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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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.

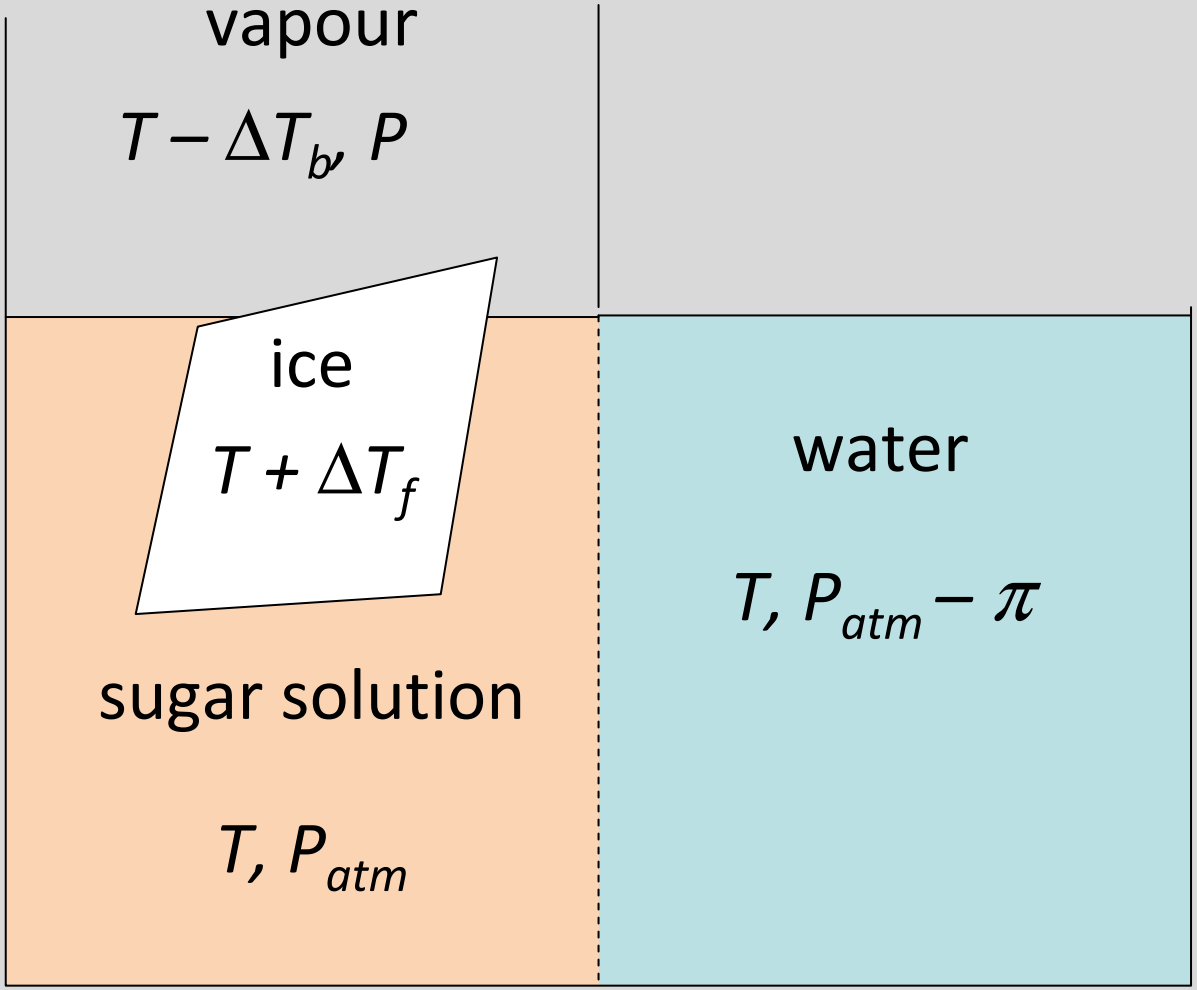
$$a_w = \frac{p}{p_{sat}}$$

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



Equilibrium

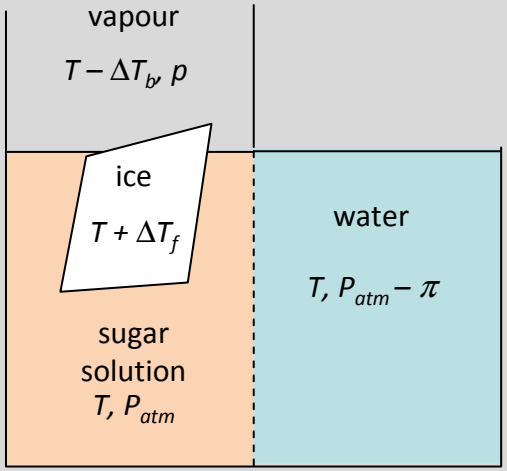
At equilibrium

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

$$\pi = -\frac{RT}{\overline{V}_w} \ln a_w$$

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

$$\overline{V}_w = 1.8 \times 10^{-5} \text{ m}^3 \text{mol}^{-1}$$

heat of vapourisation

$$\Delta h_v = 40650 \text{ J mol}^{-1}$$

heat of fusion

$$\Delta h_f = 6010 \text{ J mol}^{-1}$$

