# Water Activity Prediction

GUSTAVO V. BARBOSA-CÁNOVAS

Washington State University
Pullman, Washington , USA

# *Water Activity*

- **Water activity is a critical factor that determines shelf life, influence how fast organisms will grow in a product, and may be the most important factor in controlling spoilage.**
- **By measuring water activity, it is possible to:**
  - **predict which microorganisms will and will not be potential sources of spoilage.**
  - **have an insight on the activity of enzymes and vitamins in foods that can have a major impact their color, taste, and aroma.**

# *Water Activity: Concept*

**The water activity scale extends from 0 (bone dry) to 1.0 (pure water)**

***Water Activity = $a_w = \rho/\rho_o$***

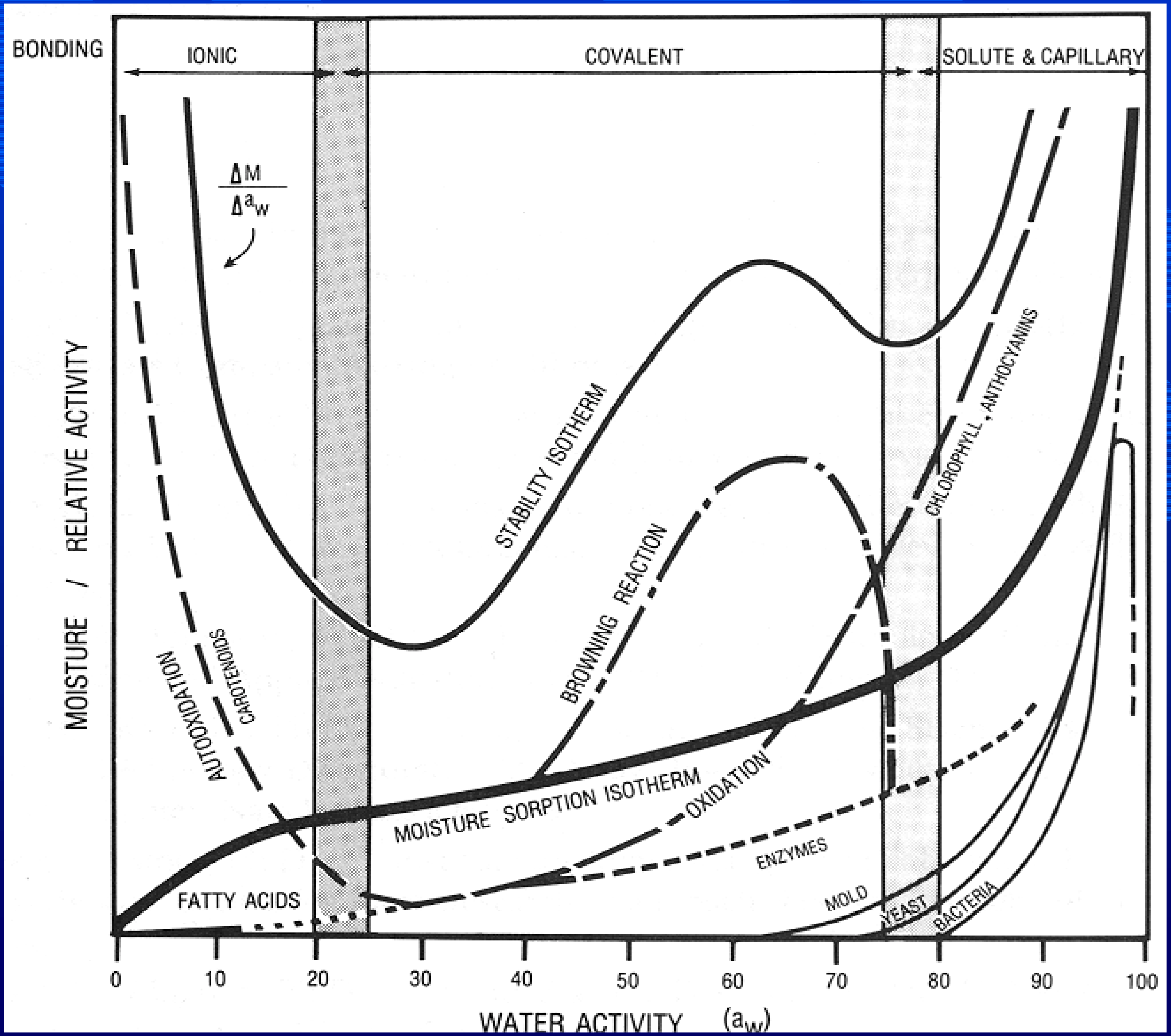
**where $\rho$ = water vapor pressure inside the food**

