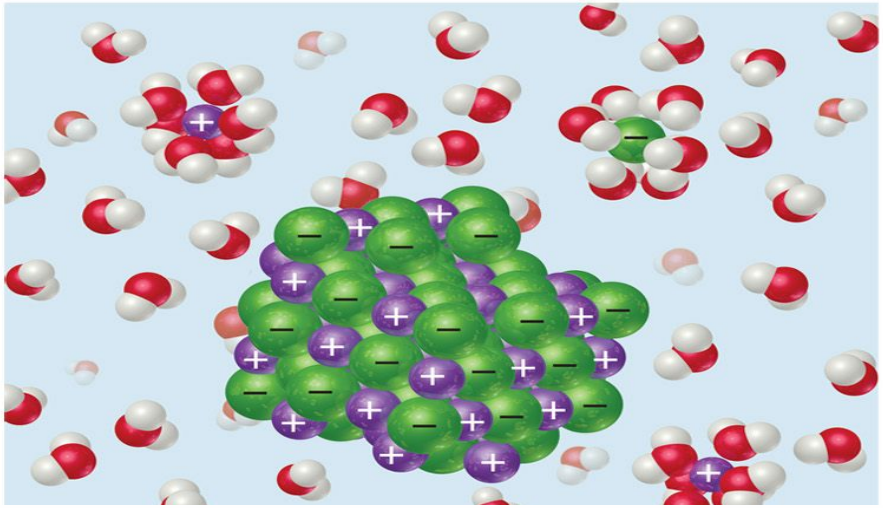


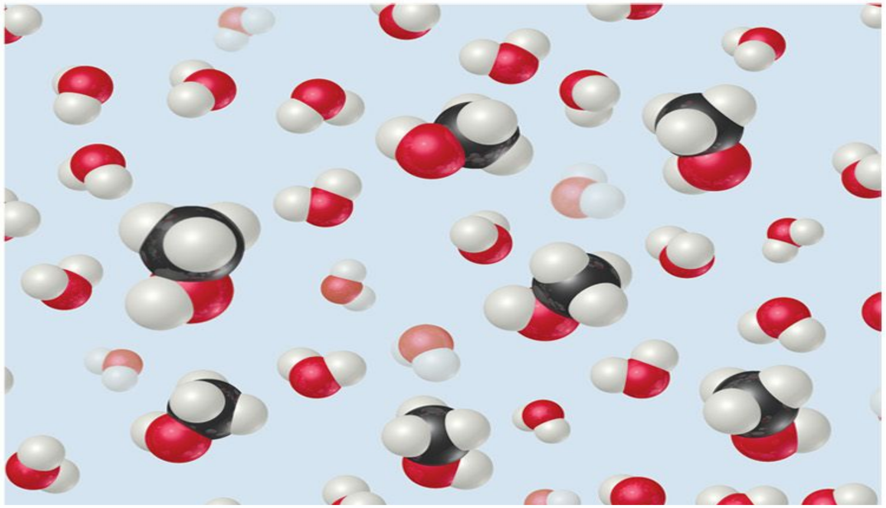


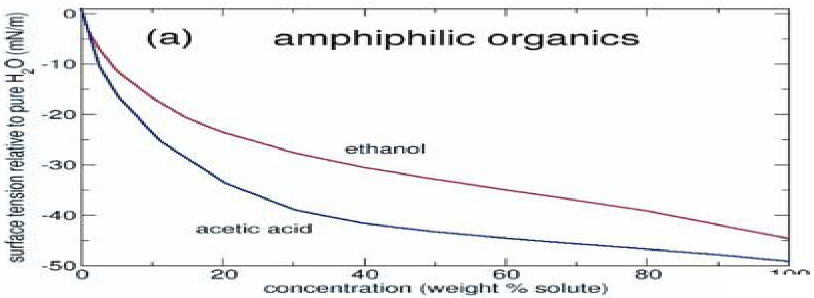




Does It Matter What to Solvate?

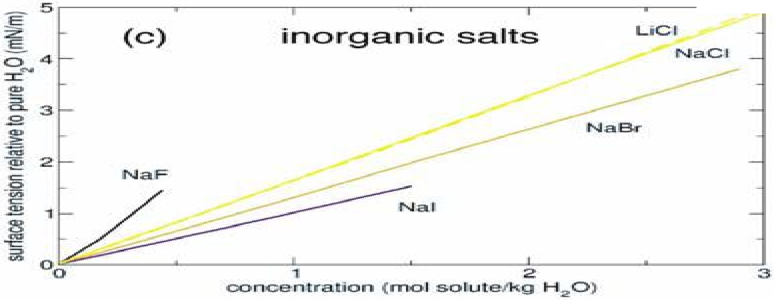




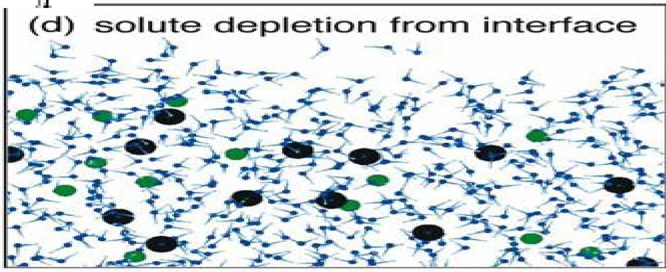


$$\frac{\partial \gamma}{\partial \ln a} < 0 \Rightarrow \Gamma > 0$$

$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_i}\right)_{T,p}.$$



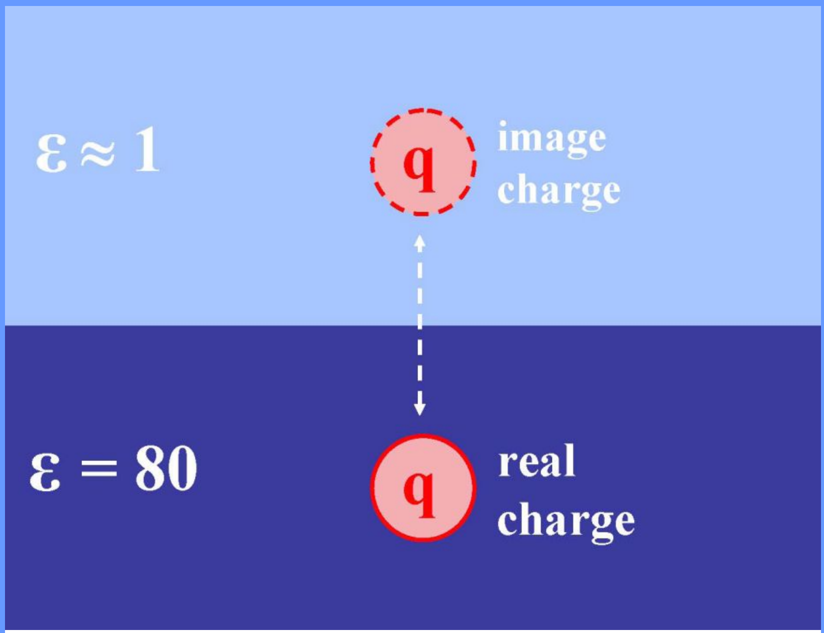
$$\frac{\partial \gamma}{\partial \ln a} > 0 \Rightarrow \Gamma < 0$$

