# Understanding Ion Selective Sensors: A Short Introduction

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# Ion Selective Sensors (1)

- Advantages of low cost and portability
- Major Types of Ion Selective Sensors
  - Glass, Crystalline and Solvent Polymeric
- Glass
  - Hydronium (pH), $Na^+$, $K^+$
- Crystalline
  - Silver ($Ag^+$), Chloride ($Cl^-$), Bromide ($Br^-$), Iodide ($I^-$), Sulfide ($S2^-$), Cyanide ($CN^-$), and Thiocyanate ($SCN^-$)

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# Ion Selective Sensors (2)

- Solvent Polymeric Cation Sensors
  - Potassium, Ammonium, Calcium, Lithium and many others
- Solvent Polymeric Anion Sensors
  - Limited, with poor performance and lifetime
- Need for improved anion sensors
- What is different about anions vs. cations?
  - Large ionic radius, oxoanions, organic anions, charge distribution & charge density

*Anal. Chem.* **2001**, *73*, 88A-97A

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# Ion Selective Sensors (3)

- *General form of Nernst Equation*
  - $E = E^{0}(T) + (RT/zF) \ln ( a(OX) / a(RED) )$
- *Simplified Form used for Testing*
  - $E = E^{0} - 0.05916 * \log_{10} [ION]$
- *Assumptions for Simplified Form*
  - *Constant Temperature (25° C)*
  - *Reduced or Oxidized species is Liquid or Gas*
  - *[ION] is the mean Molar activity of the species*
  - *DI Water and Single Electrolyte Solution*

*Pure & Appl. Chem.* **1994**, *66*, 2527-2536.

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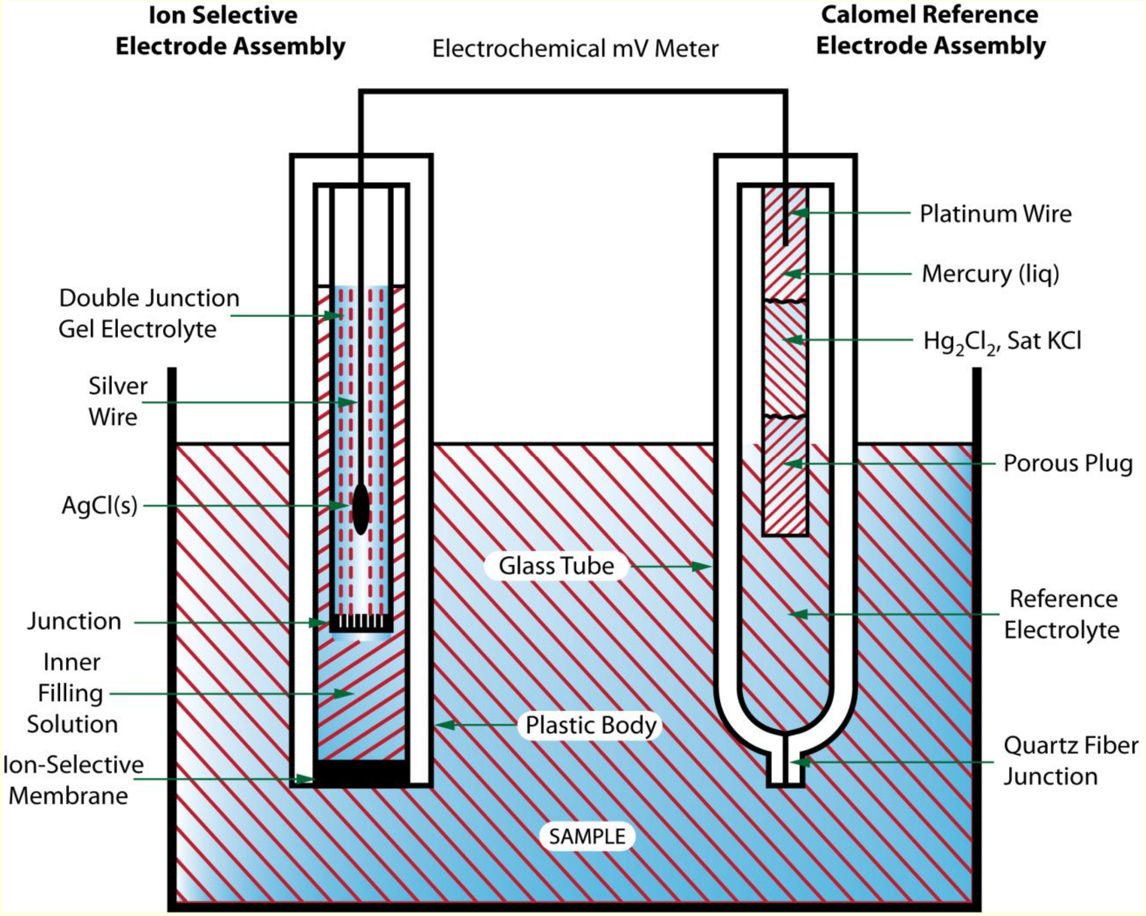
# Laboratory Measurement Testing Setup

