CHAPTER 3

METHODOLOGY

3.1 Model 1

In this work, Gibbs free energy term is given by long range (Lr) electrostatic contributions b/w ions and short range (Sr) interaction b/w all species.

Using Pitzer`s form of the Debye- Huckle (PDH) function as the electrostatic contribution to the free energy. So

$$\frac{F^{Lr}}{RT} = -(v_w n_w + \upsilon v_s n_s)\frac{4A_\varphi I}{b} ln\left(1 + bI^{1/2}\right)$$

Where n_w, n_s = no. of moles of water, salt respectively

v_s, v_w = partial molar volume (m^3/mole) of salt, solvent respectively

b = the closest approach parameter

Total no. of ions per salt $\upsilon = \upsilon_M + \upsilon_X$

Debye Huckel type constant $A_\varphi = \frac{1}{3}\left[\frac{2\pi N_A}{V_S}\right]^{1/2}\left[\frac{e^2}{4\pi\varepsilon D_S KT}\right]^{3/2}$

Where Mw = molecular weight of solvent i.e., water in gram/mol,

N_A = Avogadro number,

K = Boltzmann constant, ε = permittivity of vacuum, e = electronic charge,

D_S = dielectric constant of water, V_S = the molar volume of water

I = the ionic strength $I = \sum C_i \frac{Z_i^2}{2}$ or $I = \frac{1}{2} C\upsilon|Z_+Z_-|$

The expression for the short-range interaction contribution of aqueous salt solution is obtained from Flory- Huggins theory as given below,

$$\frac{F^{S_r}}{RT} = v_w n_W \ln\varphi_w + \upsilon v_s n_s \ln\varphi_s + \chi_{sw} v_w n_w \varphi_s$$

Where χ_{sw} = salt-water interaction parameter, which dependent on the salt concentration and temperature

$$\frac{F}{RT} = -(n_w + \nu n_s)\frac{4A_x I_x}{b}\ln\left(1 + bI_x^{1/2}\right) + n_w \ln\phi_w + \nu n_s \ln\phi_s + \chi_{sw}\, n_w \phi_s$$

where n_S and n_w represent the moles of salt hydrate and water in salt hydrate solution, respectively. r_S is the number of Kuhn segments in Salt hydrate chain. The term χ_{sw} is the generalized Flory-Huggins parameter and considered as the function of the volume fraction of the salt hydrate, ϕ_S, and temperature, T.

$$\chi_{sw}(T, \phi_S) = \sum_{i=0}^{n} b_i(T)\, \phi_S^i$$

$b_i(T)$ is temperature dependent coefficient and as expressed as:

$$b_i(T) = b_{i\alpha} + b_{i\beta}\left(\frac{1}{T} - \frac{1}{T_r}\right) + b_{i\gamma}\, ln\left({}^{T}/{}_{T_r}\right)$$

$b_{i\alpha}, b_{i\beta}$ and $b_{i\gamma}$ are constants

$b_i(T)$ is temperature dependent coefficient are calculated using non linear regression method

Derivative of Equation (1) w.r.t. moles of water and salt gives us chemical potential of water and salt hydrate respectively.

$$\frac{\mu_w - \mu_w^0}{RT} = \left(\frac{\delta \frac{F}{RT}}{\delta n_w}\right)_{n_s}$$

$$= \left(\mathrm{I_x}\ln\left(1 + bI_x^{1/2}\right)\right)\left[-\frac{\nu n_s}{n_w}\right] - \frac{(n_w + \nu n_s)}{2\left(1 + bI_x^{1/2}\right)}\frac{I_x^{-1/2}}{n_w} + \ln\phi_w$$

$$+ \phi_s\left(1 - \frac{v_w}{v_s}\right) - \chi_{sw}\phi_s^2 - \frac{\delta\chi_{sw}}{\delta\phi_s}\phi_s^2(1 - \phi_s)$$

$$\frac{\mu_s - \mu_s^0}{RT} = \left(\frac{\delta \frac{F}{RT}}{\delta n_s}\right)_{n_s}$$

$$= I_x\ln\left(1 + bI_x^{1/2}\right)\left(2 + \frac{n_w}{n_s}\right) + \left(\frac{n_w}{n_s} + \nu\right)\left(\frac{1}{\left(1 + bI_x^{1/2}\right)}\; b\frac{1}{2}I_x^{\frac{3}{2}}\right)$$

$$+ \nu\ [\ln\phi_s + \left(1 - \frac{v_S}{v_w}\right)\phi_w + \frac{v_s}{v_w}\ \chi_{sw}(1 - \phi_s)^2$$

$$+ \frac{v_s}{v_w}\phi_s(1 - \phi_s)^2\ \frac{\delta\chi_{sw}}{\delta\phi_s}$$

The condition for the phase equilibrium between two separate phases (Phase-1 and Phase-2) are given by