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But Chemists Did Not Like Logs

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Natural logs

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Natural logs

Artificial Logs

But Chemists Did Not Like Logs

$$y = \ln(x)$$

Natural logs

Artificial Logs

But Chemists Did Not Like Logs

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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

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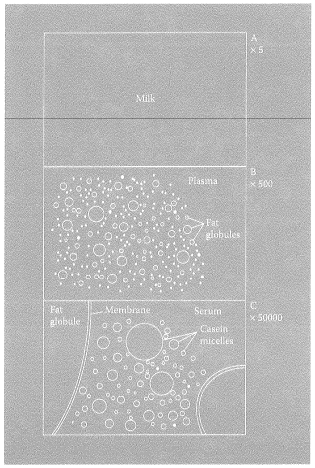

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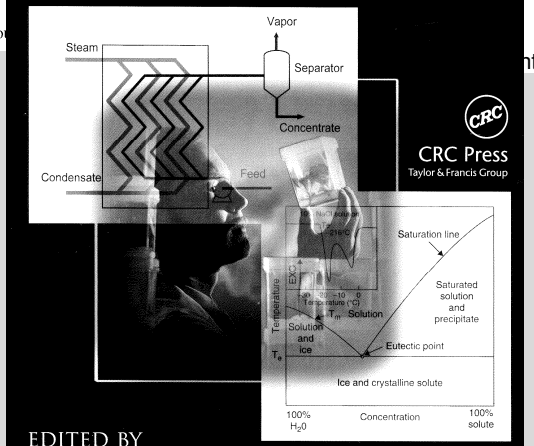

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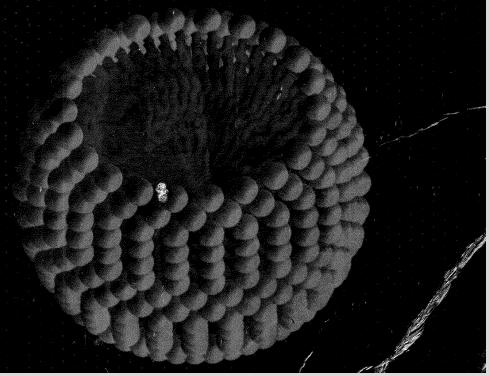
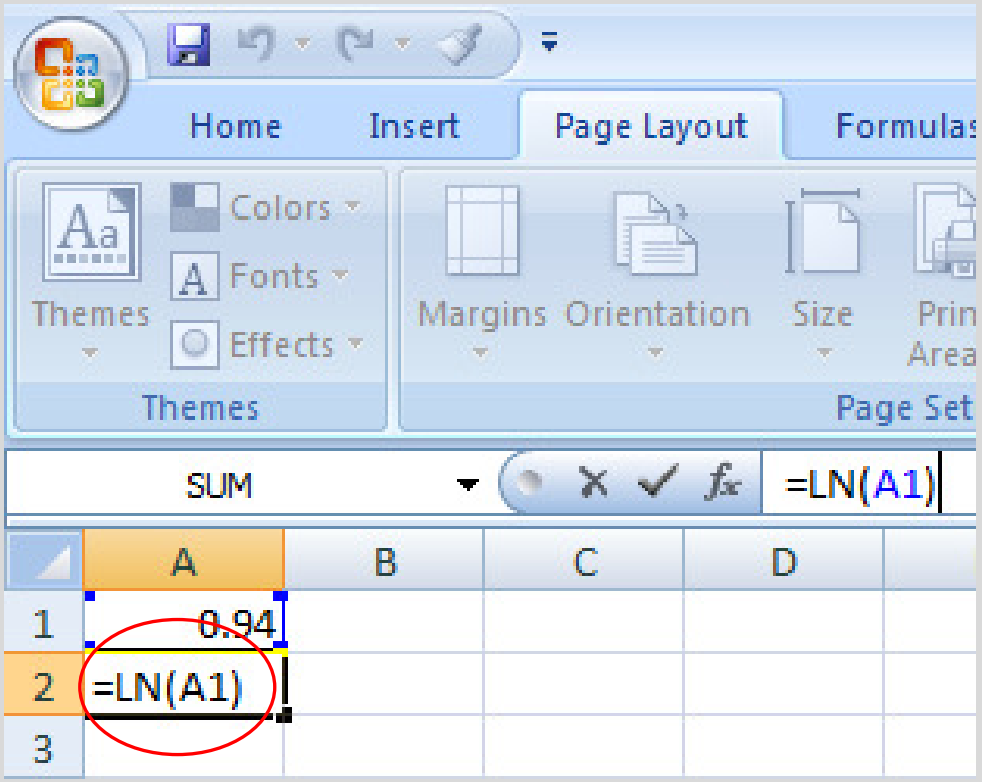