**$\rho_o$ = vapor pressure of pure water under the same conditions of temperature, etc.**

***Relative humidity = $\rho/\rho_o$***

**Each solute will affect the $a_w$ uniquely**

# WATER ACTIVITY - STABILITY DIAGRAM



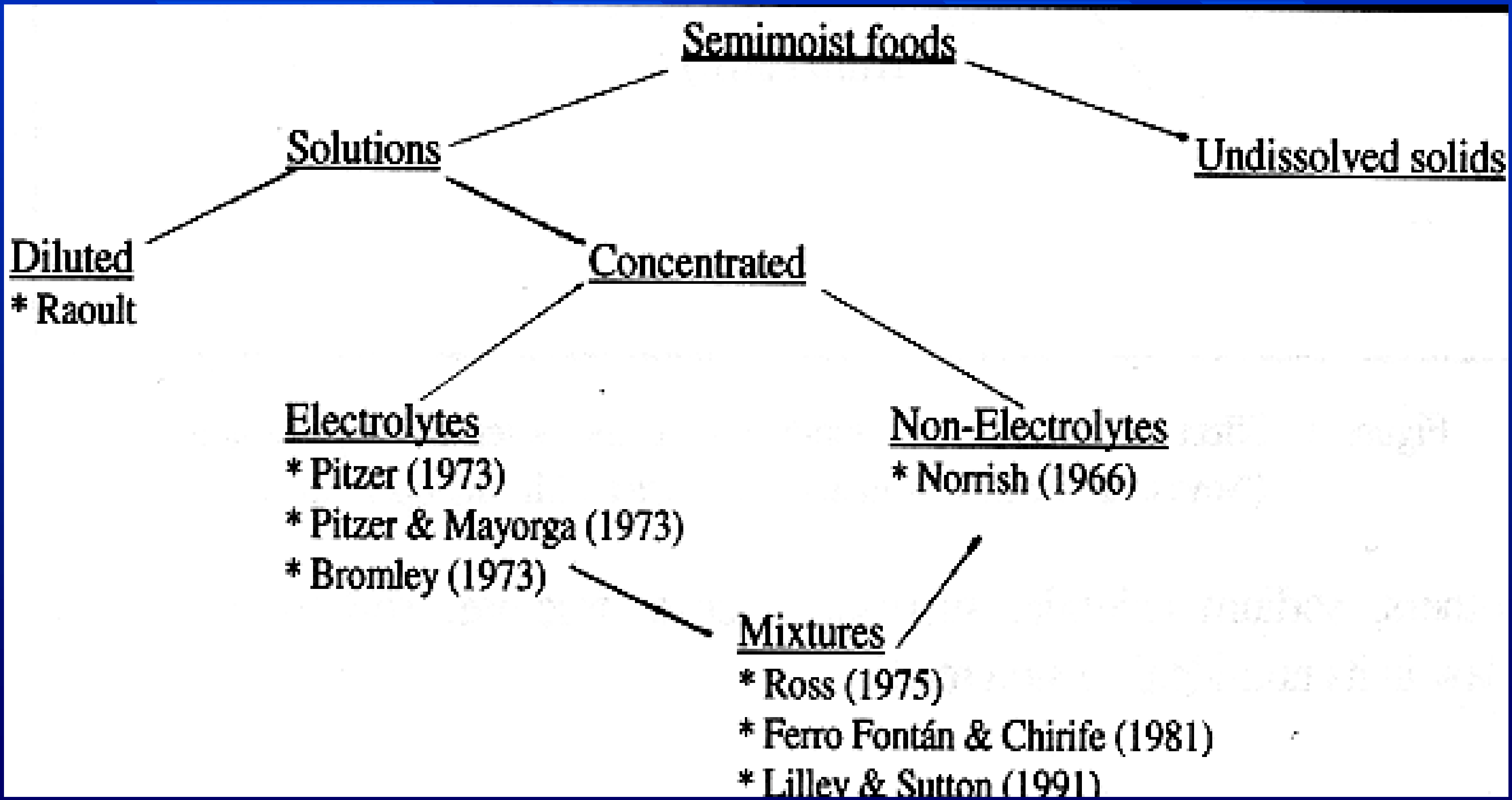
# *Water activity ($A_w$) of food products*

| *Food Product* | $A_w$ |
|---|---|
| **Fruits &Vegetables** | **0.97-1.00** |
| **Meats** | **0.95-1.00** |
| **Cheese** | **0.68-1.00** |
| **Jams & Jellies** | **0.75-0.94** |
| **Honey** | **0.54-0.75** |
| **Noodles** | **0.50** |
| **Dried Milk** | **0.20** |
| **Crackers** | **0.10** |

# *Some devices used to measure water activity in semimoist foods*

| | |
|---|---|
| ***LUFF* Aw-Wet Messer (Germany)** | Fiber-dimensional hygrometer |
| ***NOVASINA* Thermoconstanter (Switzerland)** | Electrical conductivity of immobilized salt solutions |
| ***VAISALA* Humicap (Finland)** | Electrical capacitance of polymer thin film |
| ***DECAGON* Aqualab (U.S.A.)** | Dew point by the chilled mirror technique |
| ***OTTAWA* aw-Meter (Canada)** | Thermometric device suited to establish compliance or non-compliance of test samples with a standard |
| ***NAGY* aw-Kryometer (Germany)** | Cryoscopic measurements; initial freezing point |

# *Procedure for calculation of $A_w$ in semimoist foods*



# *Prediction of Water Activity*

## By Mathematical Models

**Has been limited to aqueous solutions of electrolyte and non electrolyte solutes**

# *Raoult's Law*

$$y_i P = x_i P_i^0$$

**Where**

- **P** is the system pressure
- **$P_i^0$** is the saturation vapor pressure of the pure solvent
- **$y_i$** and **$x_i$** are the mole fraction of a particular component in the vapor and liquid phases respectively

**The application of Raoult's Law to food systems is not practical because of solvent-solute interactions.**

# *Raoult's Law*

- Assumes water activity lowering due to solute (range 0.95 to 1.0)
- All solute dissolved in all water
- No between solute interaction