$\mu_w^\alpha = \mu_w^\beta$

And $\mu_S^\alpha = \mu_S^\beta$

By solving equation simultaneously, phase diagram can be obtained.

$$\frac{\ln(1 - \phi_s^\alpha)}{\ln(1 - \phi_s^\beta)} + \left(\phi_s^\alpha - \phi_s^\beta\right)\left(1 - \frac{v_w}{v_s}\right)$$

$$- \left[\chi_{sw}(T, \phi_s^\alpha)\,\phi_s^{2\alpha} + \frac{\delta\chi_{sw}(T, \phi_s^\alpha)}{\delta\phi_s^\beta}\phi_s^{2\alpha}(1 - \phi_s^\alpha\ )\right]$$

$$- \left[\chi_{sw}\left(T, \phi_s^\beta\right)\phi_s^{2\beta} + \frac{\delta\chi_{sw}\left(T, \phi_s^\beta\right)}{\delta\phi_s^\beta}\phi_s^{2\beta}\left(1 - \phi_s^\beta\ \right)\right] = 0$$

$$
v\left[\ln\frac{\phi_s^\alpha}{\phi_s^\beta} + \left(1-\frac{v_S}{v_w}\right)\left(2-\phi_s^\alpha-\phi_s^\beta\right)\right]
+ \left[\frac{v_s}{v_w}\,\chi_{sw}\,(T,\phi_s^\alpha)(1-\phi_s^\alpha)^2 + \frac{v_s}{v_w}\phi_s^\alpha(1-\phi_s^\alpha)^2\,\frac{\delta\chi_{sw}(T,\phi_s^\alpha)}{\delta\phi_s^\alpha}\right]
+ \left[\frac{v_s}{v_w}\,\chi_{sw}\left(T,\phi_s^\beta\right)\left(1-\phi_s^\beta\right)^2 + \frac{v_s}{v_w}\phi_s^\beta\left(1-\phi_s^\beta\right)^2\,\frac{\delta\chi_{sw}\left(T,\phi_s^\beta\right)}{\delta\phi_s^\beta}\right]
= 0
$$

The critical point is given by the following conditions :

$$
\frac{\delta^2\left(\frac{F}{RT}\right)}{\delta\phi_s^2} = \frac{\delta^2\left(\frac{F}{RT}\right)}{\delta\phi_s^3}
$$

$$\frac{\delta^2\left(\frac{F}{RT}\right)}{\delta\phi_s^2} = \left(\left(\left(\left(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2} + \nu\frac{n_s}{\phi_s(1-\phi_s)}\right)\right)I_x\frac{1}{\phi_s(1-\phi_s)}\left(\ln\left(1+bI_x^{\frac{1}{2}}\right)+\frac{1}{2}\,I_x^{\frac{1}{2}}\,\frac{1}{1+bI_x^{\frac{1}{2}}}\right)\right)\right.$$

$$+(n_w+\nu n_s)\frac{I_x}{\left(\phi_s(1-\phi_s)\right)^2}\left(\ln\left(1+bI_x^{\frac{1}{2}}\right)+\frac{1}{2}\,I_x^{\frac{1}{2}}\,\frac{1}{1+bI_x^{\frac{1}{2}}}\right)$$

$$+(n_w+\nu n_s)\,I_x\frac{1}{\phi_s(1-\phi_s)}\frac{b}{1+bI_x^{\frac{1}{2}}}\,\frac{1}{4}\left(2I_x^{\frac{1}{2}}+\frac{I_x^{\frac{-1}{2}}}{b}-1\right)$$

$$+\left(\left(-\frac{v_s}{v_w}\nu\,(\frac{n_s}{\phi_s^3}\,\frac{-1+2\phi_s}{1-\phi_s})+\left(\frac{n_s}{\varphi_s^2(1-\phi_s)^2}+n_s\,\frac{2\phi_s-1}{\phi_s^2(1-\phi_s)^2}\right)\right)I_x\ln\left(1+bI_x^{\frac{1}{2}}\right)\right)$$

