

Modeling Swelling of the PVAm:CMC Complex Film

Model in MathCad 13 create by X. Feng and R. Pelton, McMaster University

Objective: estimate swelling of PVAm:CMC complex film as a function of pH, ionic strength and polymer structure.

Assumption: the complex is a hydrogel with ionic bonds forming physical cross-links

Theory

The total osmotic pressure is the sum of three components (Shibayama and Tanaka, Adv. Polym. Sci. 109 (1993) 1)

$$\Pi_{\text{tot}} = \Pi_{\text{mix}} + \Pi_{\text{el}} + \Pi_{\text{don}}$$

Π_{mix} - osmotic pressure from complex/water mixing

Π_{el} - osmotic pressure from elastic free energy

Π_{don} - osmotic pressure from Donnan potential

The swelling ratio is equal to $1/\phi_e$, where ϕ_e is the volume fraction of complexes at which Π_{tot} is equal to zero

Contribution of polymer/solvent mixing to the osmotic pressure of a polymer solution (Shibayama, Tanaka 1993)

$$\Pi_{\text{mix}} = \frac{-R \cdot T}{V_w} \cdot \left(\phi + \ln(1 - \phi) + \chi \cdot \phi^2 \right)$$

ϕ - volume fraction of polymer

V_w - molar volume of water

χ - Flory-Huggins parameter

R - gas constant

T - temperature

Contribution of elastic free energy to the osmotic pressure (Shibayama, Tanaka 1993)

$$\Pi_{\text{el}} = \frac{R \cdot T \cdot \phi_o}{V_w \cdot N_x} \cdot \left[\frac{1}{2} \frac{\phi}{\phi_o} - \left(\frac{\phi}{\phi_o} \right)^{\frac{1}{3}} \right]$$

N_x - the average number of monomer units between cross-links

ϕ_o - the volume fraction of polymer in the prepared state. Here we assume

$$\phi_o = 1$$

$$N_x = \frac{C_T}{X_T}$$

C_T - total number of polymer segments per unit volume
 X_T - number of cross-links per unit volume

$$C_T = \frac{\rho \cdot \phi}{EW_p \cdot (1 + r)} + \frac{\rho \cdot r \cdot \phi}{EW_c \cdot (1 + r)}$$

ρ - density of polymer blend
 EW_p - equivalent weight of PVAm
 EW_c - equivalent weight of CMC
 r - weight ratio of CMC to PVAm

X_T can be derived from binding equilibrium

$$K_c = \frac{X_T}{(C_p - X_T) \cdot (C_c - X_T)}$$

K_c - binding constant of PVAm to CMC
 C_p - concentration of charged amine
 C_c - concentration of charged carboxyl
 α_p - degree of ionization of PVAm
 α_c - degree of ionization of CMC

$$C_p = \frac{\rho \cdot \alpha_p \cdot \phi}{EW_p \cdot (1 + r)}$$

$$C_c = \frac{\rho \cdot r \cdot \alpha_c \cdot \phi}{EW_c \cdot (1 + r)}$$

In the presence of univalent salt, Donnan equilibrium can be expressed as

$$Na_{gel} \cdot Cl_{gel} = Na_w \cdot Cl_w$$

Na_{gel} - molarity of Na^+ inside the gel
 Cl_{gel} - molarity of Cl^- inside the gel
 Na_w - molarity of Na^+ outside the gel
 Cl_w - molarity of Cl^- outside the gel

The charge balance equations are

$$Na_{gel} = C_c - C_p + Cl_{gel} \quad Na_w = Cl_w$$

For negatively charged gel

or $Cl_{gel} = C_p - C_c + Na_{gel}$

For positively charged gel

The molarity of species leading to osmotic pressure is

$$M = Na_{gel} + Cl_{gel} - Na_w - Cl_w$$

Contribution of Donnan potential to the osmotic pressure

$$\Pi_{don} = M \cdot R \cdot T = R \cdot T \cdot \left[\left[(C_p - C_c)^2 + 4 \cdot Cl_w^2 \right]^{0.5} - 2 \cdot Cl_w \right] = RT \left[\left[(C_p - C_c)^2 + 4I^2 \right]^{0.5} - 2I \right]$$

Cl_w is equal to ionic strength (I)
(See Appendix 1 for derivation)