Ag(s)|AgCl(s)|KCl(Pt(s)|Hg(l)|$Hg_2Cl_2$(sat),KCl(Sat)|$Cl^-$(aq)|| (REFERENCE) Sat)|$KNO_3$(0.001 M)|ISE|ext.soln|| (MEASURE)

- Double junction ISE measuring electrode
- Quartz fiber calomel reference electrode used for stability and accuracy
- All test performed at 25º C

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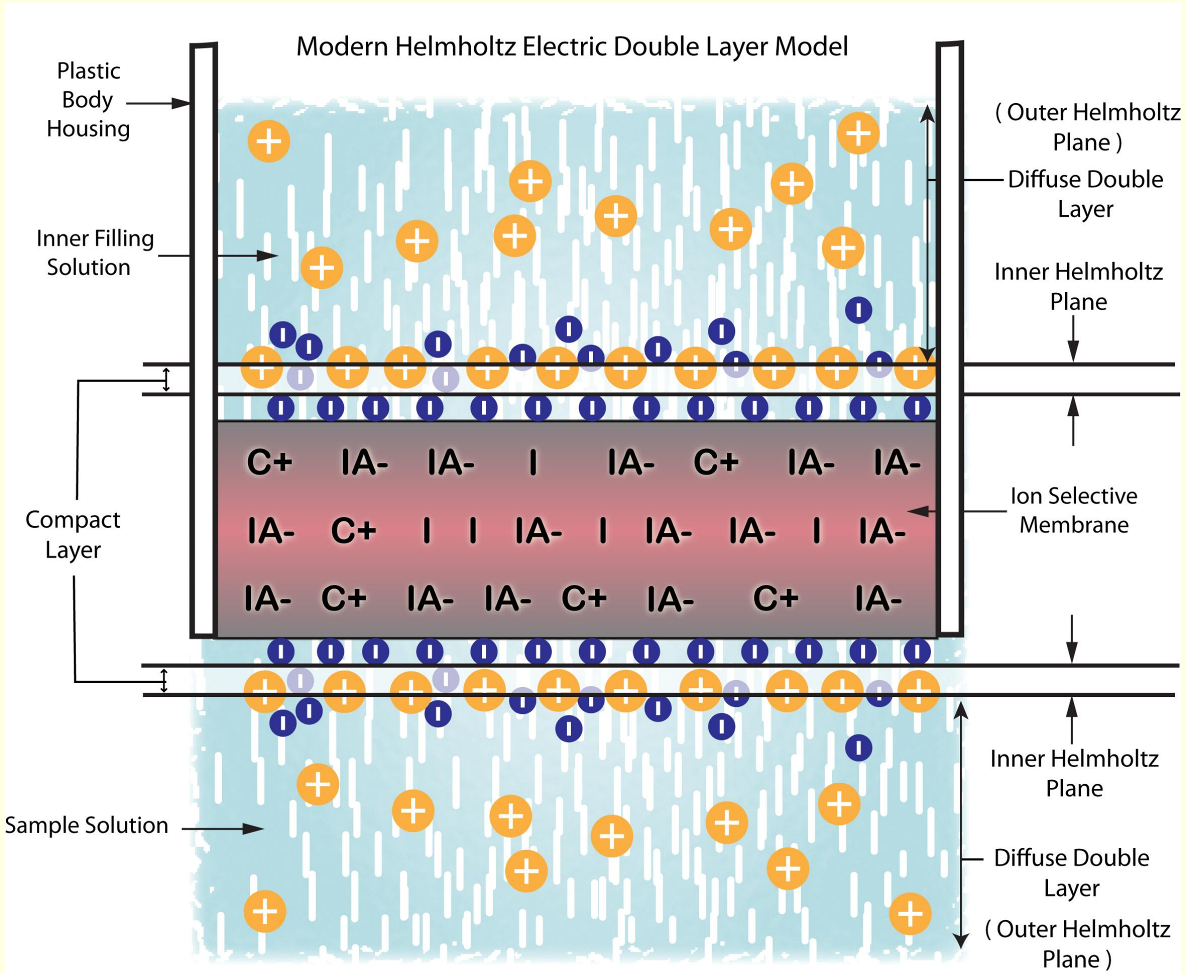
# Helmoholtz Double Layer

- Inner compact layer not solvated
- Outer diffuse layer is solvated
- Potential generated between activity at surface of inner & outer solution
- C+ is Large Cation
- I is Ionophore
- A- is Anion




*Surf. Sci.* **2003**, *540*, 401-406.
*Chem. Rev.* **1997**, *97*, 3083-3132.