$$+\left(\left(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2}+\frac{n_s}{\phi_s(1-\phi_s)}\right)\left(\frac{I_x}{\phi_s(1-\phi_s)}\right)\ln\left(1+bI_x^{\frac{1}{2}}\right)\right)$$

$$+\left(\left(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2}+\frac{n_s}{\phi_s(1-\phi_s)}\right)I_x^{\frac{3}{2}}\frac{1}{(1+bI_x^{\frac{1}{2}})}\;b\frac{1}{2}\frac{1}{\phi_s(1-\phi_s)}\right)$$

$$+-\frac{v_s}{v_w}\nu\left[\frac{n_s}{\varphi_s(1-\varphi_s)}\;\frac{1}{\phi_s^3(1-\phi_s)}\;ln(1-\phi_s)\right)+\;n_s(\;\frac{4\phi_s-3}{\phi_s^4(1-\phi_s)^4})\,ln(1-\phi_s)$$

$$+\quad n_s\frac{-1}{\phi_s^3(1-\phi_s)^2}]\;+(-2)(\left(\frac{n_s}{\varphi_s^4(1-\varphi_s)}\ln(1-\phi_s)\right)+n_s(-3)\;\phi_s^{-4}\ln\,(1-\phi_s)$$

$$+n_s\phi_s^{-3}\frac{-1}{\phi_s-1})+\;n_s\;\frac{(-1)}{\phi_s^3(1-\phi_s)^2}+n_s(-1)\;\;\frac{3\phi_s-2}{(\phi_s-1)^2\phi_s^3}]-[-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2}\,\frac{1}{(1-\phi_s)^2}$$

$$+n_w\frac{2}{(1-\phi_s)^3}\;+(\frac{v_s}{v_w}\nu)(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2}\;n_s\;\frac{1}{\phi_s^2}\;+\;n_w\;\frac{n_s}{\varphi_s(1-\varphi_s)}\;\frac{1}{\phi_s^2}+n_w n_s(2)\phi_s^{-3})$$

$$+-\frac{v_s}{v_w}\nu\left[\frac{n_s}{\varphi_s(1-\varphi_s)}\;\frac{1}{\phi_s^3(1-\phi_s)}\;ln(1-\phi_s)\right)+\;n_s(\;\frac{4\phi_s-3}{\phi_s^4(1-\phi_s)^4})\,ln(1-\phi_s)$$

$$+\quad n_s\frac{-1}{\phi_s^3(1-\phi_s)^2}]\;+(-2)(\left(\frac{n_s}{\varphi_s^4(1-\varphi_s)}\ln(1-\phi_s)\right)+n_s(-3)\;\phi_s^{-4}\ln\,(1-\phi_s)$$

$$+n_s\phi_s^{-3}\frac{-1}{\phi_s-1})+\;n_s\;\frac{(-1)}{\phi_s^3(1-\phi_s)^2}+n_s(-1)\;\;\frac{3\phi_s-2}{(\phi_s-1)^2\phi_s^3}]-[-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2}\,\frac{1}{(1-\phi_s)^2}$$

$$+n_w\frac{2}{(1-\phi_s)^3}\;+(\frac{v_s}{v_w}\nu)(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2}\;n_s\;\frac{1}{\phi_s^2}\;+\;n_w\;\frac{n_s}{\varphi_s(1-\varphi_s)}\;\frac{1}{\phi_s^2}+n_w n_s(2)\phi_s^{-3})]$$

$$\frac{\delta^3\left(\frac{F}{RT}\right)}{\delta\phi_s^3} = \Bigg(\frac{1}{1+bI_x^{\frac{1}{2}}}\frac{1}{2}\Bigg(\frac{I_x^{\frac{1}{2}}}{\phi_s(1-\phi_s)} + \frac{1}{2}I_x^{\frac{-1}{2}} - \frac{1}{4}\frac{1}{1+bI_x^{\frac{1}{2}}}I_x\frac{1}{\phi_s(1-\phi_s)}\Bigg)\Bigg)I_x\frac{1}{\phi_s(1-\phi_s)}\Bigg(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2} + \nu\frac{n_s}{\phi_s(1-\phi_s)} +$$

$$(n_w+\nu n_s)\frac{I_x}{\phi_s(1-\phi_s)}\Bigg) + \Bigg(\ln\Big(1+bI_x^{\frac{1}{2}}\Big) + \frac{1}{2}\,I_x^{\frac{1}{2}}\,\frac{1}{1+bI_x^{\frac{1}{2}}}\Bigg)\Big(\frac{I_x}{\phi_s(1-\phi_s)}\Big)\frac{1}{\phi_s(1-\phi_s)}\Bigg(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2} + \nu\frac{n_s}{\phi_s(1-\phi_s)} +$$