Sample calculation

Parameters

Physical constants

$DS := 0.7$	Degree of CMC substitution	$V_w := 1.8 \cdot 10^{-5} m^3 \cdot mol^{-1}$	Molar volume of water
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$\rho_p := 1080 kg \cdot m^{-3}$	Density of PVAm (from manufacturer BASF)	$\rho_c := 1590 kg \cdot m^{-3}$	Density of CMC (from Sigma-Aldrich)
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$EW_p := 0.092 \cdot kg \cdot mol^{-1}$	Equivalent weight of PVAm
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$$EW_c(DS) := \left[6 \cdot AM_C + 8 \cdot AM_H + 5 \cdot AM_O + (1 - DS) \cdot AM_H + DS \cdot (2 \cdot AM_C + 2 \cdot AM_O + 2 \cdot AM_H + AM_{Na}) \right] \cdot \frac{1}{DS}$$

$EW_c(0.7) = 0.3102 mol^{-1} \cdot kg$	Equivalent weight of CMC
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Adjustable model parameters

$K_c := 10^5 \frac{\text{L}}{\text{mol}}$	Binding constant in water based on the fact that polyelectrolyte complexes have a very tight binding
$\chi := 0$	Parameter for complex/water interaction
$r := 1, 2 \dots 5$	Weight ratio of CMC to PVAm

Computational parameters

$\text{pH} := 2, 2.1 \dots 10$	$\phi := 0.5$	$\rho(r) := \frac{1+r}{\frac{1}{\rho_p} + \frac{r}{\rho_c}}$	Density of polymer blend
$T := 298\text{K}$	$I := 0.1 \frac{\text{mol}}{\text{L}}$		

Calculation

$$C_p(\text{pH}, I, r, \phi) := \frac{\rho(r) \cdot \alpha_{\text{pvam}}(\text{pH}, I) \cdot \phi}{\text{EW}_p \cdot (1+r)} \quad C_c(\text{pH}, I, r, \phi) := \frac{\rho(r) \cdot r \cdot \alpha_{\text{cmc}}(\text{pH}, I) \cdot \phi}{\text{EW}_c(\text{DS}) \cdot (1+r)} \quad \text{Concentrations of charged amine and charged carboxyl}$$

$$C_T(r, \phi) := \frac{\rho(r) \cdot \phi}{\text{EW}_p \cdot (1+r)} + \frac{\rho(r) \cdot r \cdot \phi}{\text{EW}_c(\text{DS}) \cdot (1+r)} \quad \text{Total number of polymer segments per unit volume}$$

$$K_c = \frac{X_T(\text{pH}, r, \phi, I)}{(C_p(\text{pH}, I, r, \phi) - X_T(\text{pH}, r, \phi, I)) \cdot (C_c(\text{pH}, I, r, \phi) - X_T(\text{pH}, r, \phi, I))} \quad \begin{array}{l} \text{Binding constant of PVAm to CMC} \\ X_T - \text{concentration of cross-links} \end{array}$$

$$X_T(pH, r, \phi, I) := \frac{1}{2 \cdot K_c} \cdot \left[\left(K_c \cdot C_p(pH, I, r, \phi) + K_c \cdot C_c(pH, I, r, \phi) \right) \dots \right. \\ \left. + 1 - \left[\left(K_c^2 \cdot C_p(pH, I, r, \phi)^2 - 2 \cdot K_c^2 \cdot C_p(pH, I, r, \phi) \cdot C_c(pH, I, r, \phi) \right) \dots \right]^{\frac{1}{2}} \right. \\ \left. + 2 \cdot K_c \cdot C_p(pH, I, r, \phi) + K_c^2 \cdot C_c(pH, I, r, \phi)^2 \dots \right. \\ \left. + 2 \cdot K_c \cdot C_c(pH, I, r, \phi) + 1 \right]$$

The quadratic root which gives the decreased binding with ionic strength was chosen

$$N_x(pH, r, \phi, I) := \frac{C_T(r, \phi)}{X_T(pH, r, \phi, I)}$$

Average number of monomer units between crosslinks

$$\Pi_{mix}(\phi, \chi) := \frac{-R_{gas} \cdot T}{V_w} \cdot (\phi + \ln(1 - \phi) + \chi \cdot \phi^2)$$

Osmotic pressure from complex/water mixing

$$\Pi_{el}(\phi, pH, r, I) := \frac{R_{gas} \cdot T}{V_w \cdot N_x(pH, r, \phi, I)} \cdot \left(\frac{1}{2} \phi - \phi^{\frac{1}{3}} \right)$$

