

Chilling-freezing process development based on ice slurry mixtures using regular solution theory

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Abstract

The objective of this work is feasibility study related to chilling-freezing process development, associate with the freezing point of the aqueous solutions employed. Knowing the freezing point of any solution under consideration, that would be one of the important properties required for equipment design associated with any of the ice slurry and beverage industries. Yet researchers know very little about the phenomena of mixing multi-component and the accompanying phase changes. Data for freezing points for chilling-freezing solution at different composition would be predicted and compared with experimental data. A thermodynamic model based regular solution theory would be employed in order to evaluate activity coefficient expression to each phase and that would be associated with predicting the freezing point temperature of the considered chilling and freezing solutions. The chilling and freezing solutions systems considered in the present work are the aqueous solutions of Ethanol, Methanol. Experimental and theoretical data for the freezing point temperature are given in table below.

Keywords: Chilling-freezing process, thermodynamic model, freezing point, phases behaviour.

1. Introduction

There are a number of economical and technical advantages for chilling and freezing process that could be summarized as high heat transfer rates with small value of temperature gradients; fine ice crystal structure; the product surface would freeze immediately in a solid crust that would limits the osmotic temperature and give an excellent appearance; the process operation is easy to maintain (convenient for automation and the labor costs which are substantially reduced and the technology is

environmentally friendly[1]. The ability to predict equilibrium data is very important when designing equipment and understanding fluid properties. Equilibrium data is scarce and accurate methods of predicting equilibrium are needed [2].

Most of thermodynamic model used to describe vapour liquid equilibrium of aqueous solution are based on relations involving Gibbs free energy which is a large number of physical parameters may be calculated such as solute activities, partial equilibrium properties, solubility, relative volatility and others [3].

Freezing point is one of the most important thermodynamic properties. Accurate freezing point can be used to calculate other properties such as effective molecular weight, activity coefficient, enthalpy below freezing and phase diagram [4]. The freezing characteristics of aqueous binary solutions are related quite closely not only to a variety of engineering problems such as desalination of sea water and freezing on the cooled tube in the brine reservoir, but also to the other fields such as freezing of blood in medical science and freeze-dried foods in the food industry [5]. In order to know the phenomena of mixing multi-component aqueous solutions, must know precisely the thermodynamic properties of the slurries, especially the properties that related to temperature, the mass fraction, and the enthalpy [6].

In the previous work, Peralta J. M. etc. have presented a prediction model for freezing point of multi-component. UNIQUAC model was adequate for predicting the freezing point in multi-component systems [7]. Also Tello Alonso used the same model but with different systems [8].

Several attempts tried to describe the phenomena of mixing multi-component (aqueous solutions) and the accompanying phase changes by determination the properties of these solutions. This paper evaluates the activity coefficients to predict freezing point temperature where regular solution theory was used to evaluate the activity coefficient. We discuss a

prediction method for freezing point temperature of the slurries and made comparisons between theoretical and experimental data that obtained from previous publications for binary mixtures which were studied from [9].

2. Thermodynamic model

Regular solution theory selected as model for study the behaviour of solutions during freezing point depression. This model is based on activity coefficient of component in a defined liquid mixture. These may be regarded as starting from the basic thermodynamic result that [10].

$$G = H - TS \quad (1)$$

$$RT \ln \gamma_i = \left(\frac{\partial(nG_m^E)}{\partial n_i} \right)_{T,P,n_{j \neq i}} = \left(\frac{\partial(nH_m^E)}{\partial n_i} \right)_{T,P,n_{j \neq i}} - T \left(\frac{\partial(nS_m^E)}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (2)$$

Where n: Total number of moles.

n_i : Number of mole of component i.

G_m^E : Molar Gibbs function.