**http://courses.che.umn.edu/02fscn4342-1s/Lecture_Folder/Topic%207-3Color.pdf**

# *Prediction of Water Activity*

## *By Mathematical Models*

**Water activity can be estimated by different theoretical and empirical models considering the types of solutes in the solution:**

- **Electrolytes**
- **Nonelectrolytes**
- **Mixtures**

# Prediction of Water Activity

## By Mathematical Models

### Non-electrolytes solutions

- Money and Born Equation
- Grover Equation
- Norrish Equation
- Teng and Lenzi

# Prediction of Water Activity

## Money and Born Equation

$$a_w = \frac{1.0}{(1.0 + 0.27n)}$$

**where *n* is the number of moles of sugar per 100 g of water.**

✓**This empirical equation is use for calculating $A_w$ of sugar confections, such as jams, fondant creams and boiled sweets.**

# Prediction of Water Activity

## Grover Equation

$$a_w = 1.04 - 0.1\Sigma_i s_i c_i + 0.0045\Sigma_i (s_i c_i)^2$$

**where**

- ***$C_i$* is the concentration of component *i***
- ***$S_i$* is the sucrose equivalent for different ingredients such as lactose (1.0), invert sugar (1.3), 45DE corn syrup (0.8), and gelatin (1.3).**

**The Grover model is an empirical approach to estimated $A_w$ in candy formulations.**

# Prediction of Water Activity

## Norrish Equation

$$\log (a_w/x_w) = -k_i(1-x_w)^2$$

$x_w$ = mole fraction of water

$k_i$ = Norrish constant for ingredient *i*

- ✓ Norrish equation takes into account a nonideal thermodynamic approach to determine the $A_w$ of binary mixtures.
- ✓ Norrish Equation - accounts for water binding properties of the solute and is more useful for large concentrations of solute.

**Table 3.1. Value of Norrish constant K for some sugars, polyols, amino acids, and amides.**

| | K |
|---|---|
| **Sugars** | |
| Sucrose | 6.47 ± 0.06 |
| Maltose | 4.54 ± 0.02 |
| Glucose | 2.25 ± 0.02 |
| Xylose | 1.54 ± 0.04 |
| Lactose | 10.2 |
| **Polyols** | |
| Sorbitol | 1.65 ± 0.14 |
| Glycerol | 1.16 ± 0.01 |
| Mannitol | 0.91 ± 0.27 |
| Propylene glycol | 4.04 |
| Arabitol | 1.41 |
| **Amino acids and amides** | |
| α-Amino-*n*-butyric acid | 2.59 ± 0.14 |
| β-Alanine | 2.52 ± 0.37 |
| Lactamide | −0.705 ± 0.066 |
| Glycolamide | −0.743 ± 0.079 |
| Urea | −2.02 ± 0.33 |
| Glycine | −0.868 ± 0.11 |
| **Organic acids** | |
| Citric acid | 6.2 |
| Malic acid | 1.82 |
| Tartaric acid | 4.68 |

(From Chirife et al., 1980 and Chirife and Favetto, 1992).

# Example

## Norrish Equation

- The water activity of a glucose-water solution (2.44:1 wt/wt) can be estimated by means of the Norrish equation. The mole fractions are: $X_1$ = 0.804 and $X_2$ = 0.196. The Norrish constant for glucose.is 2.25. Substituting for the values in the Norrish equation results in an estimated water activity of ***0.74***.

$$\log (a_w/x_w) = -k_i(1-x_w)^2$$

# *Example*

## Norrish Equation

- **The experimental water activity of this mixture is reported as *0.78* (Teng and Seow, 1981).**
- **The use of Raoult's law gives a water activity estimate of *0.80*.**

# Prediction of Water Activity

## Teng and Lenzi Equation

$$a_w = 1 + \sum_i A_i m^i$$

**For *i*=1 to k**

**Where $A_i$ is the polynomial coefficient, *m* is the solute molality, and *k* is the degree of the polynomial**

# *Prediction of Water Activity*

## *By Mathematical Models*

**Electrolytes solutions**

- **Pitzer Equation**
- **Bromley Equation**

# Prediction of Water Activity

## Pitzer Equation

$$\Phi - 1 = |z_m z_x| F + 2m(v_m v_x/v) B_{mx} + 2m^2 [(v_m v_x)^{1.5}/v] C_{mx}$$

$$F = -0.392\, I^{0.5} / (1 + 1.2\, I^{0.5})$$

$$I = 0.5 \Sigma_i m_i z_i^2$$

$$|z_m z_x| = \Sigma_i m_i z_i^2 / \Sigma_i m_i$$

$$B_{mx} = B_{mx}(0) + B_{mx}(1) \exp(-2.0\, I^{0.5})$$

$$a_w = \exp(-0.01802 \phi \Sigma i M i)$$

Where $\phi$ **is the osmotic coefficient,** $z_m$ **and** $z_x$ **are the charges of** $m$ **and** $x$ **ions,** $v_m$ **and** $v_x$ **are the respective number of ions,** $M$ **is the solution molality. B(0), B(1),** $B_{mx}$ **and C are the Pitzer coefficients.**