Osmotic pressure from elastic free energy

$$\Pi_{don}(\phi, I, pH, r) := R_{gas} \cdot T \cdot \left[\left[\left(C_p(pH, I, r, \phi) - C_c(pH, I, r, \phi) \right)^2 + 4 \cdot I^2 \right]^{0.5} - 2 \cdot I \right]$$

Osmotic pressure from Donnan potential

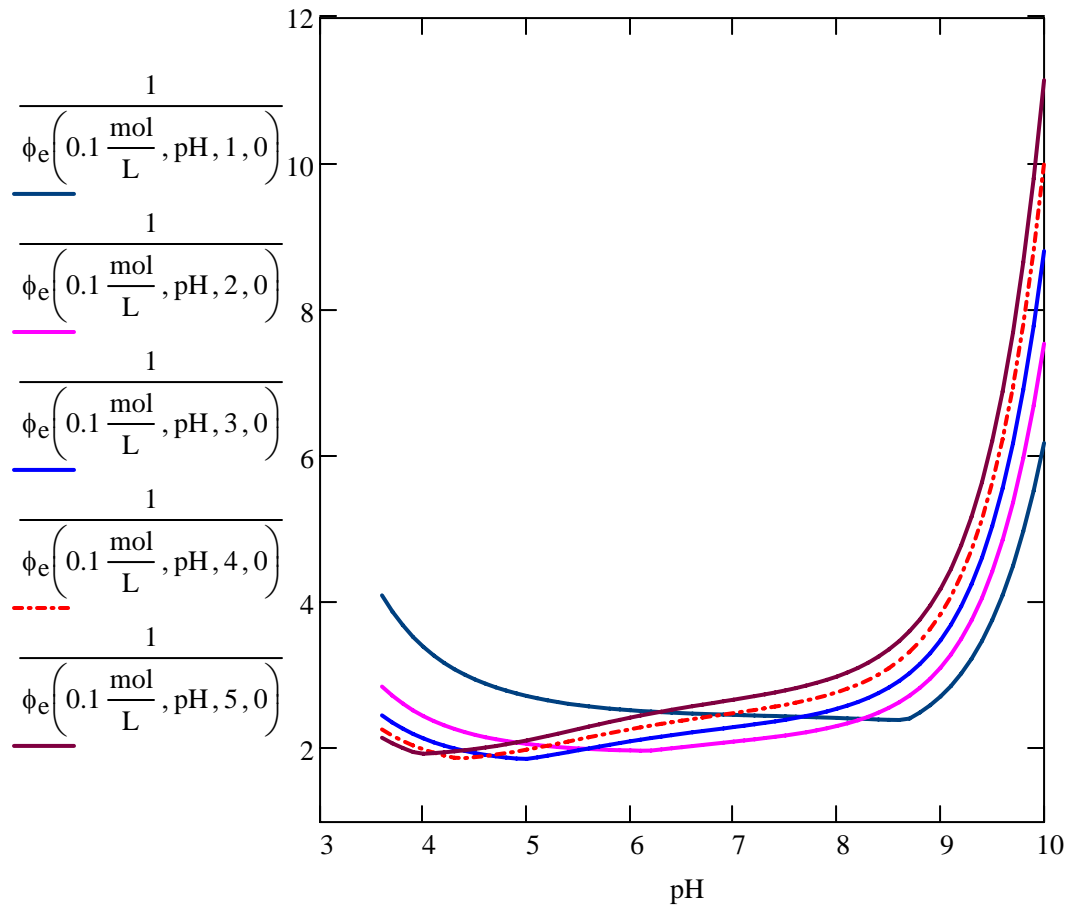
$$\Pi_T(\phi, I, pH, r, \chi) := \Pi_{don}(\phi, I, pH, r) + \Pi_{el}(\phi, pH, r, I) + \Pi_{mix}(\phi, \chi)$$