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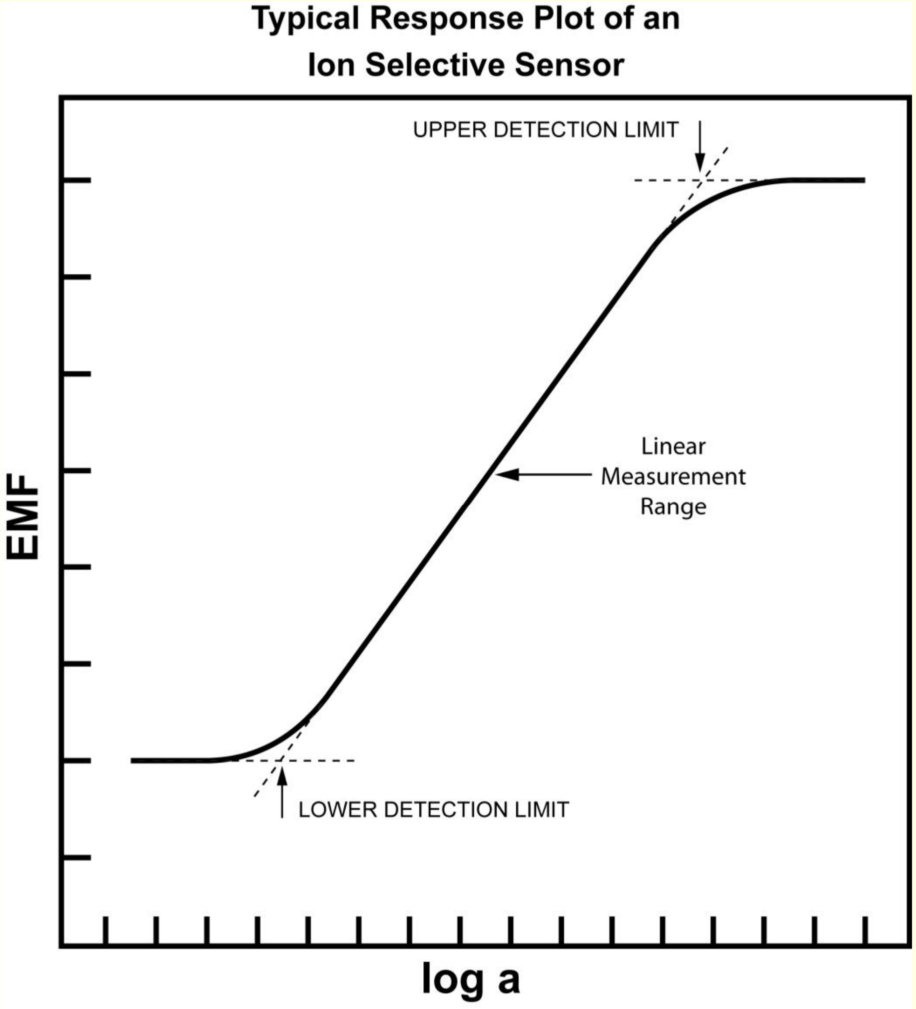
# Typical Electrochemical Response Plot

- Lowest limit of detection and linear measurement range are fundamental characteristics of any ion selective sensor
- Good lowest limit of detection is $10^{-6}$ to $10^{-7}$
- Good linear measurement range is $10^{-5}$ to $10^{-1}$




*Pure & Appl. Chem.* **1975**, *48*, 127-132.

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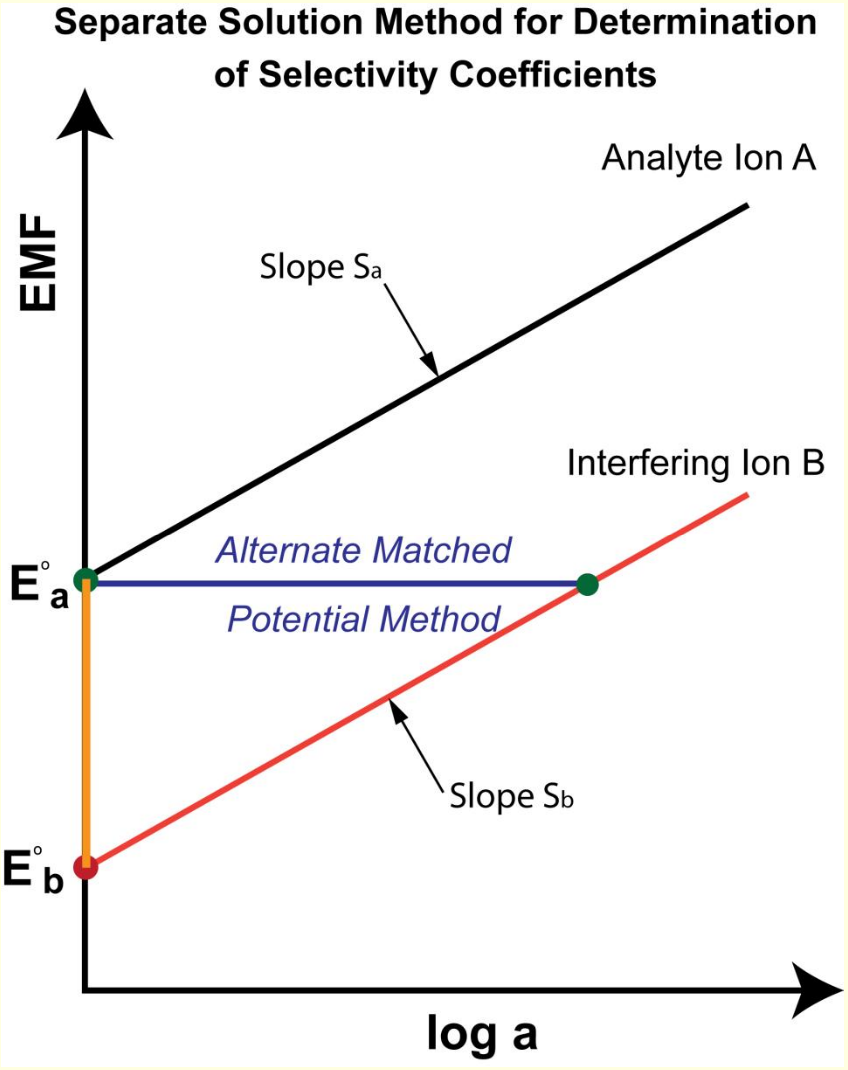
# Selectivity Coefficients (1)