# Example

## *Pitzer Equation*

**Table 3.2.** Values for Pitzer and Bromley constants for some electrolytes.

| Electrolytes | $B(0)$[a] | $B(1)$ | $C$ | $B$[b] |
|---|---|---|---|---|
| NaCl | 0.0765 | 0.2664 | 0.00127 | 0.0574 |
| LiCl | 0.1494 | 0.3074 | 0.00359 | 0.1283 |
| KCl | 0.0483 | 0.2122 | −0.0008 | 0.0240 |
| HCl | 0.1775 | 0.2945 | 0.00080 | 0.1433 |
| KOH | 0.1298 | 0.3200 | 0.0041 | 0.1131 |
| $KH_2PO_4$ | −0.0678 | −0.1042 | −0.1124 | |
| NaOH | 0.0864 | 0.2530 | 0.0044 | 0.0747 |
| $NaH_2PO_4$ | −0.0533 | 0.0396 | 0.00795 | −0.0460 |

[a] $B(0)$, $B(1)$, and $C$ are Pitzer constants.
[b] $B$ is the Bromley constant.
(From Bromley, 1973; Pitzer and Mayorga, 1973)

# Example

## Pitzer Equation

- An electrolyte 1:1 type is in solution(e.g., a solution of NaCl, 2.31 molal at 25°C).
- The Pitzer's $B_{mx}(0)$, $B_{mx}(l)$, and $C_{mx}$ parameters for NaCl are 0.0765, 0.2664, and 0.00127, respectively. The following can be defined for the ions: $z_{Na} = 1$, $z_{Cl} = 1$, $\nu_{Na} = 1$, and $\nu_{Cl} = 1$.
- The osmotic coefficient is evaluated from equation:

$$\Phi = -1000 \ln a_s / (M_s \sum \nu_r m_r)$$

# *Example*

## *Pitzer Equation*

**$m_{Na}$=2.31** **$m_{Cl}$=2.31** ***I*=2.31** **$|z_{Na}z_{Cl}|$ =1.0**

**F = -0.211** **$B_{NaCl}$ = 0.089** **Φ = 1.001**

**Water activity is evaluated from Equation:**

$$a_W = \exp(-0.01802\phi\Sigma i M i)$$

**$a_w$ = exp(-0.01802 x 1.001 X (2.31 + 2.31 a, = 0.92**

**The experimental water activity of this mixture is *0.92* (Teng and Seow, 1981).**

# Prediction of Water Activity

## Bromley Equation

$$\Phi = 1 + 2.303\,[T_1 + (0.06 + 0.6B)\,T_2 + 0.5\,B\,I]$$

$$T_1 = 0.511\,|z_m z_x|\,[1 + 2(1 + I^{0.5})\ln(1 + I^{0.5}) - (1 + I^{0.5})^2]\,/\,(I(1 + I^{0.5}))$$

$$T_2 = (1 + 2aI)\,/\,(a(1 + aI)^2) - \ln(1 + aI)/(a^2 I)$$

$$a = 1.5\,/\,|z_m z_x|$$

$$B = B_m + B_x + \delta_m \delta_x$$

Where $\phi$ **is the osmotic coefficient,** $z_m$ **and** $z_x$ **are the charges of** $m$ **and** $x$ **ions,** $v_m$ **and** $v_x$ **are the respective number of ions.** $M$ **is the solution molality,** $I$ **is the ionic strength.** $B$, $B_m$, $B_x$, $\delta_m$, $\delta_x$ **are the Bromley coefficients.**

$$a_w = \exp(-0.01802\,\phi\,\Sigma_i M_i)$$

# *Example*

## Bromley Equation

The Bromley B parameter is equal to 0.0574 for the NaCl. The ionic strength $I$=2.31 and the charge product $|z_{Na}z_{Cl}|$ =1.0.

- Substituting these values gives in the equations presented above:

$T_1$ = -0.0615 $T_2$ = -0.0226 a = 1.5

The osmotic coefficient (Φ ) and the water activity are:

$\Phi = 1.0062$ $a_w = 0.919$

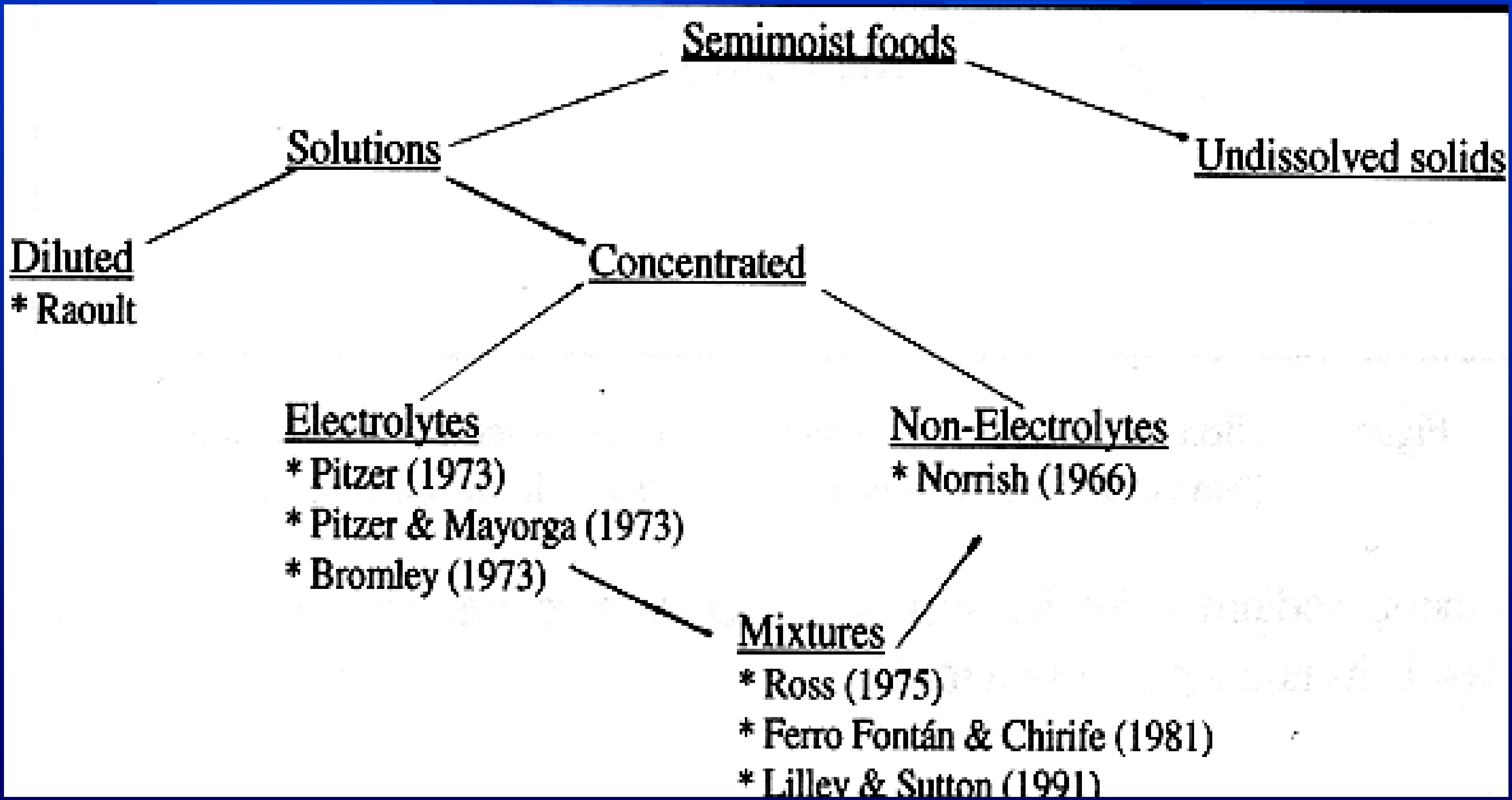
# *Prediction of Water Activity*

***By Mathematical Models***

## Multicomponents Mixtures

- **Ross Equation**
- **Ferro-Fontán-Benmergui-Chirife Equation**
- **Ferro-Chirife-Boquet Equation**
- **Lang-Steinberg Equation**
- **Pitzer-Kim Equation**

# *Procedure for calculation of $A_w$ in semimoist foods*



# Prediction of Water Activity

## Ross Equation

$$a_w = \Pi_i (a_w^0) i$$

**$a_w^0$=water activity of each component in the binary mixture**

# Prediction of Water Activity

## Ferro-Fontán-Benmergui-Chirife Equation

$$a_w = \Pi_i (a_{wi}(I))^{\frac{Ii}{I}}$$

$$I_i = 0.5 v_i m_i \left| Z_m Z_x \right|$$

**$a_{wi}(I)$= water activity of a binary solution of I at the same total ionic strength (I) of the multicomponent solution. $I_i$ is the ionic strength of component $i$ in the mixture, $v_i$ is the total of ions of the solute $i$ in solution, $m_i$ is the molality of the solute, and $z_m$ and $z_x$ are the charges of $m$ and $x$ ions.**

# *Prediction of Water Activity*

## Ferro-Chirife-Boquet Equation

$$(a_w)_m = X_1 \exp\left(-K_m X_2^2\right)$$

$$K_m = \sum_{s=1}^{n} K_s C_s \left(\frac{M_t}{M_s}\right) \qquad M_t = \left[\sum_{s=1}^{n}\left(\frac{C_s}{M_s}\right)\right]^{-1}$$

**$X_1$ and $X_2$ are the molar fractions of the solvent and solutes, $K_s$ is the Norrish K value for each solute in the mixture, $C_s$ is the weight ratio of each solute to the total of solids in the mixture, and $M_s$ is the molecular weight of each component**

# *Example*

## Ferro-Chirife-Boquet Equation

**A solution of glucose (5.96% wt/wt) and sucrose (46.01%wt/wt) has a measured water activity of 0.926 (Teng and Seow,198l). The K values of glucose and sucrose are 2.25 and 6.47, respectively. The $K_m$ and $M_t$ values are evaluated from equations mentioned above.**

$K_m = 5.65$ $M_t = 310.82$

**Then, the predicted water activity using Ferro-Chirife-Boquet equation is *0.923*.**

# *Prediction of Water Activity*

## Lang-Steinberg Equation

$$Log(1-a_w)=(MW-\sum a_i w_i)/\sum b_i w_i$$

**Where $a_i$ and $b_i$ are the Smith equation constants for each component *i* in the mixture. *M* is the moisture content of the mixture, *W* is the total dry material of the mixture, $w_i$ is the dry material of each component *i* in the mixture.**

✓ **The model may predict water activities over the range 0.30 to 0.95 of a multicomponent mixture**

# *Example*

## Lang-Steinberg Equation

**A mixture of starch (0.79 g/g of total sample) and sucrose (0.09 g/g of total sample) has a moisture con- tent of 0.219 g of water/g of solids at an aw of 0.90. The Smith constants for each component are (Lang and Stein- berg, 1981):**