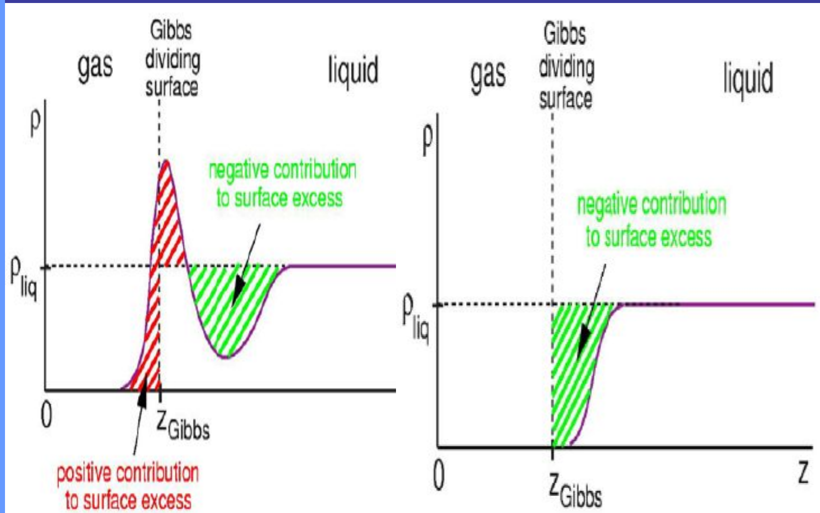


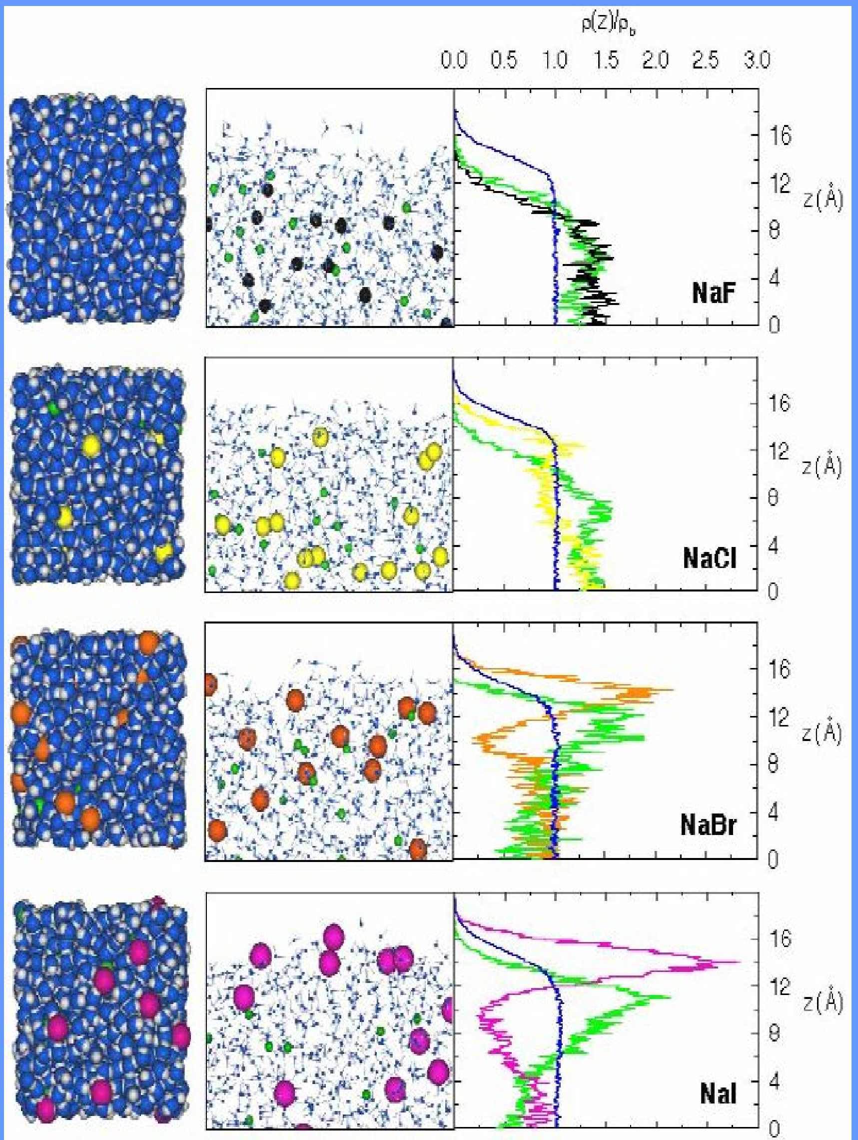
Theories of Electrolyte Solutions

- Small, non-polarizable ions are repelled from the interface.
- Large, polarizable ions show propensity to the interface.