- Separate (Single) Solution Methods
- Practical Slope Method Refinement
- $E = E°_A + S_A \log_{10} a_A$
- $E = E°_B + S_B \log_{10} a_B$
- $K^{pot}_{A,B}(PSM) = 10^{(E°b - E°a)/Sa}$
- Alternate Matched Potential Method

*Pure & Appl. Chem.* **2008**, *80*, 85-104.
*Chin. Chem. Lett.* **2002**, *13*, 355-358.



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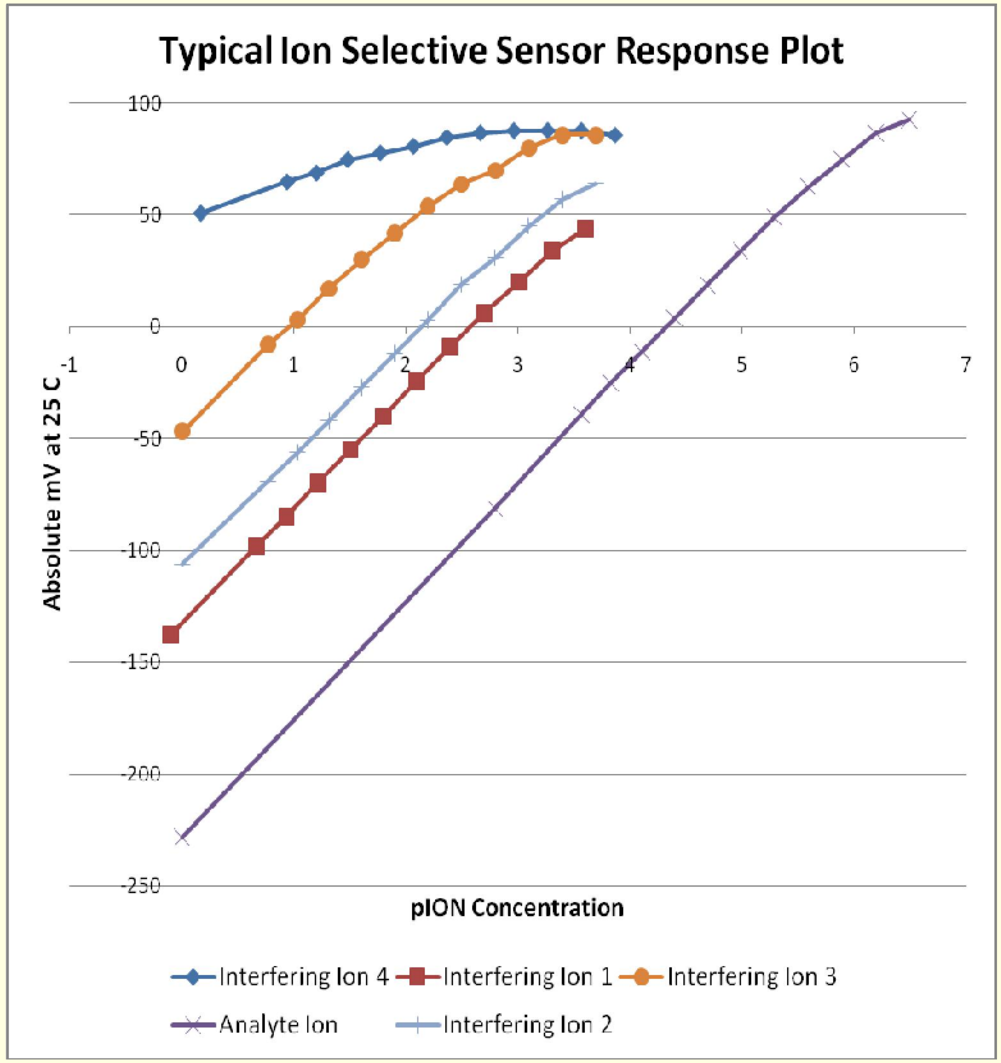
# Selectivity Coefficients (2)