**Starch: $a_i$ = 0.0989 $b_i$ = -0. 1485**

**Sucrose: $a_i$ = -0.5944 $b_i$ = 1.2573**

# *Example*

## Lang-Steinberg Equation

**Rearranging the data in terms of the Lang and Steinberg model:**

**$M$=0.29gofwater/g of solid**

**$W$=0.89g of solids**

**$(a_i w_i)_{starch}$= 0.08 g of water**

**$(a_i w_i)_{sucrose}$ = -0.06 g of water**

**$(b_i w_i)_{starch}$=-0.12g of water**

**$(b_i w_i)_{sucrose}$=0.13g of water**

**Replacing the above values in Lang-Steinberg equation and taking the $\log_{10}$ to base 10:**

$$a_w = 0.90$$

# Prediction of Water Activity

## Pitzer-Kim Equation

$$\phi - 1 = \left(\sum m_i\right)^{-1} \left\{ IF' - F) + \sum_i \sum_j m_i m_j (\lambda_{ij} + I\lambda'_{ij}) + 2\sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} \right\}$$

$$F = -0.392\, I^{0.5} / (1 + 1.2\, I^{0.5})$$

$$F' = dF / dI$$

$$\lambda'_{ij} = d\lambda_{ij} / dI$$

**Where m is the molality of a particular ion (i,j,or k). $\lambda_{ij}$ is the second virial coefficient, $\mu_{ijk}$ is the third virial coefficient, and $I$ is the ionic strength.**

# Example

## Pitzer-Kim Equation

An aqueous solution of NaCl (9.29% wt/wt) and LiCl (1.57% wt/wt) has an experimental water activity of 0.9312 (Tsong and Seow, 1981). Pitzer and Kim equation can be expressed as

$$\Phi - 1 = (\Sigma m_i)^{-1}\{2IF + 2\,\Sigma_i\Sigma_j m_i m_j (B_{ij} + C_{ij}(\Sigma mz)/(z_i z_j)^{0.5}\}$$

where $B_{ij}$, $F$ and $I$ are evaluated by

$$F = -A\frac{I^{0.5}}{\left(1 + bI^{0.5}\right)}$$

$$I = 0.5\Sigma_i m_i z_i^2 \quad \text{and} \quad |z_m z_x| = \Sigma_i m_i z_i^2 / \Sigma_i m_i$$

$$B_{mx} = B_{mx}(0) + B_{mx}(1)\exp(-\alpha I^{0.5})$$

# Example

## Pitzer-Kim Equation

$I = 2.198$ $F = -0.2087$ $B_{NaCL} = 0.0902$ $B_{LiCl} = 0.1652$

$C_{NaCl} = 0.00127$ $C_{LiCl} = 0.0036$ $\sum m_i = 4.408$ $\sum mz = 4.408$

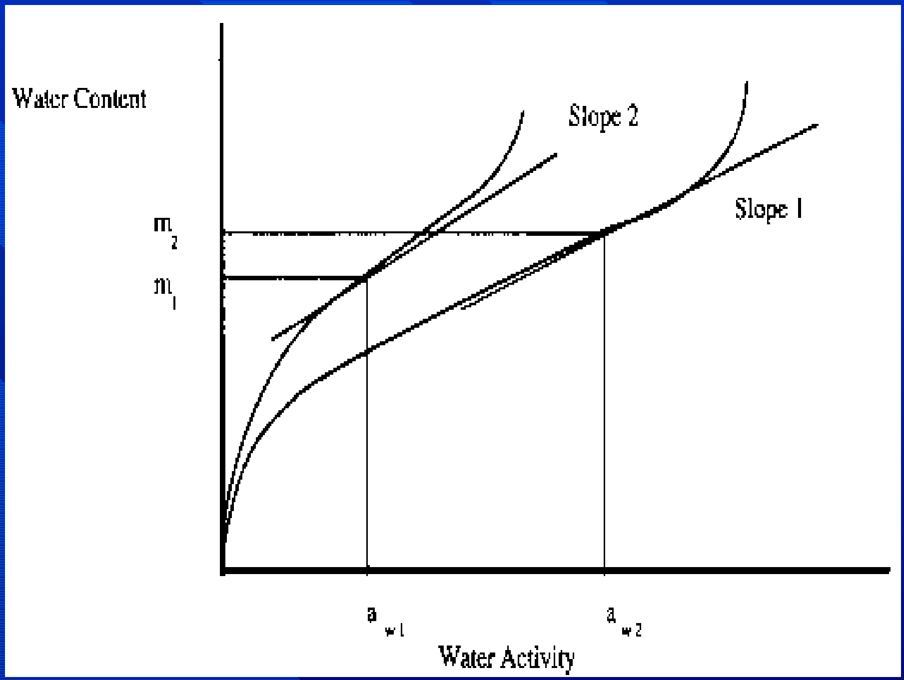
- **The predicted values for the osmotic coefficient and water activity are the following:**

$\Phi = 1.0811$ $a_w = 0.92$

# *Prediction of Water Activity*

## Salwin-Slawson Equation

$$a_w = \frac{\sum_i a_i s_i w_i}{\sum_i s_i w_i}$$




**Where a$_i$ is the initial water activity of component *i* used in the mixture, $s_i$ is the sorption isotherm slope of component *i* at the mixture temperature, and $w_i$ is the dry weight of component *i*.**

# Prediction of Water Activity

## Roa-Tapia Model

**Based on the concept proposed by Salwin and Slawson, and the linear relationship of Favetto and Chirife (1985).**

$$a_{wM} = 1 - \sum_{i} K_i m_i$$

**Where $a_wM$= water activity in equilibrium state o final of a complex mixture, $k$ = constant of Faveto and Chirife equation at 25°C[kg w/g mol], $m$ = molality and $i$= number of solutes in a complex mixture.**