P. Jungwirth and D. J. Tobias, J. Phys. Chem. B 2001, 10468

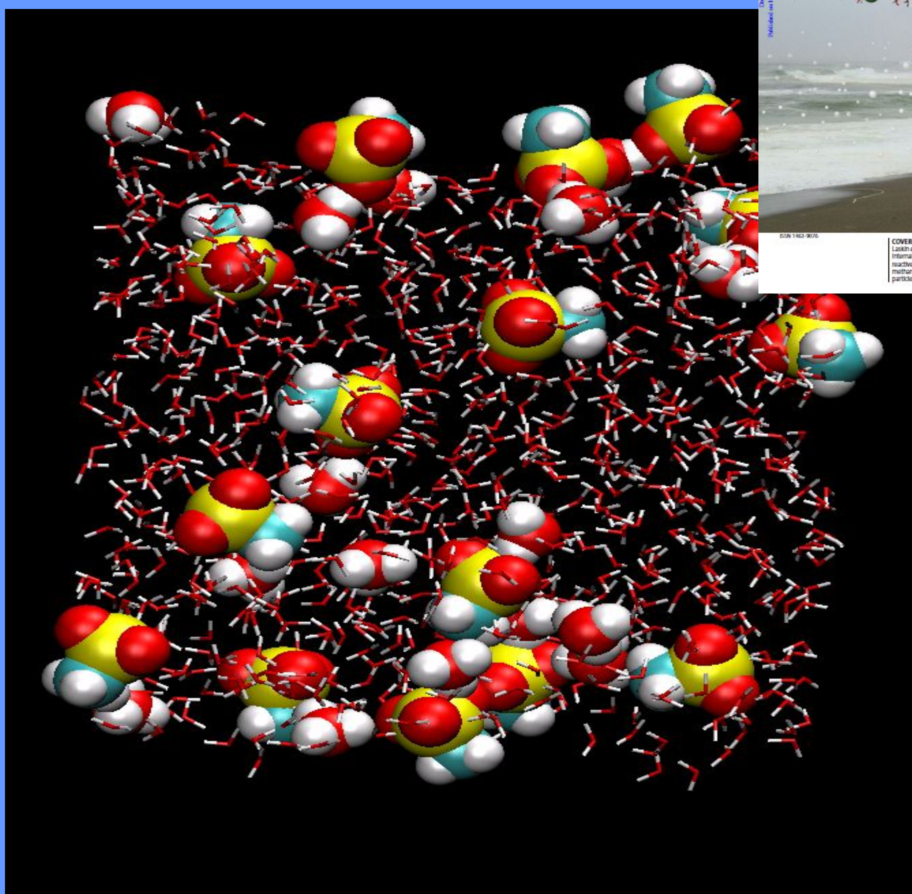


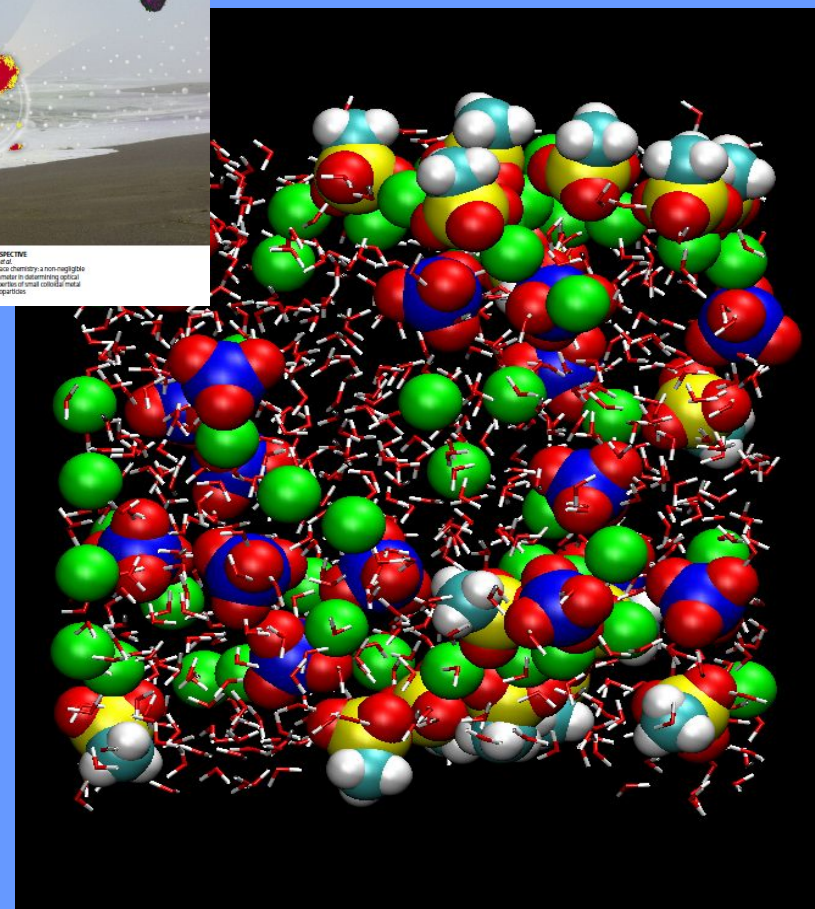




Vrbka, L.; Mucha, M.; Minofar, B.; Jungwirth, P.; Brown, E. C.; Tobias, D. J. Current Oppinion in Interface and Colloid Science, 9 (2004) 67

Solvation of CH_3SO_3 & ($CH_3SO_3 + SO_4^{2-}$)





Liu Y.; Desyaterik Y.; Wang H.; Minofar B.; Jungwirth P.; Laskin A.; Phys. Chem. Chem. Phys., 2011, **13**, 11778-11778

Bubble Coalescence

Coalescence is the merging of two or more droplets, bubbles or particles into one.
Simple electrolytes can stabilize bubbles against coalescence in aqueous solutions.
It depends on the combination of cation and anion.

α cations (Na^+, K+, Mg^{2+}, NH_4^+)

α anions (OH^-, F^-, Cl^-, Br^-, SO_4^{2-})

β anions (ClO_4^-, CH_3COO^-, SCN^-)

β cations (H^+, $(CH_3)_4N^+$) attracted to the interface

αα and ββ anion-cation pairs causes inhibition of bubble coalescence

αβ and βα anion-cation pairs pairs no inhibition of bubble coalescence

Inhibition when a bulk solvated or a surface active ion pair is present in solution. Creating an effectively uncharged interface is the key point for inhibition of bubble coalescence

Current Opinion in Colloid & Interface Science, 2004, 9 (1-2), 178-184

Why Biomolecules In Non-Aqueous Media?

Water molecules can mediate enzymatic catalysis directly by taking part in the reaction or indirectly through providing a solvation medium for reactants, transition state, and products.

Proteins have been extracted from aqueous solution into organic media using surfactant molecules at concentrations below their critical micelle concentration.

Nonhazardous bio-catalysts for chemical synthesis has become attractive alternative for pharmaceutical compounds because many compounds of interest to the pharmaceutical industries have poor solubility in water.

Organic media alters the enzymatic activity in solution by:

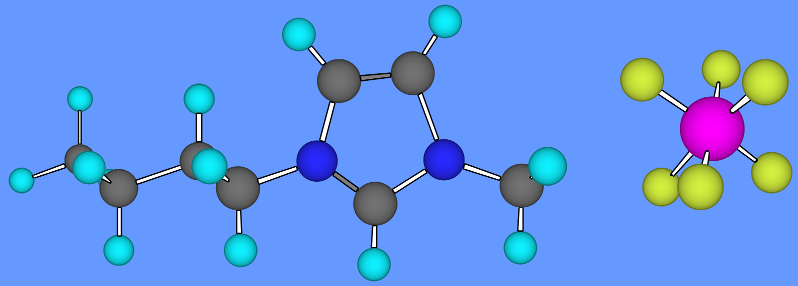
1) Poor compatibility between the solvent and enzymatic transition state
2) Reduced protein flexibility
3) Ground-state stabilization of the substrate
4) water stripping
5) Partial denaturation of the enzyme
6) ion-pairing

Thermodynamic activity of water in the bulk of organic media correlates well with the enzyme activity thus it is a qualitative indicator of amount of water available for the hydration of enzyme.

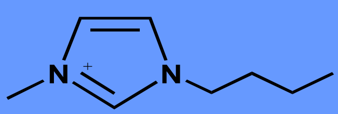
Definition of Ionic liquids

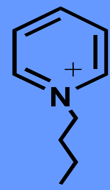
Ionic Liquids are defined as materials containing only ionic species without any neutral molecules and having a low melting point (usually less than 100°C).