- Anion Ion Selective Sensor Response Plot
- Interfering Ion 1, 2 & 3 use PSM method
- Interfering Ion 4 uses Matched Potential
- Absolute Response to All Ions Converges near Lowest Limit of Detection (at about +100 mV for this plot)



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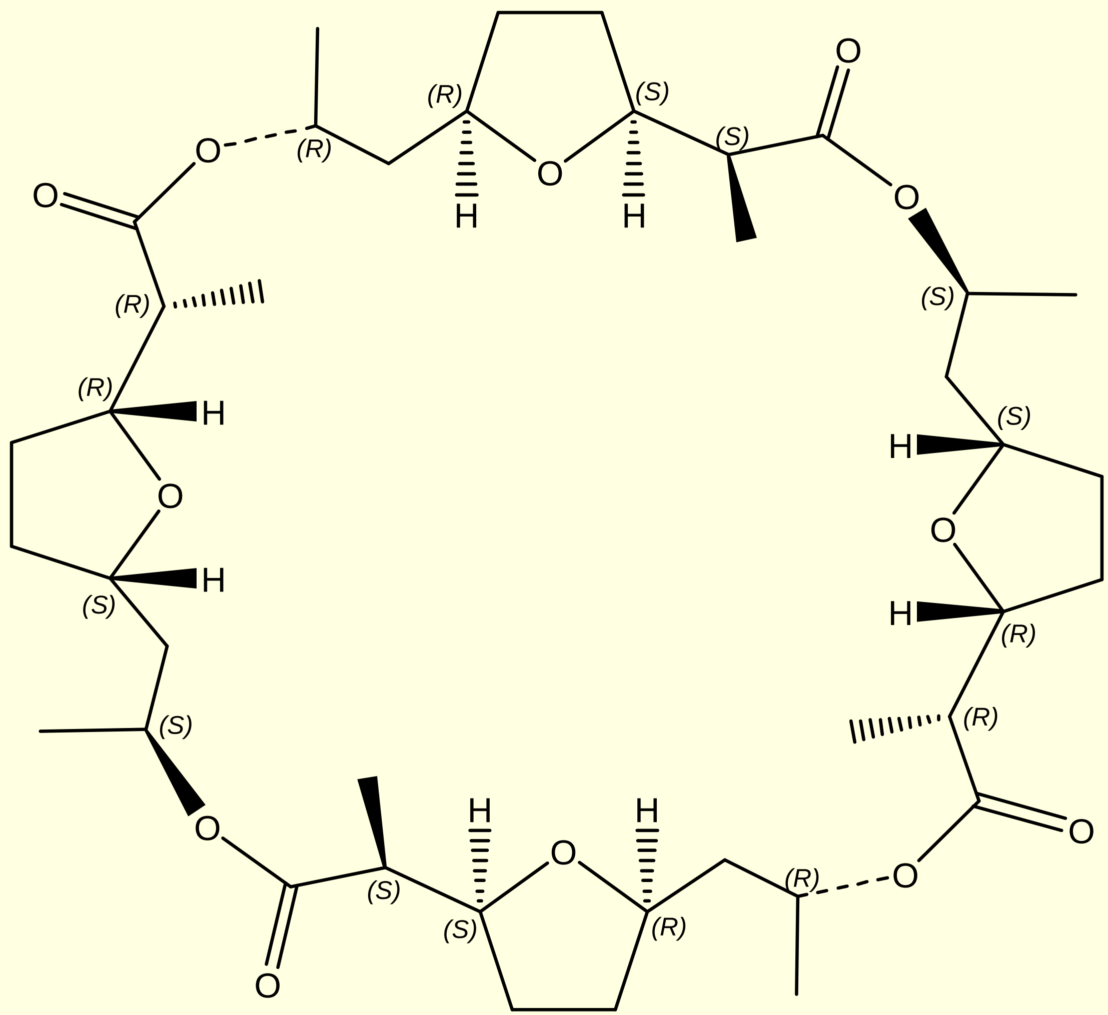
# Visualization of Binding for the Classical Ionophore Nonactin (1)

- Naturally Occurring Ionophore
- Highly symmetric meso compound
- Conformation is flexible



*Anal. Chem.* **2003**, *75*, 152-156.