But now everyone can calculate a log



Properties of Milk

We use

$a_w = x_w$ *water activity = mole fraction*

For pure solutions we use $a_w = \gamma x_w$ *where* γ *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

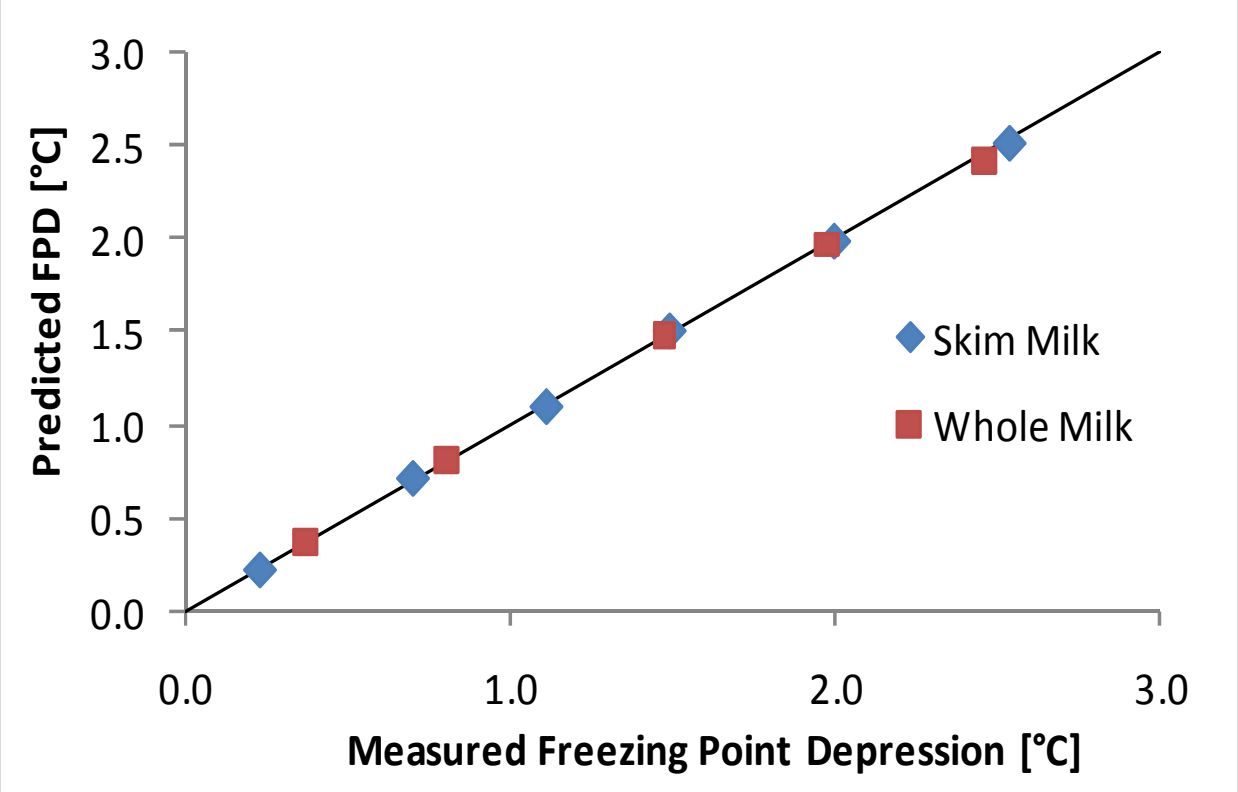
TABLE 3
FPD Data and Effective Concentrations for Whole Milk, Skim milk and Mixed milk