Rika Hagiwara and Yasuhiko Ito
Journal of Fluorine Chemistry 105 (**2000**) 221-227.



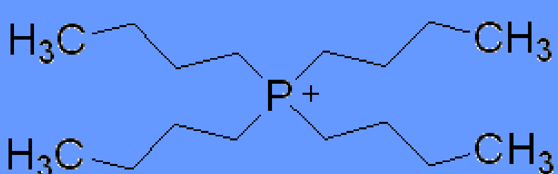
Cations and Anions of Ionic liquids



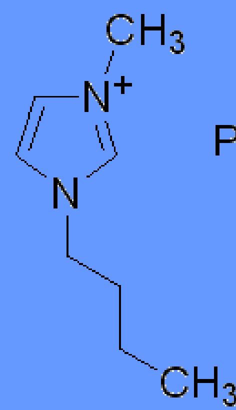


Ph $N^+(CH_3)_3$ Phosphonium ion

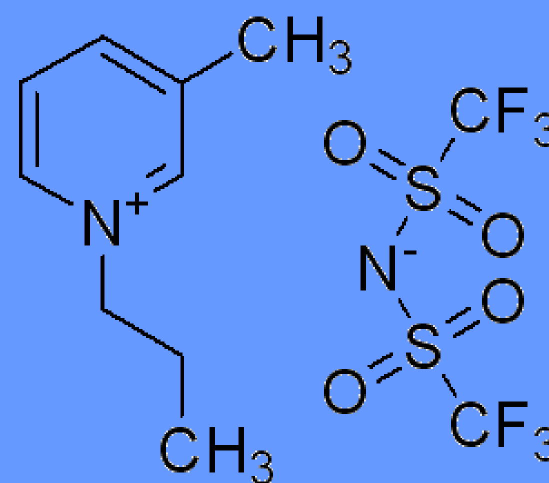
BF_4^- PF_6^- $Al_2Cl_7^-$ $(CF_3SO_2)_2N^-$ CF_3COO^- $[CH_3SO_3]^-$

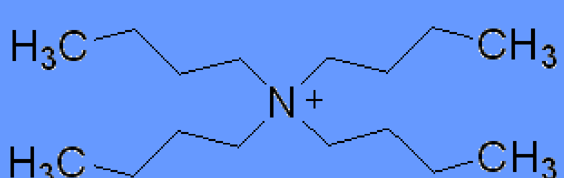


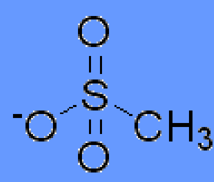
Cl^-



PF_6^-







Principle is to use large non-symmetrical ions => lower lattice energy

Properties of Ionic liquids

- Negligible vapor pressure
- Non-volatile
- Non-flammable
- High thermal, chemical and electrochemical stability
- Liquid over a wide temperature range
- Dissolution of many organic and inorganic compounds
- Variable miscibility with water and organic solvents

Applications of Ionic Liquids

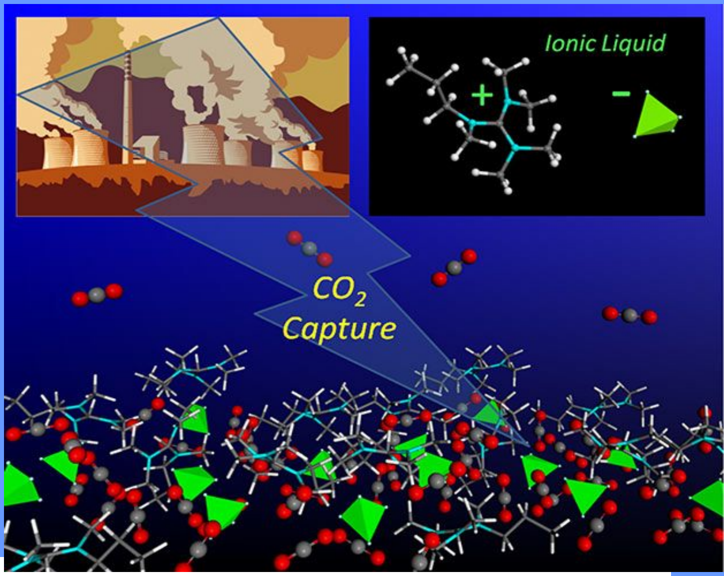
Applications in process engineering

Synthetic chemistry (oxidation, hydrogenations, etc.)

Absorption of gases (oxygen and carbon dioxide most studied)

Recently applied to the removal of SO_2 from flue gases

Batteries, fuel cells, solar cells: high conductivity, low viscosity



Applications in biotechnology

Protein crystallization

Enzyme catalysis

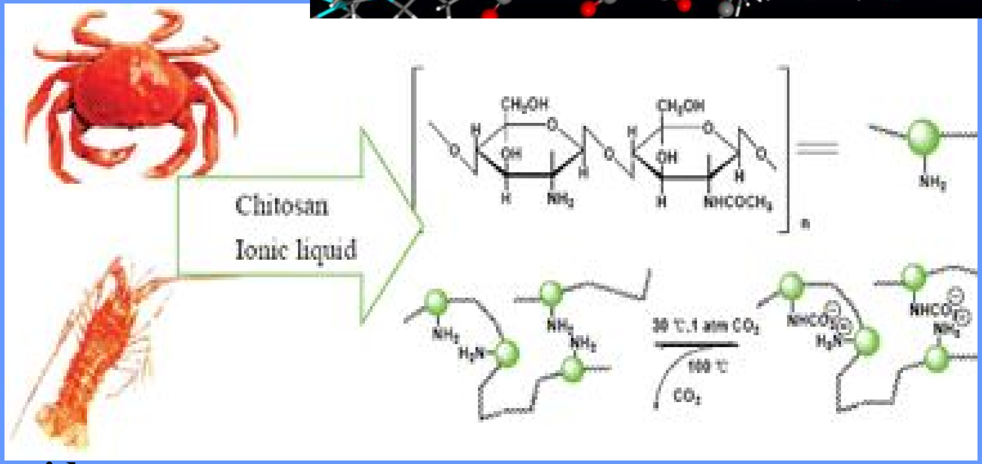
Protein synthesis

Peptide synthesis

Natural product isolation and purification

Dissolution of biomass materials

Cellulose is soluble in some water free ionic liquids.



A new method to cleaner and more efficient CO2 capture. PHYSorg.com. 22 Jul 2009.