$$(n_w+\nu n_s)\frac{I_x}{\phi_s(1-\phi_s)}\Bigg) + \Bigg(\ln\Big(1+bI_x^{\frac{1}{2}}\Big) + \frac{1}{2}\,I_x^{\frac{1}{2}}\,\frac{1}{1+bI_x^{\frac{1}{2}}}\Bigg)I_x\Bigg(-\,\frac{2\phi_s-1}{\left(\phi_s(1-\phi_s)\right)^2}\Bigg)\Bigg(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2} + \nu\frac{n_s}{\phi_s(1-\phi_s)} +$$

$$(n_w+\nu n_s)\frac{I_x}{\phi_s(1-\phi_s)}\Bigg) + \Bigg(\ln\Big(1+bI_x^{\frac{1}{2}}\Big) + \frac{1}{2}\,I_x^{\frac{1}{2}}\,\frac{1}{1+bI_x^{\frac{1}{2}}}\Bigg)I_x\frac{1}{\phi_s(1-\phi_s)}\Bigg(\Bigg(-\frac{v_s}{v_w}\nu(\frac{n_s}{\phi_s(1-\phi_s)}\;\phi_s^{-2} +$$

$$n_s(-2\phi_s^{-1})) + \nu((\frac{n_s}{\phi_s(1-\phi_s)}\Big)\frac{1}{\phi_s(1-\phi_s)} + n_s\Bigg(-\,\frac{2\phi_s-1}{\left(\phi_s(1-\phi_s)\right)^2}\Bigg) + \Bigg(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2} + \nu\frac{n_s}{\phi_s(1-\phi_s)}\Bigg)\frac{I_x}{\phi_s(1-\phi_s)} +$$

$$(n_w+\nu n_s)\;\Big(\frac{I_x}{\phi_s(1-\phi_s)}\Big)\frac{1}{\phi_s(1-\phi_s)}\Bigg) + (n_w+\nu n_s)I_x\Bigg(-\,\frac{2\phi_s-1}{\left(\phi_s(1-\phi_s)\right)^2}\Bigg)\Bigg) + \frac{1}{4}b\Bigg(\Bigg(-\Bigg(1+$$

$$bI_x^{\frac{1}{2}}\Bigg)^{-2} b\,I_x^{-\frac{1}{2}}\Bigg)(n_w+\nu n_s)\Bigg(2\,I_x^{\frac{3}{2}} + \frac{I_x^{\frac{1}{2}}}{b} - 1\Bigg) + \frac{1}{1+bI_x^{\frac{1}{2}}}\Bigg(\Bigg(-\frac{\frac{v_s}{v_w}\nu n_s}{\phi_s^2} + \nu\frac{n_s}{\phi_s(1-\phi_s)}\Bigg)\Bigg)\Bigg(2\,I_x^{\frac{3}{2}} + \frac{I_x^{\frac{1}{2}}}{b} - 1\Bigg)\Bigg) +$$

$$\frac{1}{1+bI_x^{\frac{1}{2}}}\,(n_w+\nu n_s)\Bigg(\Bigg(3\,I_x^{\frac{1}{2}} + \frac{1}{2}\frac{1}{b}I_x^{\frac{-1}{2}}\Bigg)\Bigg)\Bigg(\Bigg(\Bigg(\Big(\frac{n_s}{\phi_s(1-\phi_s)}\Big)\;\Bigg(-\frac{v_s}{v_w}\nu\;\Big(\frac{-1+2\phi_s}{(1-\phi_s)\,\phi_s^3}\Big) + \Big(\frac{2}{\phi_s(1-\phi_s)^2}\Big)\Bigg)\;I_x\ln\Bigg(1+$$

$$bI_x^{\frac{1}{2}}\Bigg)\Bigg)\Bigg)\Bigg)(\Bigg(\Bigg(n_s\;(\frac{\delta}{\delta\phi_s}\;\Bigg(-\frac{v_s}{v_w}\nu\;\Big(\frac{6\,\phi_s^2-8\phi_s+3}{\phi_s^4(1-\phi_s)^2}\Big) + \Big(2\;\frac{3\phi_s+1}{\phi_s^2(\phi_s-1)^3}\Big)\Bigg)\,)\;I_x\ln\Bigg(1+$$