# *Prediction of Water Activity*

## By Computer Programs

- **Vega-Mercado H., Romanach B., Barbosa-Cánovas G.V. et al, *Developed an Interactive Computer Program* to accurately predict the Aw of multicomponent systems containing fiber, proteins and fats**

# *Prediction of Water Activity*

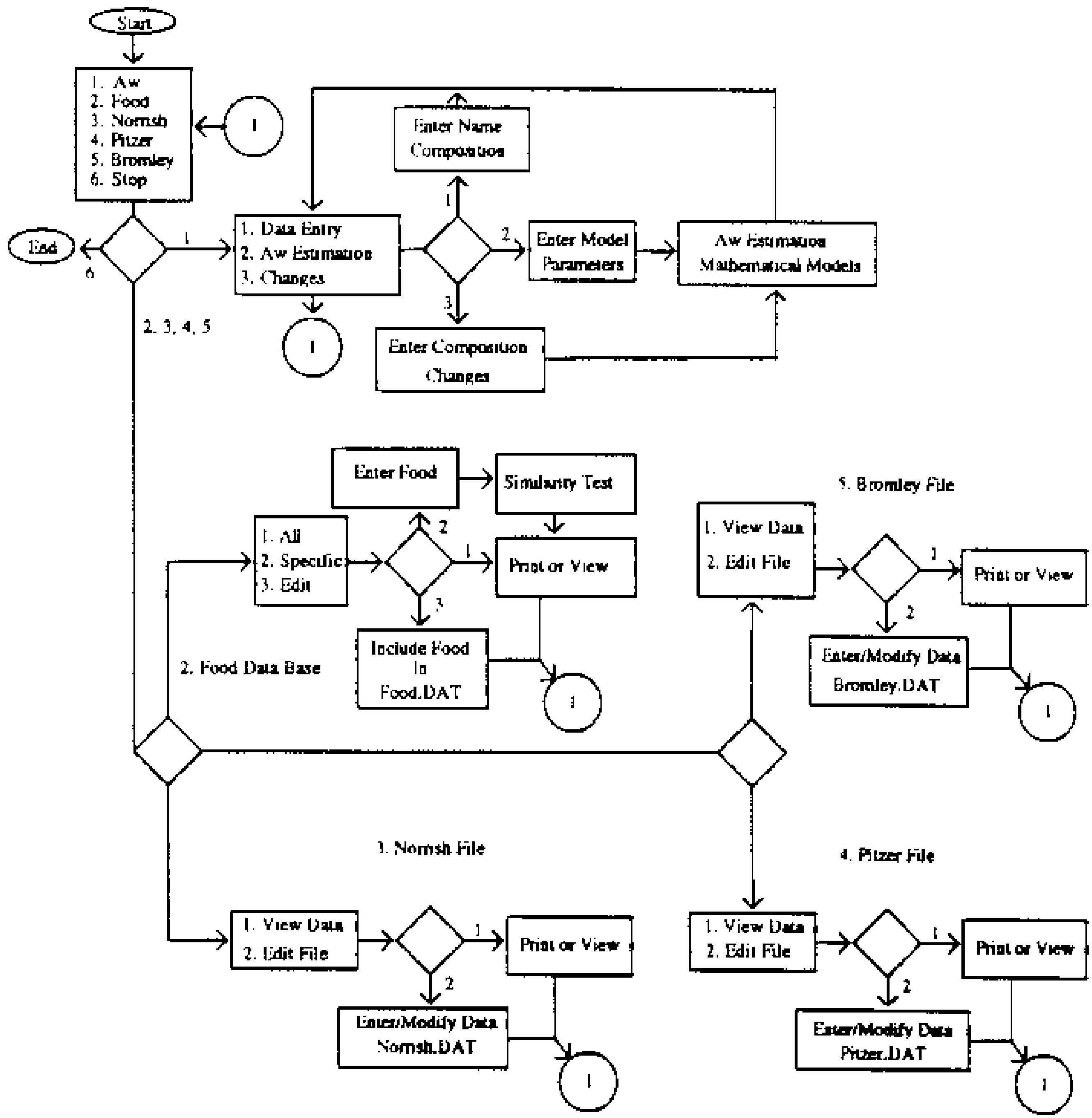
## By Computer Programs

- **Program Capabilities**
  - **Predict $A_w$ of model food systems by several well accepted equations (Bromley, Pitzer, Norrish, Ferro-Cherife-Boquet, Ross, Ferro Benmergui-Cherife)**
  - **Establish similarity levels between foods of known $a_w$ and composition to new products where composition is available**

# *Prediction of Water Activity*

## By Computer Programs

- **Program Capabilities**
  - **Calculate deviation factors based on previously established similarity levels, where the presence of fibers, fats and proteins is taken into account**
  - **Programmed in MS-DOS QBASIC 1.0, available from the authors**