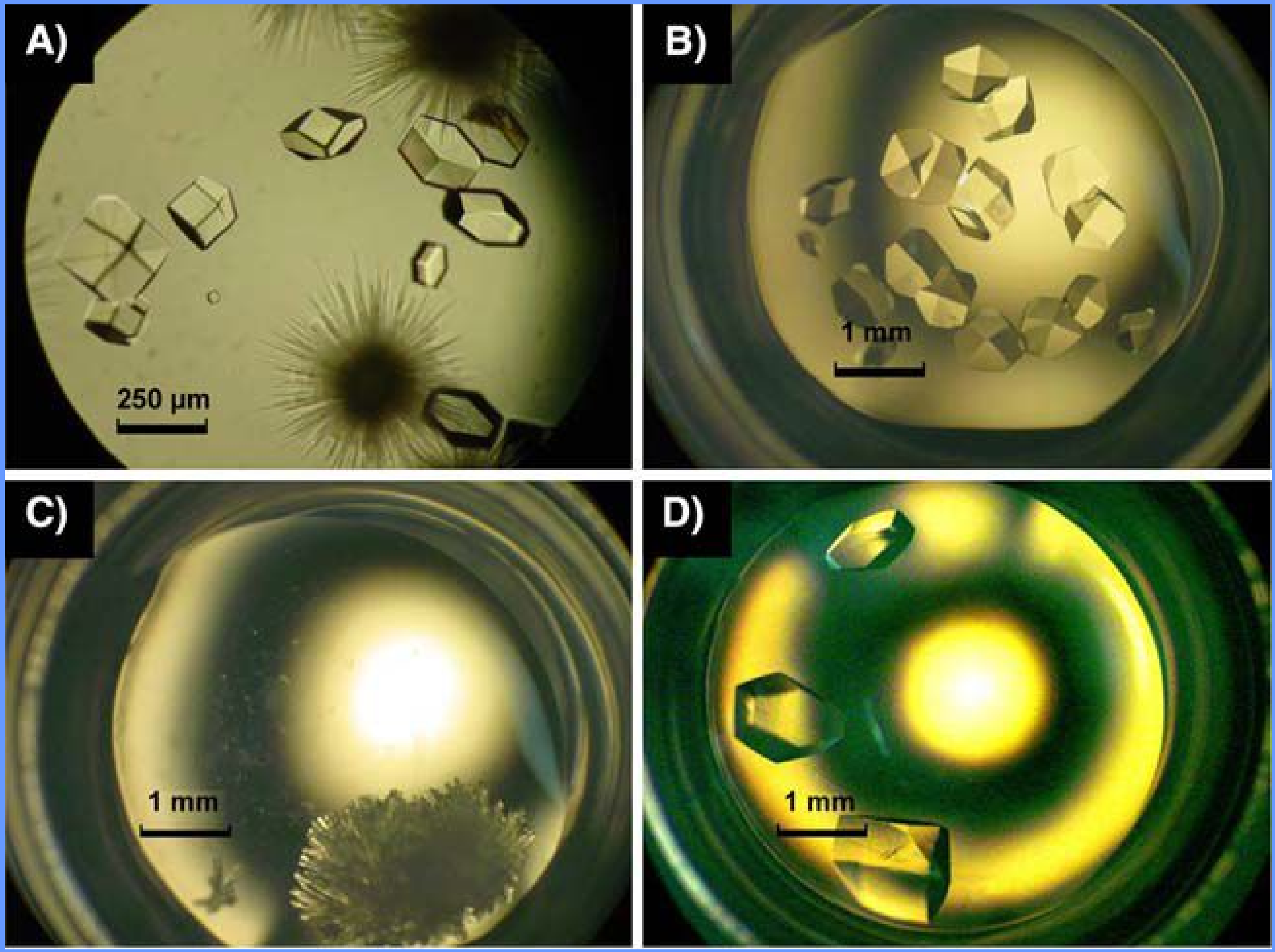
Haibo Xie , Suobo Zhang and Shenghai Li, *Green Chem.*, 2006,8, 630-633

Anthony *et al.*, *J. Phys. Chem. B 109* (**2005**) 6366-6374.

Jess *et al.*, *Chem. Commun.* (**2001**) 2494; Chen *et al.*, *Energy & Fuels 18* (**2004**) 1862;

Zhang *et al.*, *Ind. Eng. Chem. Res. 43* (**2004**) 614, Han *et al.*, *Angew. Chem. Int. Ed. 43* (**2004**) 2415.