$$bI_x^{\frac{1}{2}}\Bigg)\Bigg)\Bigg)\Bigg(\Bigg(n_s\;\Bigg(-\frac{v_s}{v_w}\nu\;\Big(\frac{-1+2\phi_s}{(1-\phi_s)\,\phi_s^3}\Big) + \Big(\frac{2}{\phi_s(1-\phi_s)^2}\Big)\Bigg)\;(\frac{\delta}{\delta\phi_s}I_x)\;\ln\Bigg(1+$$

$$bI_x^{\frac{1}{2}}\Bigg)\Bigg)\Bigg)\Bigg(\Bigg(n_s\;\Bigg(-\frac{v_s}{v_w}\nu\;\Big(\frac{-1+2\phi_s}{(1-\phi_s)\,\phi_s^3}\Big) + \Big(\frac{2}{\phi_s(1-\phi_s)^2}\Big)\Bigg)\;I_x\Bigg(I_x^{\frac{3}{2}}\frac{1}{\Big(1+bI_x^{\frac{1}{2}}\Big)}\;b\frac{1}{2}\Bigg)\Bigg)\Bigg)\Bigg) +$$

$$\Bigg(\Bigg(\;\Bigg(-\frac{v_s}{v_w}\nu\;\Big(\frac{n_s}{\phi_s^3}\;\frac{-1+2\phi_s}{1-\phi_s}\Big) + \Big(\frac{n_s}{\phi_s^2(1-\phi_s)^2} + n_s\;\frac{2\phi_s-1}{\phi_s^2(1-\phi_s)^2}\Big)\Bigg)\;(\frac{I_x}{n_s})\ln\Bigg(1+bI_x^{\frac{1}{2}}\Bigg)\Bigg)\Bigg) +$$

$$\Bigg(\Bigg(\;\Bigg(-\frac{v_s}{v_w}\nu\;\Big(\frac{n_s}{\phi_s^3}\;\frac{-1+2\phi_s}{1-\phi_s}\Big) + \Big(\frac{n_s}{\phi_s^2(1-\phi_s)^2} + n_s\;\frac{2\phi_s-1}{\phi_s^2(1-\phi_s)^2}\Big)\Bigg)\;I_x\;\Bigg(I_x^{\frac{3}{2}}\frac{1}{\Big(1+bI_x^{\frac{1}{2}}\Big)}\;b\frac{1}{2}\Bigg)\Bigg)\Bigg) +$$

$$\Big(\frac{n_s}{\phi_s(1-\phi_s)}\Big)\Bigg(-\frac{\frac{v_s}{v_w}\nu}{\phi_s^2} + \frac{1}{\phi_s(1-\phi_s)}\Bigg)\Big(\frac{1}{\phi_s(1-\phi_s)}\Big)I_x\;\ln\Bigg(1+bI_x^{\frac{1}{2}}\Bigg) + n_s\Bigg(\frac{\delta}{\delta\phi_s}\Bigg(2\frac{\frac{v_s}{v_w}\nu}{\phi_s} +$$

$$\frac{1}{\phi_s(1-\phi_s)}\Bigg)\Bigg)\Big(\frac{1}{\phi_s(1-\phi_s)}\Big)I_x\;\ln\Bigg(1+bI_x^{\frac{1}{2}}\Bigg) + n_s\Bigg(-\frac{\frac{v_s}{v_w}\nu}{\phi_s^2} + \frac{1}{\phi_s(1-\phi_s)}\Bigg)\Big(\frac{2\phi_s-1}{\phi_s^2(1-\phi_s)^2}\Big)I_x\;\ln\Bigg(1+bI_x^{\frac{1}{2}}\Bigg) +$$

$$n_s\Bigg(-\frac{\frac{v_s}{v_w}\nu}{\phi_s^2} + \frac{1}{\phi_s(1-\phi_s)}\Bigg)\Big(\frac{1}{\phi_s(1-\phi_s)}\Big)(\frac{I_x}{n_s})\quad\ln\Bigg(1+bI_x^{\frac{1}{2}}\Bigg) + n_s\Bigg(-\frac{\frac{v_s}{v_w}\nu}{\phi_s^2} +$$

$$\frac{1}{\phi_s(1-\phi_s)}\Bigg)\left(\frac{1}{\phi_s(1-\phi_s)}\right) I_x^{\frac{5}{2}} \frac{1}{\left(1+bI_x^{\frac{1}{2}}\right)}\ b\frac{1}{2} + b\frac{1}{2}\ \Bigg[\ \Bigg(\left(\frac{n_s}{\phi_s(1-\phi_s)}\right)\left(-\frac{\frac{v_s}{v_w}v}{\phi_s^2} + \frac{1}{\phi_s(1-\phi_s)}\right)\ I_x^{\frac{3}{2}} \frac{1}{\left(1+bI_x^{\frac{1}{2}}\right)}\ \frac{1}{\phi_s(1-\phi_s)}\ \Bigg) +$$