Total osmotic pressure

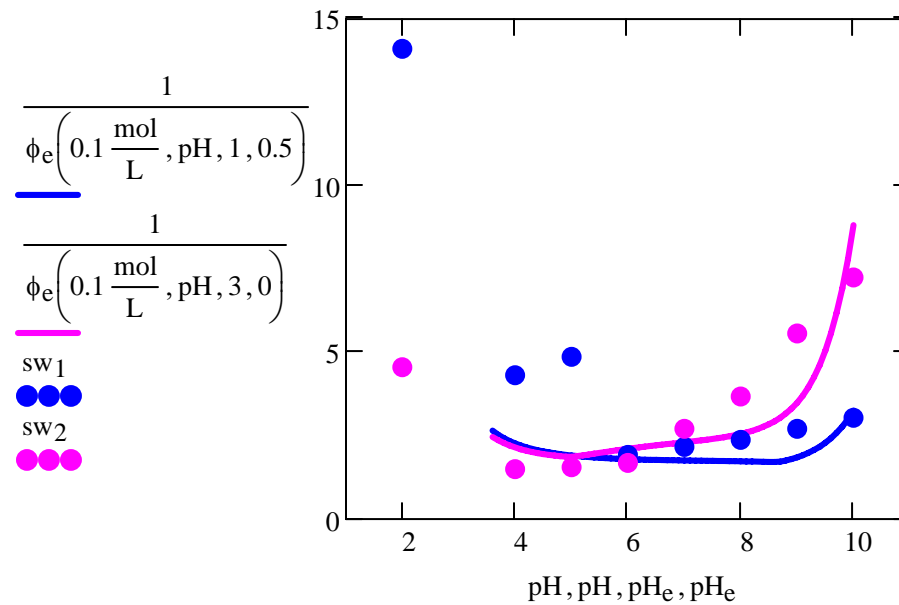
Here we use the root function to iteratively find the volume fraction ϕ_e

$$\phi_e(I, pH, r, \chi) := \text{root}(\Pi_T(\phi, I, pH, r, \chi), \phi)$$

Results: 1:1 to 5:1 films at ionic strength of 0.1 and $\chi = 0$

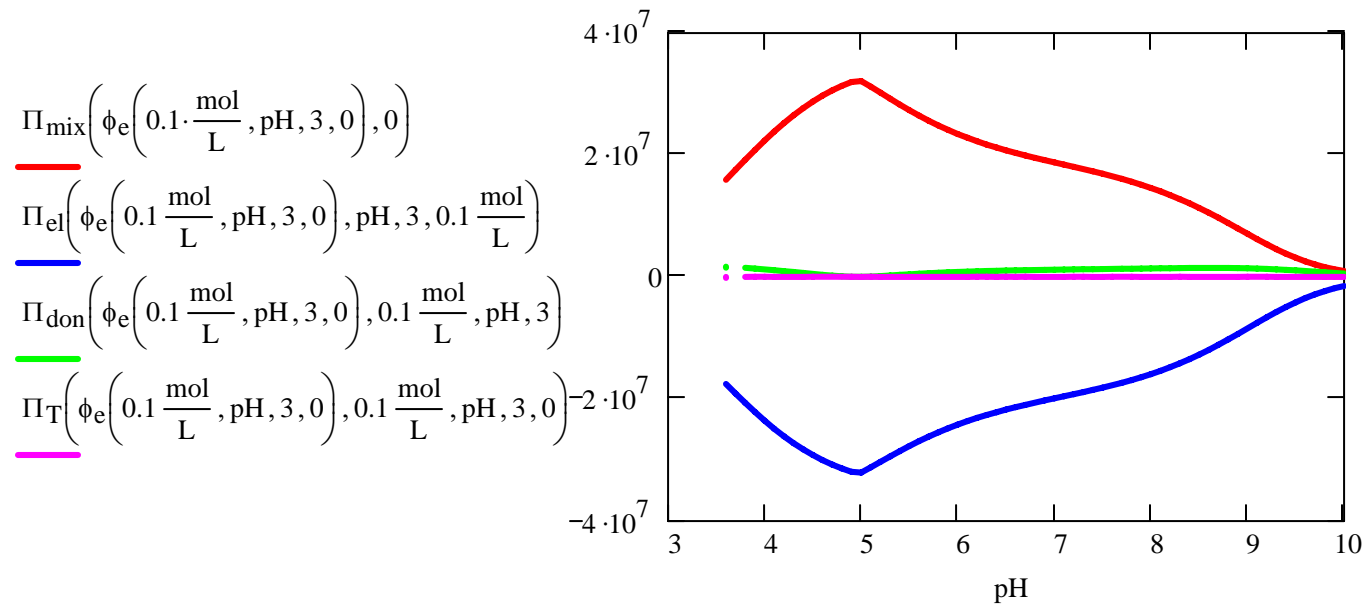


Comparison of modeling results with experimental data
 Example: 1:1 film and 3:1 film



Fitting is good at intermediate pH. For 1:1 films, fit is good at $\chi = 0.5$, whereas for 3:1 films, good fit is at $\chi = 0$.