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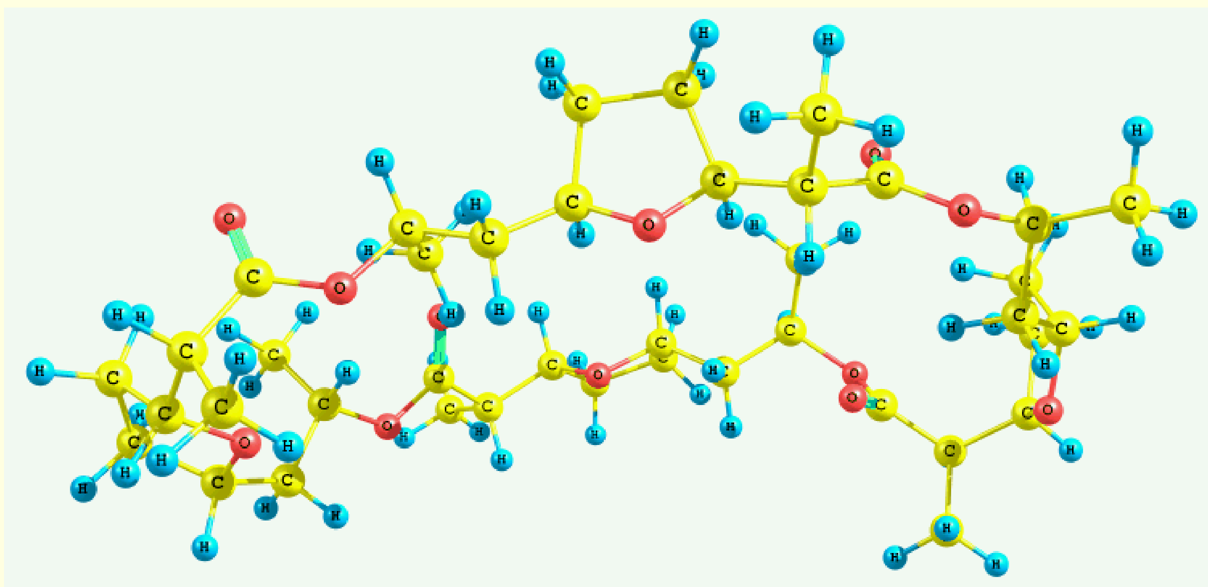
# Visualization of Binding for the Classical Ionophore Nonactin (2)

- Unbound conformation is “relaxed” and almost planar
- Lack of strong intramolecular non-bonding dipole or hydrogen bonding interactions means a very loose and nonactin is a flexible molecule when no ion is present
- Assumes many optimal conformation for different ions



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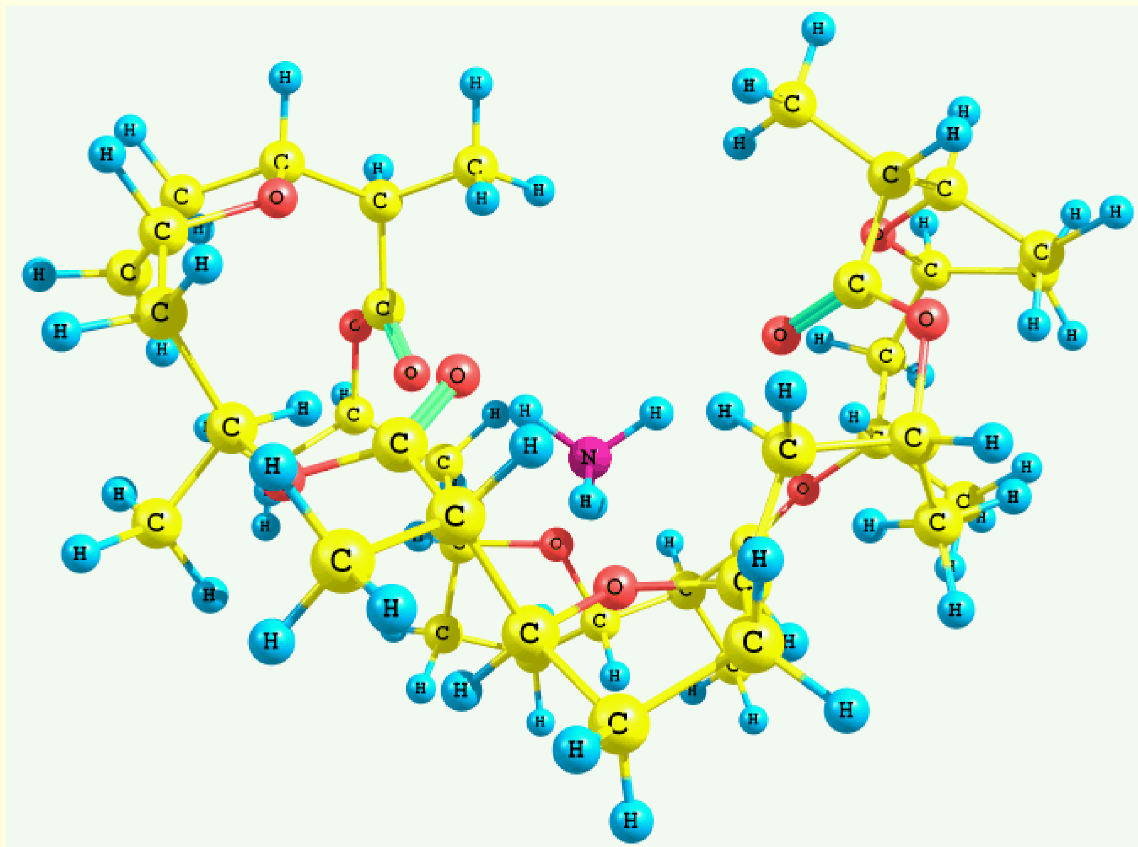
# Visualization of Binding for the Classical Ionophore Nonactin (3)

- Puckered conformation bound to ammonium
- Preorganization with ion bound
- Good overlap of oxygens to stabilize charged ammonium hydrogens



*J. Am. Chem. Soc.* **2002**, *124*, 5374-5379.