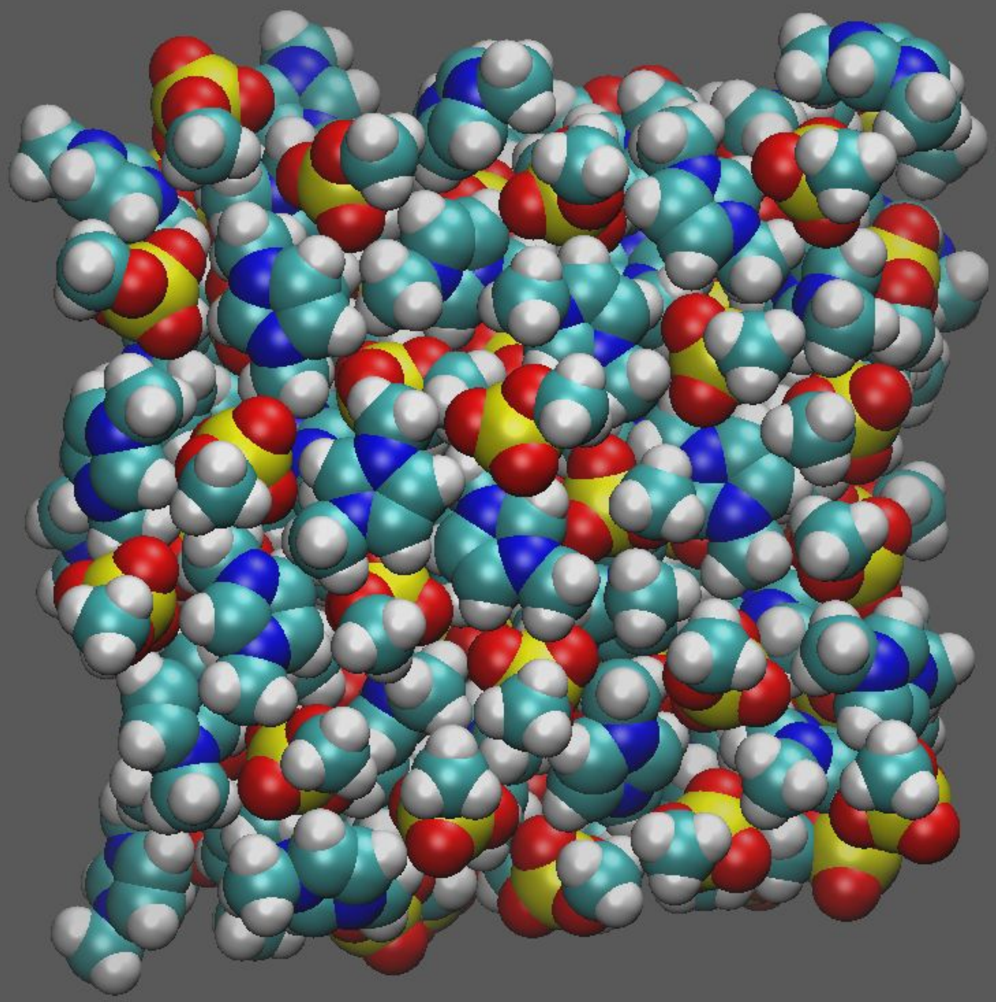
Protein Crystallization with ILs

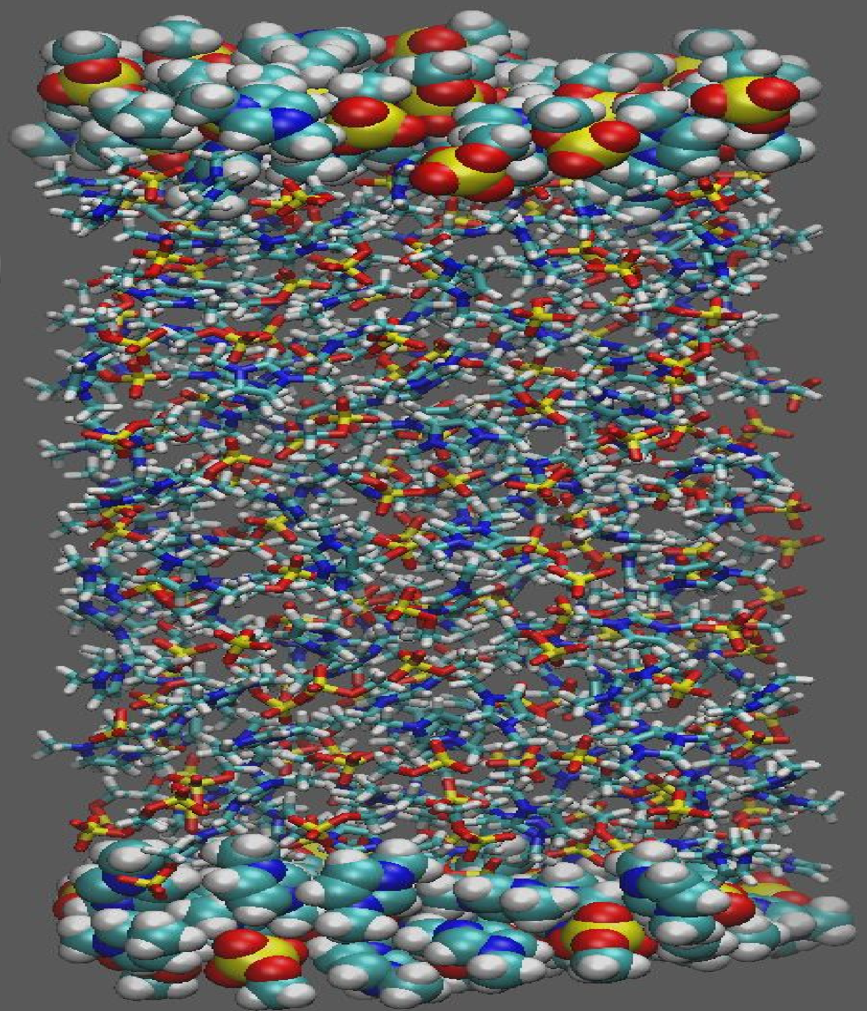


Microphotographs of lysozyme crystals in sitting-drops with 50 mM acetate buffer. (A) No IL, pH = 4.0, tetragonal crystals. (B) 62.5 g ethanolammonium formate ,pH = 6.7 (C) ethylammonium nitrate l, pH = 5.4, (D) choline dihydrogenphosphate ,pH = 5.2