Relative contribution of each component to the total swelling at various pH
 Example: 3:1 film, ionic strength of 0.1, $\chi = 0$



The two dominant terms are mixing and elastic contributions. pH changes the crosslinking which influences the elastic term. The mixing term then compensates, by varying ϕ_e . The Donnan term is not very important.

Appendix 1 Deriving the equation for contribution of Donnan potential to the osmotic pressure

$$Na_{gel} \cdot Cl_{gel} = Na_w \cdot Cl_w$$

Eqn 1

Donnan equilibrium

$$Na_{gel} = C_c - C_p + Cl_{gel}$$

$$Na_w = Cl_w$$

Eqn 2

Charge balance for negatively charged gel

$$M = Na_{gel} + Cl_{gel} - Na_w - Cl_w$$

Eqn 3

The molarity of species leading to osmotic pressure

$$\Pi_{don} = M \cdot R \cdot T$$

Eqn 4

Contribution of Donnan potential to the osmotic pressure

Substituting the charge balance equations (eqn 2) into the Donnan equilibrium (Eqn 1) and solving the quadratic to eliminate the ion concentrations in the gel because we can assume the salt concentration in the external solution is known and constant - i.e. a large reservoir.

$$Na_{gel} \cdot Cl_{gel} = Na_w^2$$

$$(\omega + Cl_{gel}) \cdot Cl_{gel} = Na_w^2$$

$$\omega = C_c - C_p$$

$$(\omega + Cl_{gel}) \cdot Cl_{gel} = Na_w^2 \text{ solve, } Cl_{gel} \rightarrow \left[\begin{array}{l} \frac{-1}{2} \cdot \omega + \frac{1}{2} \cdot \left(\omega^2 + 4 \cdot Na_w^2 \right)^{\frac{1}{2}} \\ \frac{-1}{2} \cdot \omega - \frac{1}{2} \cdot \left(\omega^2 + 4 \cdot Na_w^2 \right)^{\frac{1}{2}} \end{array} \right]$$

$$Cl_{gel} = \frac{-1}{2} \cdot \omega + \frac{1}{2} \cdot \left(\omega^2 + 4 \cdot Na_w^2 \right)^{0.5}$$

Cl_{gel} must be a positive number

$$Na_{gel} = \omega + Cl_{gel} = \omega + \frac{-1}{2} \cdot \omega + \frac{1}{2} \cdot (\omega^2 + 4 \cdot Na_w^2)^{0.5}$$

$$M = Na_{gel} + Cl_{gel} - Na_w - Cl_w = Na_{gel} + Cl_{gel} - 2 \cdot Cl_w$$

Substituting into Eqn 3

$$M := M$$

$$M = Na_{gel} + Cl_{gel} - 2 \cdot Cl_w \text{ substitute } Na_{gel} = \omega + \frac{-1}{2} \omega + \frac{1}{2} (\omega^2 + 4 Na_w^2)^{0.5} \rightarrow M = \frac{1}{2} \cdot \omega + \frac{1}{2} \cdot (\omega^2 + 4 \cdot Na_w^2)^{0.5} + Cl_{gel} - 2 \cdot Cl_w$$

$$M = \frac{1}{2} \omega + \frac{1}{2} (\omega^2 + 4 Na_w^2)^{0.5} + Cl_{gel} - 2 Cl_w \text{ substitute } Cl_{gel} = \frac{-1}{2} \omega + \frac{1}{2} (\omega^2 + 4 Na_w^2)^{0.5} \rightarrow M = (\omega^2 + 4 \cdot Na_w^2)^{0.5} - 2 \cdot Cl_w$$

$$\Pi_{don} = M \cdot R \cdot T = R \cdot T \cdot \left[(\omega^2 + 4 \cdot Cl_w^2)^{0.5} - 2 \cdot Cl_w \right] = RT \left[\left[(C_p - C_c)^2 + 4I^2 \right]^{0.5} - 2I \right]$$

Substituting into Eqn 4

For positively charged gel, charge balance is as follows

$$Cl_{gel} = C_p - C_c + Na_{gel}$$

$$Na_w = Cl_w$$

Eqn 5

Following same procedures as above, we can obtain same equation for Π_{don} .