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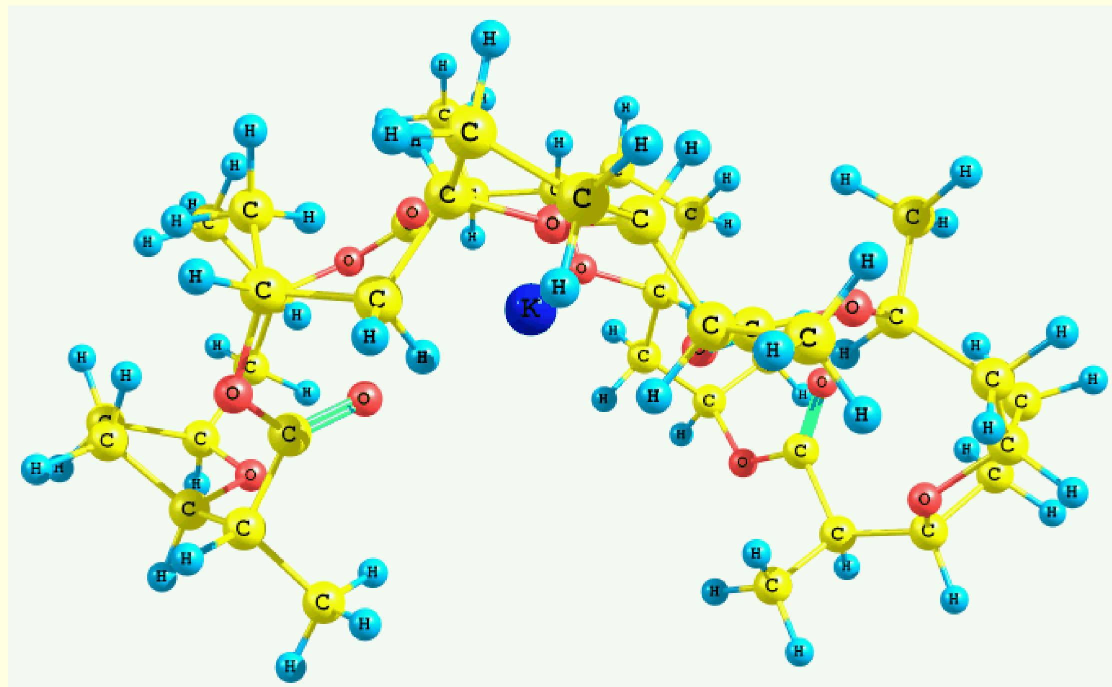
# Visualization of Binding for the Classical Ionophore Nonactin (4)

- Difference in structure between bound and unbound is the “preorganization”
- Difference in binding affinity between $NH_4^+$ and $K^+$ is basis for selectivity coefficient



*J. Am. Chem. Soc.* **1992**, *114*, 7542-7549.

# Anion Selective Sensors (1)

- Solvent polymeric ion selective electrodes based on the classical ion exchange quaternary ammonium salt tridodecylmethylammonium chloride salt (TDDMACl), the potentiometric response follows the **Hofmeister series**
  - $ClO_4^-$ > $SCN^-$ > Salicylate > $I^-$ > $NO_3^-$ > $NO_2^-$ > $Br^-$ > $Cl^-$, $HSO_3^-$ > $CH_3COO^-$, $HCO_3^-$ > $HSO_4^-$
- Perchlorate is the most lipophobic (protein destabilizing and denaturing) and bisulfate is the most lipophilic (protein stabilizing)

*Arch. Exp. Pathol. Pharmakol.* **1888**, *24*, 247-260.
*Curr. Opin. Chem. Biol.* **2006**, *10*, 658-663.

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# Anion Selective Sensors (2)

- Hofmeister series is a ranking of the natural “perm” selectivity of these various anions to biological like membranes including solvent polymeric
- Building anti-Hofmeister selective anion receptors presents some very serious difficulties, and is thus an area of intensive research interest.
- Detecting perchlorate and thiocyanate (high in series) is relatively easy, while detecting bicarbonate and bisulfate (low in series) is quite difficult and in fact very few good ionophores exist for them.

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# What are Ionophores?

- Ionophores are molecules that selectively bind and transport ions across a membrane
- An ideal Ionophore would be:
  - Neutral in charge (to minimize leaching)
  - Highly selective (1,000 times or better selectivity)
  - Have a large linear response range ($10^{-7}$-1 Molar)
  - Soluble in common organic solvents (i.e. THF)
  - Insensitive to Reduction & Oxidation
  - Able to operate over a broad pH range (1-13)
  - Stable for a long period of time (6-12 months)
  - Able to operate over a wide temperature range (5-50 °C or better)

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# What Type of Ionophores Exist?