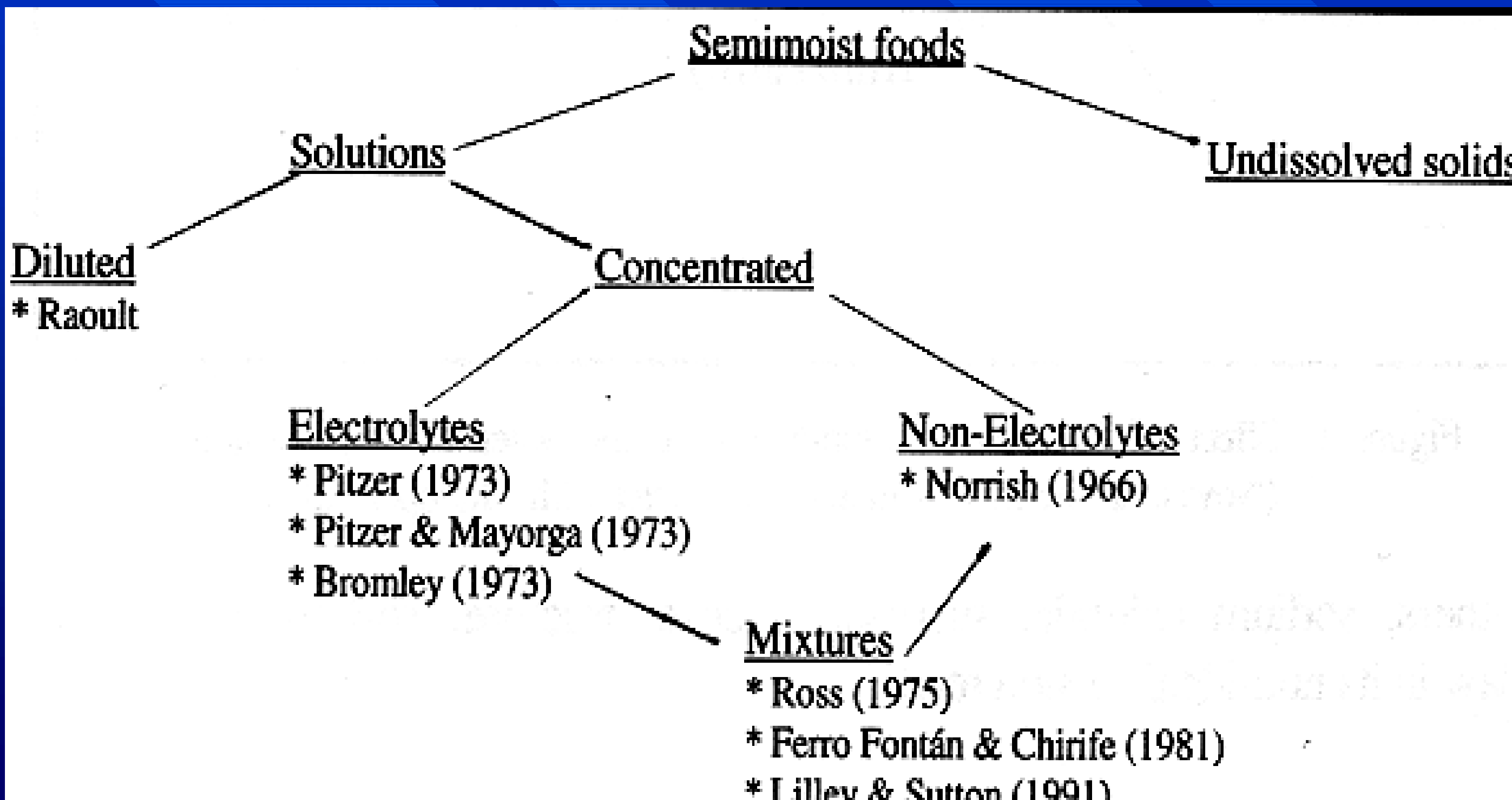

Start
1. Aw
2. Food
3. Nomsh
4. Pitzer
5. Bromley
6. Stop
End
6
1
2, 3, 4, 5
1. Data Entry
2. Aw Estimation
3. Changes
Enter Name
Composition
Enter Model
Parameters
Aw Estimation
Mathematical Models
Enter Composition
Changes
2. Food Data Base
1. All
2. Specific
3. Edit
Enter Food
Similarity Test
Print or View
Include Food
In
Food.DAT
5. Bromley File
1. View Data
2. Edit File
Print or View
Enter/Modify Data
Bromley.DAT
3. Nomsh File
1. View Data
2. Edit File
Print or View
Enter/Modify Data
Nomsh.DAT
4. Pitzer File
1. View Data
2. Edit File
Print or View
Enter/Modify Data
Pitzer.DAT

# *Prediction of Water Activity*

## By Computer Programs

- The accuracy of the predicted $a_w$ is affected when the algorithm is applied to food systems which contain fats and proteins.
- Food products containing *fats and proteins* show a deviation factor of 1.07, on average, after one iteration.
- The discrepancy in $a_w$ values, $a_{wpred}$ and $a_{wrep}$, can be explained in terms of water bound on proteins or associated with fatty mesomorphic structures.

# *Procedure for calculation of $A_w$ in semimoist foods*



- *http://courses.che.umn.edu/02fscn4342-1s/default.html*
- *http://fscn.che.umn.edu/Ted_Labuza/PDF_files/Presentations/Aw&Kinetics.pdf*
- *http://fscn.che.umn.edu/Ted_Labuza/PDF_files/Presentations/AwTgKinetics.pdf*
- *http://fscn.che.umn.edu/Ted_Labuza/PDF_files/Presentations/Multidomain.pdf*
- *http://courses.che.umn.edu/02fscn4342-1s/Lecture_Folder/Topic%202-Water%20bonding3color.pdf*

*Thank you!!*