Appendix 2 Experimental swelling data

$$\begin{array}{ccc}
 \text{pH}_e \equiv \begin{pmatrix} 2 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \end{pmatrix} & \text{sw}_1 \equiv \begin{pmatrix} 14.1 \\ 4.31 \\ 4.86 \\ 1.92 \\ 2.16 \\ 2.37 \\ 2.70 \\ 3.03 \end{pmatrix} & \text{for 1:1 film}
 \end{array}
 \quad
 \begin{array}{ccc}
 \text{sw}_2 \equiv \begin{pmatrix} 4.55 \\ 1.49 \\ 1.55 \\ 1.68 \\ 2.70 \\ 3.67 \\ 5.56 \\ 7.24 \end{pmatrix} & \text{for 3:1 film}
 \end{array}$$

Appendix 3 Modeling ionization behavior of PVAm

$\alpha \equiv 0.9$ Degree of ionization of PVAm

$$\text{pK}_{\text{pvam}}(I) \equiv 8.4 + \frac{3.5 \cdot \frac{I}{\frac{\text{mol}}{\text{L}}}}{0.8 + 2 \cdot \frac{I}{\frac{\text{mol}}{\text{L}}}}$$

The intrinsic equilibrium constant as a function of ionic strength. We derived this empirically by fitting Katchalsky's experimental data - only valid for 1:1 salt from 0 to 1 M

$A \equiv 47$ Nearest neighbor interaction energy which is not sensitive to ionic strength

$$x(\alpha) \equiv \frac{A \cdot (2 \cdot \alpha - 1) - 2 \cdot \alpha + \left[A^2 \cdot (2 \cdot \alpha - 1)^2 + 4 \cdot A \cdot \alpha \cdot (1 - \alpha) \right]^{0.5}}{2 \cdot (A - 1)}$$

Fraction of doublets

$$\text{pH}_{\text{pvam}}(\alpha, I) \equiv \text{pK}_{\text{pvam}}(I) + \log \left[\frac{\alpha}{1 - \alpha} \cdot \frac{(1 - 2 \cdot \alpha + x(\alpha))^2}{(\alpha - x(\alpha))^2} \right] \quad \text{pH as function of } \alpha$$

$$\alpha_{\text{pvam}}(\text{pH}, I) \equiv \text{root}(\text{pH}_{\text{pvam}}(\alpha, I) - \text{pH}, \alpha) \quad \alpha \text{ as a function of pH}$$

Appendix 4 Modeling ionization behavior of CMC

$$\alpha \equiv 0.9 \quad \text{Degree of ionization of CMC}$$

$$\text{pH} = \text{pK}_a + n \cdot \log \left(\frac{\alpha}{1 - \alpha} \right) \quad \text{Extended Henderson-Hasselbalch equation}$$

$$n(I) \equiv 1.10 - 0.23 \log \left(\frac{I}{\frac{\text{mol}}{\text{L}}} \right)$$

$$\text{pK}_{\text{cmc}}(I) \equiv 3.22 - 0.37 \log \left(\frac{I}{\frac{\text{mol}}{\text{L}}} \right)$$

Empirical equations for n and pK_a as a function of ionic strength, derived by fitting Aggeryd's experimental data for DS 0.79 CMC and modified to fit our experimental data for DS 0.7 CMC - only valid for 1:1 salt from 0.01 to 0.5 M

$$\text{pH}_{\text{cmc}}(\alpha, I) \equiv \text{pK}_{\text{cmc}}(I) + n(I) \cdot \log \left(\frac{\alpha}{1 - \alpha} \right) \quad \text{pH as a function of } \alpha$$

$$\alpha_{\text{cmc}}(\text{pH}, I) \equiv \frac{1}{10^{\frac{\text{pK}_{\text{cmc}}(I) - \text{pH}}{n(I)} + 1}}$$

α as a function of pH

Parameters used in the calculation

$$R_{\text{gas}} \equiv 8.314 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\text{AM}_{\text{C}} \equiv 12.011 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{H}} \equiv 1.0079 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{O}} \equiv 15.994 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{N}} \equiv 14.0067 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{S}} \equiv 32.06 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{Na}} \equiv 22.98977 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{Cl}} \equiv 35.453 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{Ca}} \equiv 40.08 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{K}} \equiv 39.0983 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{AM}_{\text{P}} \equiv 30.973761 \cdot \frac{\text{gm}}{\text{mole}}$$