Milk	x_s *(wt%)*	X_s *(wt%)*	*FPD (°C)*
Whole milk	9·146	6·889	0·365
	17·994	13·888	0·801
	28·673	22·808	1·475
	34·816	28·191	1·975
	39·654	32·568	2·461
Skim milk	4·318	4·285	0·230
	12·455	12·368	0·700
	17·951	17·833	1·110
	23·064	22·921	1·489
	28·383	18·220	1·995
	33·416	33·238	2·534

Simple Spreadsheet Calculation

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

Data Analysis Results

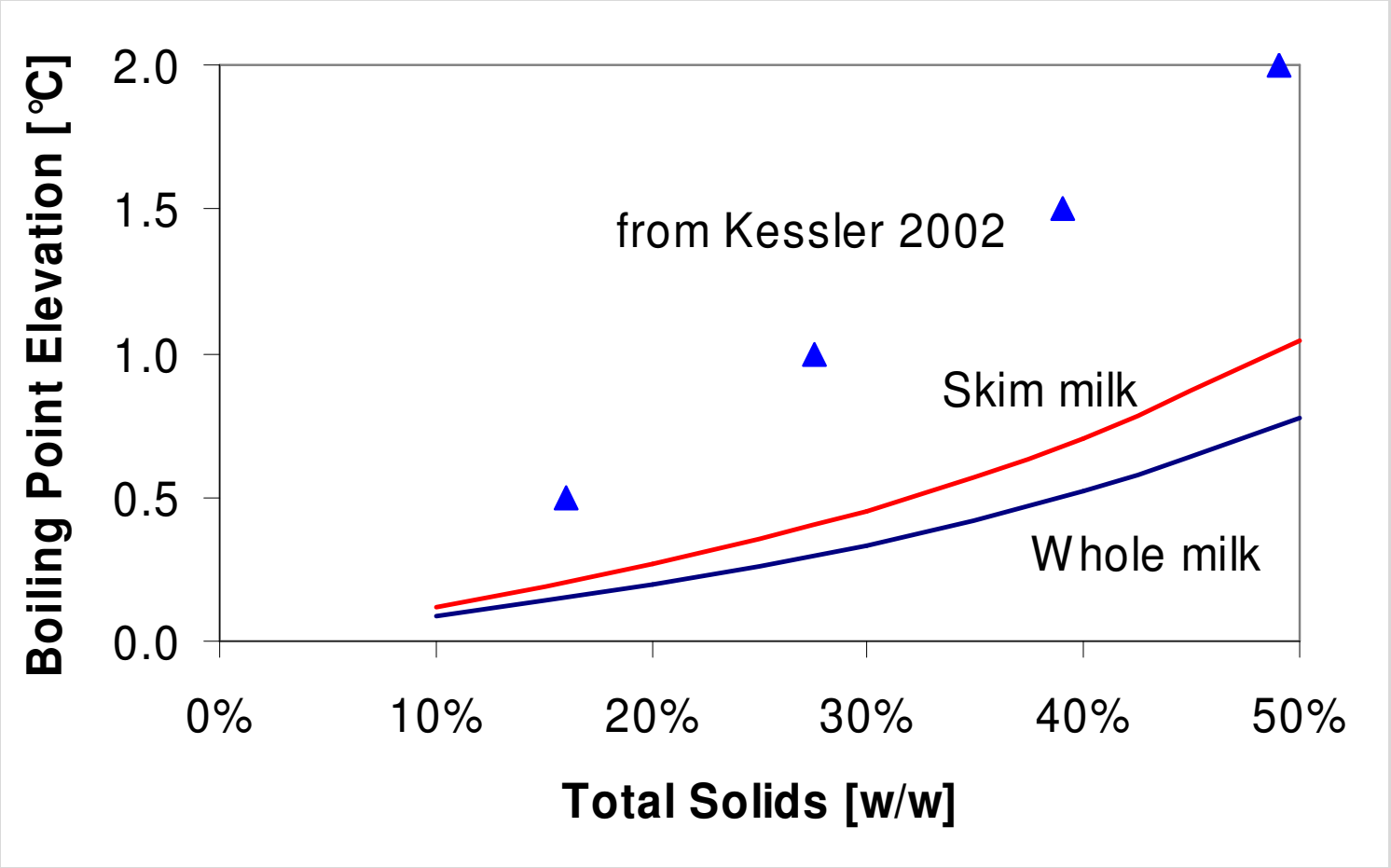


Minerals	67 g/mol	Lactose	342 g/mol
Whey protein	16000 g/mol	Fat, Casein	1,000 kg/mol

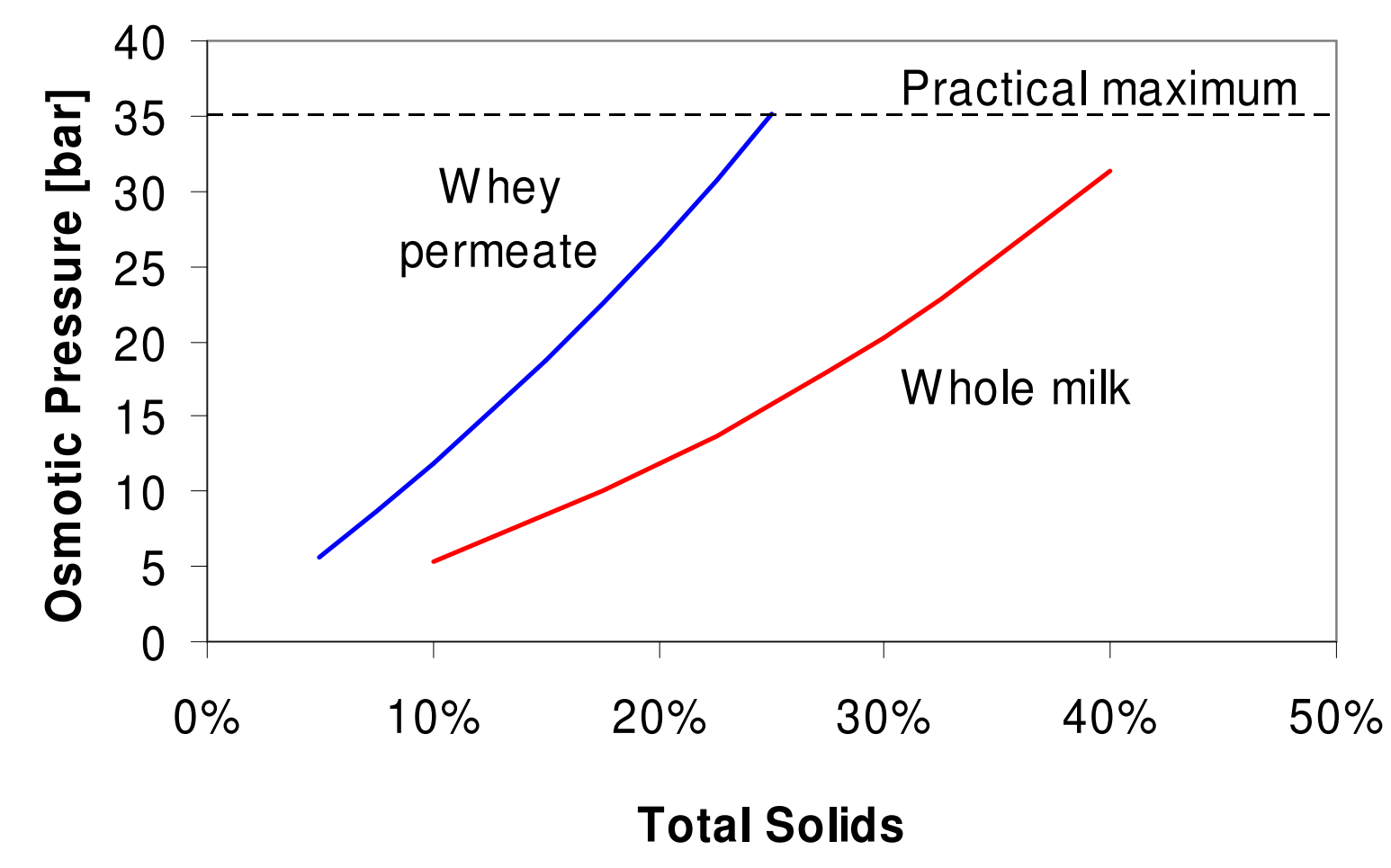
More Data

- 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)