Dariusch Hekmat et al. *Biotechnol Lett* (2007) 29:1703–1711

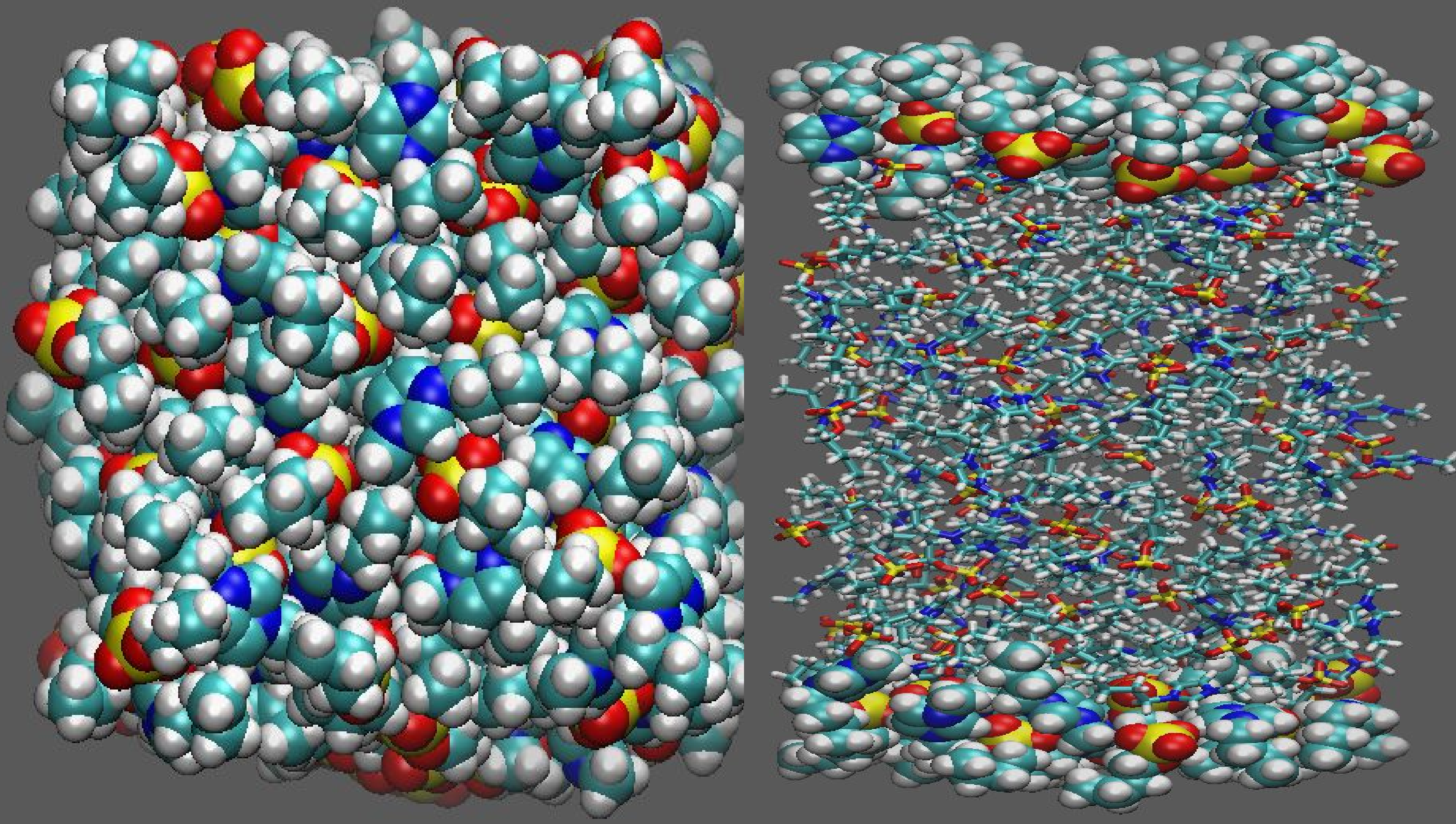
Surface of Pure Ionic Liquids





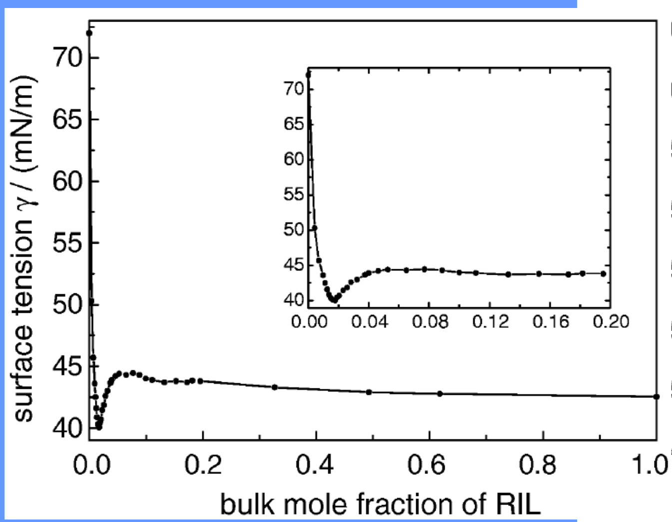
Snapshots from MD simulations for [MMIM][MS]

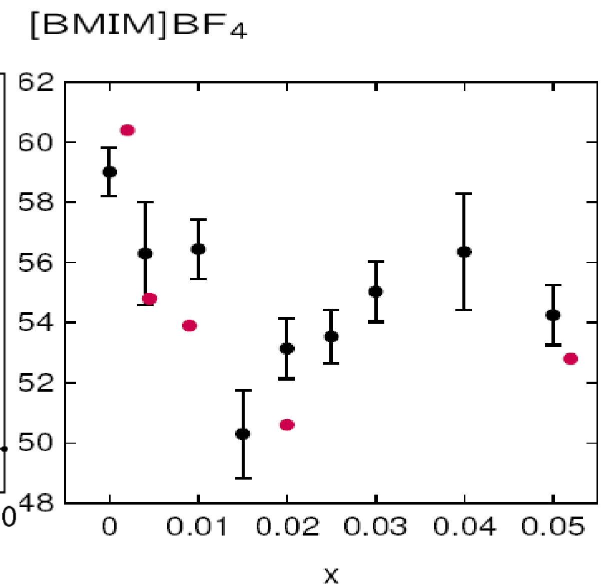
Surface of Pure Ionic Liquids

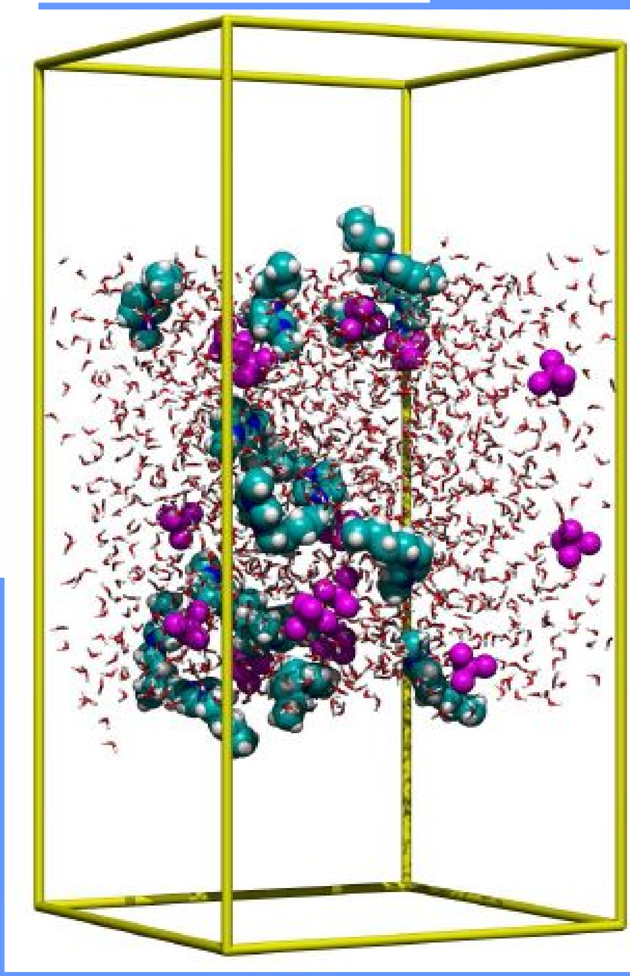


Snapshots from MD simulations for [BMIM][BS]

Surface of Aqueous Solution of ILs







$$\gamma = \frac{1}{2} L_x \left\langle P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right\rangle$$