$$\Bigg(\ n_S\ \left(\frac{\delta}{\delta\phi_s}\left(2\frac{\frac{v_s}{v_w}v}{\phi_s} + \frac{2\phi_s-1}{(\phi_s-1)^2\phi_s^2}\right)\right)\ I_x^{\frac{3}{2}} \frac{1}{\left(1+bI_x^{\frac{1}{2}}\right)}\ \frac{1}{\phi_s(1-\phi_s)}\ \Bigg) + \Bigg(\ \Bigg(-\frac{\frac{v_s}{v_w}v}{\phi_s^2} +$$

$$\frac{1}{\phi_s(1-\phi_s)}\Bigg)\left(\frac{3}{2}\right)\frac{I_x^{\frac{3}{2}}}{n_s}\frac{1}{\left(1+bI_x^{\frac{1}{2}}\right)}\ \frac{1}{\phi_s(1-\phi_s)}\ \Bigg) + \Bigg(\ n_S\ \left(-\frac{\frac{v_s}{v_w}v}{\phi_s^2} + \frac{1}{\phi_s(1-\phi_s)}\right)\ I_x^2\left(\frac{1}{2}\frac{b}{\left(1+bI_x^{\frac{1}{2}}\right)^2}\right)\frac{1}{\phi_s(1-\phi_s)}\ \Bigg) +$$

$$n_S\ \left(-\frac{\frac{v_s}{v_w}v}{\phi_s^2} + \frac{1}{\phi_s(1-\phi_s)}\right)\ I_x^{\frac{3}{2}}\frac{1}{\left(1+bI_x^{\frac{1}{2}}\right)}\left(\frac{2\phi_s-1}{(\phi_s-1)^2\phi_s^2}\right) + +v[n_s\ \ ln\phi_s\frac{1}{\left(\phi_s(1-\phi_s)\right)^3} + n_s\ \frac{1}{\phi_s^3(1-\phi_s)^2} +$$

$$n_s ln\phi_s\left(\frac{-3\phi_s+1}{(\phi_s-1)^3\phi_s^2}\right) + n_s\ \frac{1}{\phi_s^3(1-\phi_s)^2} + n_s\left(\frac{-3\phi_s+2}{(\phi_s-1)^2\phi_s^3}\right) + \frac{n_s}{\phi_s^3(1-\phi_s)^3}ln\phi_s\ 1-2\phi_s + n_s\ \left(\frac{1}{\phi_s^3}\right)\ 2\frac{2\phi_s-1}{(\phi_s-1)^2} +$$

$$n_s\ ln\phi_s(-2)\left(\frac{3\phi_s^2-3\phi_s+1}{(\phi_s-1)^3\phi_s^3}\right) + n_s\ \frac{(-1)}{\phi_s^5(1-\phi_s)^2} + n_s\left(\frac{5\phi_s-4}{(\phi_s-1)^2\phi_s^5}\right) + \frac{\delta}{\delta\phi_s}\ \left(\left(\frac{\delta^2\chi_{sw}}{\delta\varphi_s^2}\right)(n_w)(\varphi_s)\ +\right.$$

$$\left(\frac{\delta\chi_{sw}}{\delta\varphi_s}\right)\left(-\frac{\frac{v_s}{v_w}vn_s}{\phi_s}\right) + \left(\frac{\delta\chi_{sw}}{\delta\varphi_s}\right)(n_w) - \frac{v_s}{v_w}v\Bigg[\frac{\delta\chi_{sw}}{\delta\varphi_s}\ \left(\frac{n_S}{\phi_s} + n_w\right) + \chi_{sw}\Bigg(\ n_s\frac{1}{\phi_s^2(1-\phi_s)} +\ n_s\phi_s^{-2} + n_w +$$

$$\left.\left(-\frac{\frac{v_s}{v_w}vn_s}{\phi_s^2}\right)\Bigg)\ \right]$$

3.2 Model 2

We assume that the molar gibbs energy of mixing contains an electrostatic contribution given by a Deybe Huckel-type function and a contribution from extended Flory-Huggins theory ,as follows:

$$\frac{\Delta G}{RT} = \frac{\Delta G^{DH}}{RT} + \frac{\Delta G^{FH}}{RT}$$

Where superscripts DH and FH denote Deybe Huckel and Flory Huggins Contribution, respectively