- Naturally Produced Ionophores
  - Usually produced by bacteria or other microbes
  - These molecules are often also antibiotics and are usually long-chain macrocyles
  - Examples:
    - Nonactin (NH4+), Valinomycin (K+), …
- Small Molecule (Synthesized) Ionophores
  - These molecules typically mimic naturally occurring active sites of proteins or antibiotics
  - Examples:
    - Crown Ethers, Salens, Cryptands…

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# What are Ionophores Used For?

- Ionophores are used for a wide variety of tasks but we shall focus on their use as neutral carriers for ion selective electrodes for use in aqueous analytical electrochemistry
- Ionophores have been reported to selectivity detect ions in aqueous solutions in suitable solvent polymeric and silicone membranes
- We shall only consider the ubiquitous solvent polymeric type membranes, as they are currently the only viable platform for cost effective ion selective electrodes

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# What is a solvent polymeric membrane?

- Typical solvent polymeric membranes consist of the following components:
  - Ionophore soluble in THF
    - Typically 1-10% by weight *(typically ~3-5%)*
  - High molecular weight PVC
    - Typically ~20-50% by weight *(typically ~30%)*
  - Selected plasticizers (solvent mediators) improve ionophore solubility & lower membrane resistance
    - Typically ~50-80% by weight *(typically ~60%)*
  - Selected lipophilicity additives
    - Only required for measurement in blood or serum
    - Typically only 0.5-2% by weight

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# How is the Quality of an Ion Selective Electrode Characterized? (Part 1)

- Lowest Limit of Detection
  - $10^{-6}$ or $10^{-7}$ M or better is excellent for most ions
  - This lowest limit of detection is primarily a function of the thermodynamics of complexation between the ionophore and the analyte ion
  - Lowest limit of detection value can vary with the plasticizer & lipophilicity additives that are employed
- Linear Measurement Range
  - Typical Values are $10^{-5}$ to $10^{-1}$ Molar
  - Concentration range in which a Nernstian response is observed for a given pH and temperature range

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# How is the Quality of an Ion Selective Electrode Characterized? (Part 2)

- Selectivity Coefficients for Interfering Ions
  - These values can vary with the plasticizer and lipophilicity additives that are employed
  - These values are highly dependent upon the method used to determine selectivity coefficients
  - Typical values range from 10-100 fold selectivity ratios (poor to average) to 1,000-10,000 fold selectivity ratios (Excellent)
- Speed of Response
  - A function of the kinetics of ionophore complexation & PVC membrane formulation

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# How is the Quality of an Ion Selective Electrode Characterized? (Part 3)

- Valid pH Range
  - This is usually a combination of the acid/base chemistry exhibited by the ionophore and the PVC matrix sensitivity
- Thermal Stability
  - Function of reactivity and decomposition of the ionophore
- Drift *(Measured in mV per day)*
  - This is an equilibrium issue arising from whether the membrane is changing in characteristics
    - Membrane is absorbing water into PVC matrix, ionophore is migrating out of membrane, asymmetry of ion mobility
- Lifetime *(Constant Inline Use or Periodic Lab Use)*
  - This is typically an indication of the stability of the ionophore
    - Lifetime diminished by reduction & oxidation chemistry, photosensitivity, and sensitivity to hydrolysis

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# What are some areas of development for Ion Selective Measurement (Cations)?

- Successful measurements utilizing naturally produced ionophores and well known small molecule ionophores. *Partial List:*
  - $Na^{+}$, $Li^{+}$ (several known, including crown ethers)
  - $K^{+}$ (Valinomycin)
  - $NH_4^{+}$ (Nonactin)
  - $Ca^{2+}$ (several known)
- Areas of Difficulty. *Partial List:*
  - Heavy Metal Ions Including:
  - $Cu^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Fe^{2+,3+}$ …
  - $Mg^{2+}$ (poor selectivity), $Ag^{+}$ (non silver-halide)

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# What are some areas of development for Ion Selective Measurement (Anions)?

- Poor Performance for anion selective electrodes other than those covered by the silver-halide & monocrystal series. *Complete List:*
  - Fluoride ($F^-$), Chloride ($Cl^-$), Bromide ($Br^-$), Iodide ($I^-$), Cyanide ($CN^-$), Thiocyanate ($SCN^-$), Silver ($Ag^+$), Sulfide ($S^{2-}$)
- PVC Electrodes Requiring Improvement *Partial List Only:*
  - Perchlorate ($ClO_4^-$) - Environmental Remediation
  - Nitrate ($NO_3^-$) - Water Quality in Agriculture
  - Phosphate ($PO_4^{3-}$), Sulfate ($SO_4^{2-}$), Nitrite ($NO_2^-$), (Various Uses)

# Further Technical Papers and Information

- A more extensive technical paper expounding upon the topics overviewed in this short introduction to ion selective sensors slideshow and adding many other topics of related interest can be accessed from following URL:
  - http://www.astisensor.com/ISE_Tech/pH_ise_slides_papers.html
- If you should have any further questions about understanding and using ion selective sensors please contact Advanced Sensor Technologies, Inc. via the proper contact form accessible via the URL link below:
  - http://www.astisensor.com/cgi-bin/ttx.cgi