L_x, L_y, L_z are the dimensions of thae periodic simulation box.z

P_{xx},P_{yy} and P_{zz} are x, y and z components of the pressure tensor

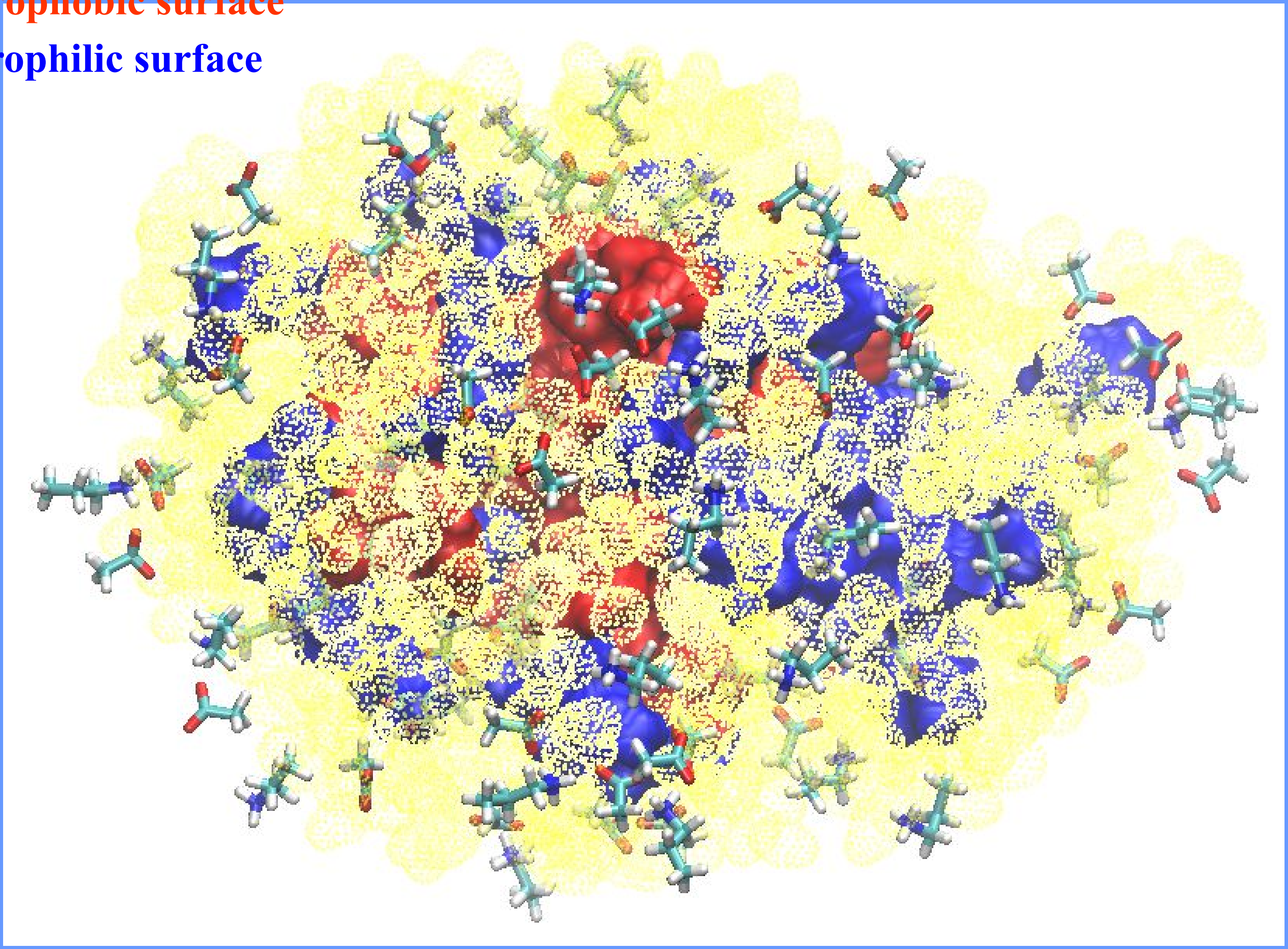
Sung et al., *Chem. Phys. Lett.* 406, 495 (2005)

Picalek, J.; Minofar, B.; Kolafa, J.; Jungwirth, P.: *PCCP*, 10 (2008) 5765

Lysozyme in 20% Propyl Ammonium Acetate

Hydrophobic surface

Hydrophilic surface



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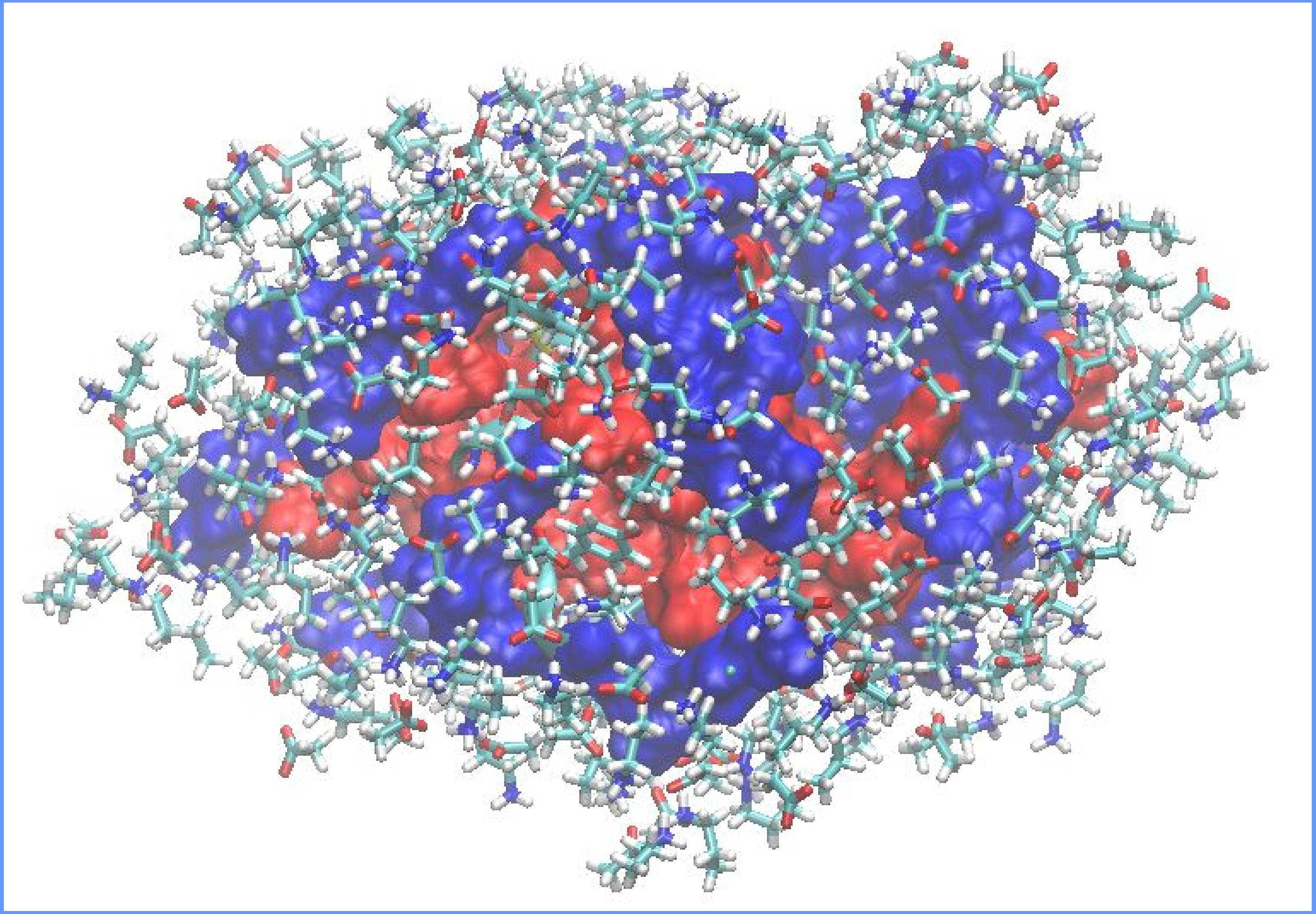

Photo by : Saeed Abbasi