Pizer's form of the Deybe-Huckel type function as the electrostatic contribution to the molar Gibbs energy of mixing is given by

$$\frac{\Delta G^{DH}}{RT} = \phi_1 (\frac{W}{1000}) \left[-A_{\Phi} \left(\frac{4I}{b}\right) \ln \left(1 + bI^{\frac{1}{2}}\right) \right]$$

Where $I = \frac{1}{2} \left[\frac{\phi_2 \left(\frac{1000}{W}\right)}{\phi_1} \right] |z_m z_x|$

$$The\ values\ for\ A_{\Phi} = 0.392\ and\ b = 1.2\ at\ 25^0 C$$

The electrostatic contribution does not contain adjustable parameters.

The Flory-Huggins contribution to the molar Gibbs energy of mixing is given by the following

$$\frac{\Delta G^{FH}}{RT} = \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + g_{12}(\phi_2)\phi_1\phi_2$$

Where the first two terms and the last term on the right hand side of equation represent, respectively, the configurational entropy of mixing and the residual free-energy, mostly enthalphic ,interaction between water and salt ion .

g_{12} refers the interaction between water and ion. It is interaction parameter.

For a binary salt water system Deybe Huckel and Flory Huggins contribution are combined to give the molar Gibbs energy of mixing given by

$$\frac{F}{RT} = \phi_1\left(\frac{W}{1000}\right)\left[-A_{\Phi}\left(\frac{4I}{b}\right)\ln\left(1 + bI^{\frac{1}{2}}\right)\right] + \phi_1 \ln\phi_1 + \phi_2 \ln\phi_2 + g_{12}(\phi_2)\phi_1\phi_2$$

$$g_{12}(\phi_2) = \sum c_k \phi_2^{k-1}$$

The condition for the phase equilibrium between two separate phases (Phase-1 and Phase-2) are given by

$$\ln a_w = \frac{\mu_w - \mu_w^0}{RT} = \left(\frac{\delta \frac{F}{RT}}{\delta n_w}\right)_{n_s} = \frac{2\ A_{\Phi} I^{\frac{3}{2}}}{1 + bI^{\frac{1}{2}}} + \ln\phi_1 + (\phi_1^2 g_{12} - \phi_1\phi_2 g_{12}')$$

$$\ln \beta_w = \frac{\mu_s - \mu_s^0}{RT} = \left(\frac{\delta \frac{F}{RT}}{\delta n_s}\right)_{n_s} = c\left[\left(\left(\frac{v}{n_w}(1-\phi_2)\right) I\ \ln\left(1 + bI^{\frac{1}{2}}\right)\right) + (1-\phi_2)\left(c_1 \frac{v}{n_w}\frac{1}{1-\phi_2}\right)\ln\left(1 + bI^{\frac{1}{2}}\right)\right.$$
$$\left. +\ I^{\frac{1}{2}}\frac{1}{1 + bI^{\frac{1}{2}}} b\frac{1}{2}\ \left(c_1 \frac{v}{n_w}\right)\right] + -\frac{v}{n_w}(1-\phi_2)\left(\ln\left(\frac{\phi_2}{1-\phi_2}\right) + 2\right) + \frac{\delta g_{12}(\phi_2)}{\delta\phi_2}\frac{v}{n_w}\ (1-\phi_2)\phi_2$$
$$+ g_{12}(\phi_2)\left(\frac{\delta}{\delta n_p}\phi_1\right)\phi_2 + g_{12}(\phi_2)\phi_1\left(\frac{\delta}{\delta n_p}\phi_2\right)$$

$$c = \left(\left(\frac{W}{1000}\right) - A_{\Phi}\left(\frac{4}{b}\right)\right)\ ;\ c_1 = \frac{1}{2}\left(\frac{1000}{W}\right)|z_m z_x|$$

$\mu_w^{\alpha} = \mu_w^{\beta}$

And $\mu_S^{\alpha} = \mu_S^{\beta}$

By solving equation and simultaneously, phase diagram can be obtained.