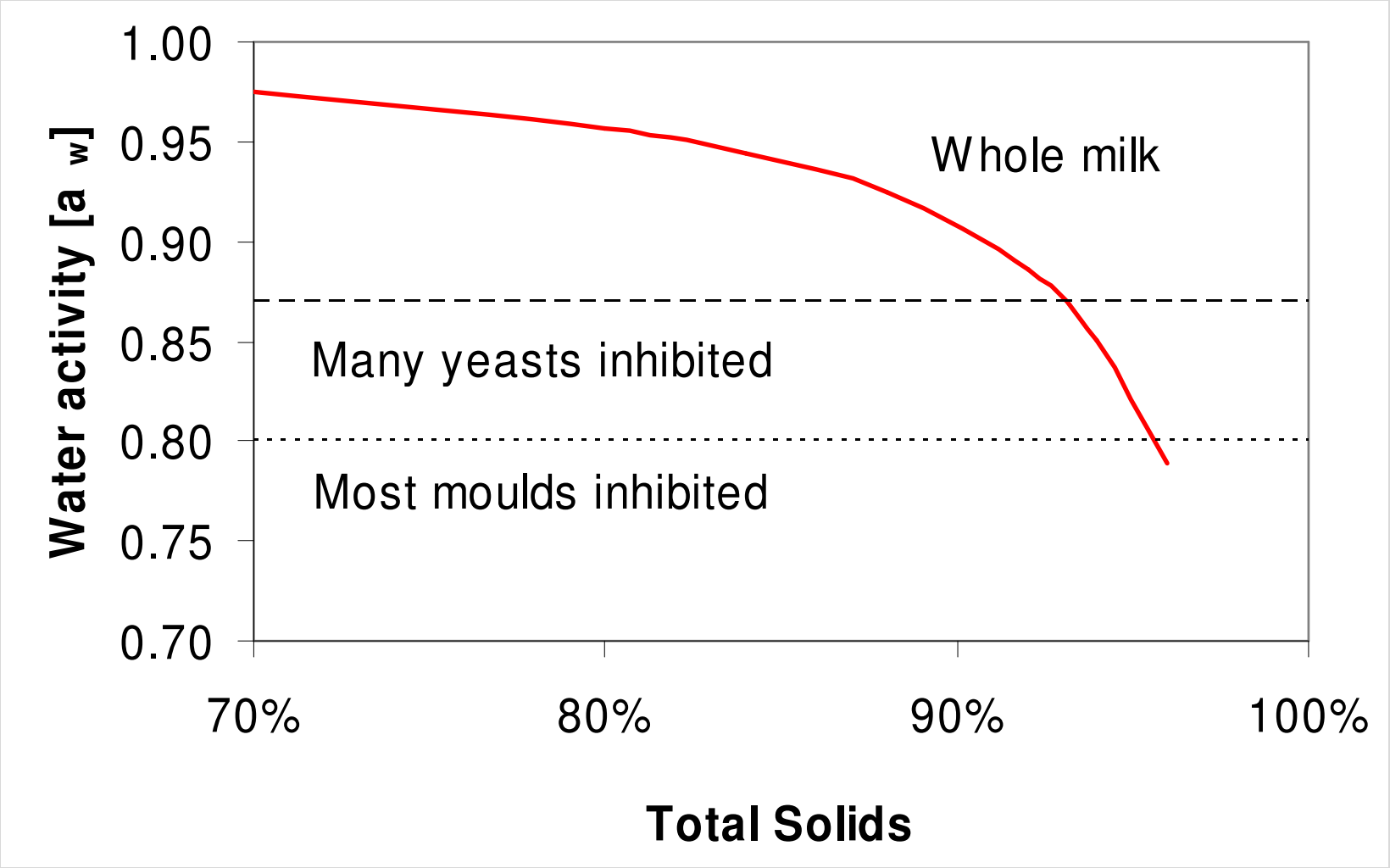
Boiling Point Elevation



Osmotic Pressure



Water Activity



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