Water Activity and Prediction of Colligative Properties: Forgotten Theory

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Water Activity

Not just the controlling variable for spoilage
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Not just the controlling variable for spoilage

Water activity, \( a_w \), is the key variable for determination of the Colligative Properties:

- Boiling point elevation
  - (Vapour pressure)
- Freezing point depression
- Osmotic pressure
Applications of Properties

• Boiling Point Elevation
  – Strongly affects evaporator design and performance at high concentrations

• Osmotic Pressure
  – A limiting factor in reverse osmosis of whey permeate and milk

• Freezing Point Depression
  – The easiest and most accurate measurement. Used to detect dilution of raw milk
Definitions

Water activity is often defined as the ratio of the vapour pressure of water (over a sample) to the vapour pressure over pure water at the same temperature.

\[ a_w = \frac{p}{p_{sat}} \]

It is also known from

\[ RH = a_w \times 100\% \]

Relative humidity is water activity expressed as a percentage rather than as a decimal, i.e., they are the same.
Equilibrium

vapour
\[ T - \Delta T_b, P \]

ice
\[ T + \Delta T_f \]
sugar solution
\[ T, P_{atm} \]

water
\[ T, P_{atm} - \pi \]
At equilibrium

Chemical potential of water = solution (osmosis)

Chemical potential of solution = ice (freezing)

Chemical potential of solution = vapour (evaporation)

This leads to ....
Colligative Properties

Osmotic pressure
\[ \pi = -\frac{RT}{V_w} \ln a_w \]

Boiling point elevation
\[ \Delta T_b = -\frac{RT_{wb}^2}{\Delta h_v} \ln a_w \]

Freezing point depression
\[ \Delta T_f = \frac{RT_{wf}^2}{\Delta h_f} \ln a_w \]

molar volume
\[ \bar{V}_w = 1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \]

heat of vapourisation
\[ \Delta h_v = 40650 \text{ J mol}^{-1} \]

heat of fusion
\[ \Delta h_f = 6010 \text{ J mol}^{-1} \]
Colligative Properties

Osmotic pressure

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But Chemists Did Not Like Logs
But Chemists Did Not Like Logs

Natural logs
But Chemists Did Not Like Logs

Natural logs

Artificial Logs
But Chemists Did Not Like Logs

\[ y = \ln(x) \]

Natural logs  Artificial Logs
But Chemists Did Not Like Logs

Natural Logs

Artificial Logs
Instead ...

They assumed **dilute** solutions and they used molality, $m$ (moles of solute per unit mass)

$$\Delta T_f = K_f \cdot m \cdot i$$

where $K_f$ is the **cryoscopic constant** and $i$ is the number of entities (e.g., ions) a molecule splits into when dissolved.

$$\Delta T_b = K_b \cdot m \cdot i$$

where $K_b$ is the **ebullioscopic constant**

$$\pi = C \cdot R \cdot T$$

where $C$ is the molar concentration of the solute in solution.
• These equations have been taught for over 50 years.
• Nearly all physical chemistry books include them
• The connection with $a_w$ has been lost
• The connection between the properties has been lost
• We are only interested when concentrations are high
• Accuracy has been lost
But now everyone can calculate a log
Properties of Milk

We use

\[ a_w = x_w \quad \text{water activity = mole fraction} \]

For pure solutions we use \( a_w = \gamma x_w \) where \( \gamma \) is the activity coefficient

All we need is the molecular mass of components

Then fit experimental data by finding the “best” molecular mass of milk minerals
Freezing point depression

- Data from Ping, Chen and Free “Measurement and Data Interpretation of the Freezing Point Depression of Milks” J Food Eng 1996