Phase Diagram equations

$$(1-\phi_2^{\alpha})\left(\ln\left(\frac{\phi_2^{\alpha}}{1-\phi_2^{\alpha}}\right) + 2\right) - \left(1-\phi_2^{\beta}\right)\left(\ln\left(\frac{\phi_2^{\beta}}{1-\phi_2^{\beta}}\right) + 2\right)$$
$$+ \left(\frac{\delta g_{12}(\phi_2^{\alpha})}{\delta\phi_2^{\alpha}}\ (1-\phi_2^{\alpha})^2\phi_2^{\alpha} + g_{12}(\phi_2^{\alpha})\left(\ \left(-3\phi_2^{\alpha} + 2\phi_2^{\alpha\,2} + 1\right)\right)\right)$$
$$- \left(\frac{\delta g_{12}\left(\phi_2^{\beta}\right)}{\delta\phi_2^{\beta}}\ \left(1-\phi_2^{\beta}\right)^2\phi_2^{\beta} + g_{12}\left(\phi_2^{\beta}\right)\left(\ \left(-3\phi_2^{\beta} + 2\phi_2^{\beta\,2} + 1\right)\right)\right)$$
$$+ \left[\left(((1-\phi_2^{\alpha}))I^{\alpha}\ \ln\left(1 + bI^{\alpha\frac{1}{2}}\right)\right) +\ (c_1)\ \ln\left(1 + bI^{\alpha\frac{1}{2}}\right) +\ I^{\alpha\frac{1}{2}}\frac{1}{1 + bI^{\alpha\frac{1}{2}}} b\frac{1}{2}\ \ (c_1)\right]$$
$$- \left[\left(\left(\left(1-\phi_2^{\beta}\right)\right)I^{\beta}\ \ln\left(1 + bI^{\beta\frac{1}{2}}\right)\right) +\ (c_1)\ \ln\left(1 + bI^{\beta\frac{1}{2}}\right)\right.$$
$$\left. +\ I^{\beta\frac{1}{2}}\frac{1}{1 + bI^{\beta\frac{1}{2}}} b\frac{1}{2}\ \ (c_1)\right]$$

$$\ln\left(\frac{1-\phi_2^\alpha}{1-\phi_2^\beta}\right)+\left[\left(\phi_2^\alpha \quad g_{12}(\phi_2^\alpha)-\left(\phi_2^{\alpha\,2}-\ \phi_2^{\alpha\,3}\right)\frac{\delta g_{12}(\phi_2^\alpha)}{\delta\phi_2^\alpha}\right) -\left(\phi_2^\beta \quad g_{12}(\phi_2^\beta)-\left(\phi_2^{\beta\,2}-\ \phi_2^{\beta\,3}\right)\frac{\delta g_{12}(\phi_2^\beta)}{\delta\phi_2^\beta}\right)\right]+\left[\frac{I^{\alpha^{\frac{3}{2}}}}{1+bI^{\alpha^{\frac{1}{2}}}}-\frac{I^{\beta^{\frac{3}{2}}}}{1+bI^{\beta^{\frac{1}{2}}}}\right]$$

Critical Point equations

$$\frac{\delta^2(\frac{F}{RT})}{\delta\phi_2^2}\ =\frac{\delta^3(\frac{F}{RT})}{\delta\phi_2^3}$$

$$\frac{\delta^2(\frac{F}{RT})}{\delta\phi_2^2}=-I\ln\left(1+bI^{\frac{1}{2}}\right)+c_1\ln\left(1+bI^{\frac{1}{2}}\right)+I^{\frac{1}{2}}\frac{1}{1+bI^{\frac{1}{2}}}\,\frac{1}{2}\frac{c_1}{1-\phi_2}+\ln\frac{\phi_2}{1-\phi_2}+\ \frac{\delta g_{12}(\phi_2)}{\delta\phi_2}\ \ (\phi_2-\phi_2^2) + g_{12}(\phi_2)\ (1-2\phi_2)$$

$$\frac{\delta^3(\frac{F}{RT})}{\delta\phi_2^3}=\frac{1}{1-\phi_2}+\frac{1}{\phi_2}+\frac{\delta^2 g_{12}(\phi_2)}{\delta\phi_2^2}\ (\phi_2-\phi_2^2)+\frac{\delta g_{12}(\phi_2)}{\delta\phi_2}\ 2\ (1-2\phi_2)-\ 2\ g_{12}(\phi_2) +\frac{c_1}{(1-\phi_2^2)}\left(-\ln\left(1+bI^{\frac{1}{2}}\right)-\frac{I}{1+bI^{\frac{1}{2}}}\right)+c_1\ \frac{I}{1+bI^{\frac{1}{2}}}\ b\frac{1}{2}\ I^{\frac{-1}{2}}\frac{c1}{(1-\phi_2)^2}$$