<table>
<thead>
<tr>
<th>Milk</th>
<th>$x_r$ (wt%)</th>
<th>$X_r$ (wt%)</th>
<th>FPD (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole milk</td>
<td>9.146</td>
<td>6.889</td>
<td>0.365</td>
</tr>
<tr>
<td></td>
<td>17.994</td>
<td>13.888</td>
<td>0.801</td>
</tr>
<tr>
<td></td>
<td>28.673</td>
<td>22.808</td>
<td>1.475</td>
</tr>
<tr>
<td></td>
<td>34.816</td>
<td>28.191</td>
<td>1.975</td>
</tr>
<tr>
<td></td>
<td>39.654</td>
<td>32.568</td>
<td>2.461</td>
</tr>
<tr>
<td>Skim milk</td>
<td>4.318</td>
<td>4.285</td>
<td>0.230</td>
</tr>
<tr>
<td></td>
<td>12.455</td>
<td>12.368</td>
<td>0.700</td>
</tr>
<tr>
<td></td>
<td>17.951</td>
<td>17.833</td>
<td>1.110</td>
</tr>
<tr>
<td></td>
<td>23.064</td>
<td>22.921</td>
<td>1.489</td>
</tr>
<tr>
<td></td>
<td>28.383</td>
<td>18.220</td>
<td>1.995</td>
</tr>
<tr>
<td></td>
<td>33.416</td>
<td>33.238</td>
<td>2.534</td>
</tr>
</tbody>
</table>

TABLE 3
FPD Data and Effective Concentrations for Whole Milk, Skim milk and Mixed milk
# Simple Spreadsheet Calculation

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Skim milk concentrate</td>
<td>40%</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Mass fraction</td>
<td>Molecular mass</td>
<td>moles/kg</td>
<td>Mole fraction</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Fat</td>
<td>0.33%</td>
<td>1000000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>5</td>
<td>Protein casein</td>
<td>12.57%</td>
<td>1000000</td>
<td>0.0001</td>
<td>0.0000</td>
</tr>
<tr>
<td>6</td>
<td>Whey Prot</td>
<td>3.14%</td>
<td>16000</td>
<td>0.0020</td>
<td>0.0001</td>
</tr>
<tr>
<td>7</td>
<td>Lactose</td>
<td>20.71%</td>
<td>342</td>
<td>0.6055</td>
<td>0.0176</td>
</tr>
<tr>
<td>8</td>
<td>Minerals</td>
<td>3.24%</td>
<td>67</td>
<td>0.4841</td>
<td>0.0141</td>
</tr>
<tr>
<td>9</td>
<td>water</td>
<td>60.00%</td>
<td>18</td>
<td>33.3333</td>
<td>0.9683</td>
</tr>
<tr>
<td>10</td>
<td>Total</td>
<td></td>
<td></td>
<td>34.4250</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Heat of evaporation</td>
<td>42468 J mol⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Heat of freezing</td>
<td>6010 J mol⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Molar volume</td>
<td>1.80E-05 m³ mol⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Water activity</td>
<td>0.968</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Osmotic P (10°C) /bar</td>
<td>42.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>BPE (60°C) /°C</td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>FPD pred /°C</td>
<td>3.33</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Data Analysis Results

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minerals</td>
<td>67 g/mol</td>
</tr>
<tr>
<td>Lactose</td>
<td>342 g/mol</td>
</tr>
<tr>
<td>Whey protein</td>
<td>16000 g/mol</td>
</tr>
<tr>
<td>Fat, Casein</td>
<td>1,000 kg/mol</td>
</tr>
</tbody>
</table>

Measured Freezing Point Depression [°C] vs. Predicted FPD [°C]

- Skim Milk
- Whole Milk
More Data

• The data of Radewonuk et al. (J Dairy Sci 1983) for FPD of non-fat reconstituted milk, evaporated milk and RO milk was also examined.

• The MW of the minerals was found to be 68 ±1 g/mol (67 from the previous data)
Boiling Point Elevation

from Kessler 2002

Skim milk
Whole milk
Osmotic Pressure

![Graph showing osmotic pressure vs total solids for whey permeate and whole milk. The graph indicates a practical maximum of osmotic pressure at around 35 bars.](image)

Whey permeate

Whole milk

Practical maximum
Water Activity

![Graph showing water activity (a_w) vs total solids.

- The graph illustrates the relationship between water activity and total solids in whole milk.
- It indicates that many yeasts are inhibited at a water activity of approximately 0.85.
- Most moulds are inhibited at a water activity below 0.80.

Water activity [a_w]

- 1.00
- 0.95
- 0.90
- 0.85
- 0.80
- 0.75
- 0.70

Total Solids

- 70%
- 80%
- 90%
- 100%

Whole milk

Many yeasts inhibited

Most moulds inhibited
Conclusions

• Water activity, freezing point depression, boiling point elevation and osmotic pressure are intimately linked by theory.

• The connection between them is very useful for property predictions.

• Chemists and Food Scientist can now calculate natural logarithms and should use the best equations.