H_m^E & S_m^E : Molar excess enthalpy of mixing & molar excess entropy of mixing respectively.

$$\ln \gamma_i = (\ln \gamma_i)^{\text{Extract}} + (\ln \gamma_i)^{\text{Solute}} \quad (3)$$

$$(\ln \gamma_i)^{\text{Extract}} = \frac{1}{RT} \left(\frac{d(nH_{\text{mixing}}^{\text{Excess}})}{dn_i} \right)_{T,P,n_{j \neq i}} \quad (4)$$

$$= \left(\frac{\phi_j^2 \times V_{mi}}{R \times T} \right) (d_i - \delta_{ij} d_j)^2 + 2l_{ij} d_i d_j - \delta_{ij} d_j$$

Where

$$\delta_{ij} = \left[\left(\frac{U_{mi}^0}{V_{mi}} \right) \left(\frac{U_{mj}^0}{V_{mj}} \right) \right]^{\frac{1}{2}} \quad (5)$$

$$d_i = \left[\frac{(U_{mi}^0 + U_{mi})}{V_{mi}} \right]^{\frac{1}{2}} \quad (6)$$

d_i is the well known ‘‘solubility parameter’’ of component (i). U_{mi}^0 and U_{mi} are the molar internal energy of the fluid component (i) and the same fluid at the same temperature but a very low pressure. These parameters are calculated by the same equations but for component (j), as well. Eq. (3) may be compared with the expression given by the Vander Waals approach [11].

$$(\ln \gamma_i)^{\text{Extract}} = \left(\frac{\phi_j^2 \times V_{mi}}{R \times T} \right) ((d_i - d_j)^2 + 2l_{ij} d_i d_j) \quad (7)$$

It differs from this only in the term δ (which is usually close to unity) and in the replacement of the area function ϕ_j^v by the volume function,

$$\phi_j^v = \frac{(x_i \times V_{mj})}{(x_i \times V_{mi} + x_j \times V_{mj})} \quad (8)$$

Where (V_{mi}) is the molar volume of the pure liquid (i). For a non-spherical molecule of type (i), quantity (q_i) is defined such that (Zq_i) is the number of interactions made by a molecule of this type with surrounding molecules. A monomer has (Z) interactions with nearest neighbour molecules (following X-ray diffraction information for simple fluids Z is normally given a value of 10). (q_i) is termed the area function for the molecule. For a linear molecule,

$$q_i = r_i - \left(\frac{x_i(r_i - 1)}{Z} \right) \quad (9)$$

$$(\ln \gamma_i)^{\text{Extract}} = \sum_{K=1}^N \theta_K^{(i)} (\ln \Gamma_K - \ln \Gamma_K^{(i)}) \quad (10)$$

$$\ln \Gamma_K = \sum_{m=1}^N \theta_m \left[1 - \ln \left(\sum_{m=1}^N \theta_m \Psi_{mK} \right) - \sum_{m=1}^N \frac{\theta_m \Psi_{Km}}{\sum_{n=1}^N \theta_n \Psi_{nm}} \right] \quad (11)$$

$$\Psi_{mK} = e^{\left(\frac{-a_{mn}}{T} \right)} \quad (12)$$

Q_K is the area function for group K and θ_m is the area fraction of group m. $\ln \Gamma_K^{(i)}$ is defined similarly except that the group area fractions refer to the pure liquid i and not to the mixture.

$$(\ln \gamma_i)^{\text{Solute}} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + L_i + \frac{\theta_i}{x_i} \sum_j x_j l_j \quad (13)$$

Where M, θ_i and ϕ_i are the number of components in the solution, the area fraction for component i in the solution and the segment fraction, respectively.

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (14)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} ; \quad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

Also there is another arrangement for Eq. (13),

$$\ln \gamma_i^{\text{Solute}} = \ln \frac{\phi_i}{x_i} - \left(\frac{Zq_i}{2} \right) \times \ln \left[1 + \left(\frac{2\theta_i}{Zq_i} \right) \left(\frac{r_i}{r_j} - 1 \right) \right] \quad (15)$$

In the present work activity coefficient is calculated using Eqs. (3), (10) and (13). The freezing

point of pure solvent is a temperature at which the liquid and solid phases of substance of specified composition are in equilibrium at atmospheric pressure, so that the chemical potential (μ) for the ideal solution must be the same for the both phases.

$$\mu_{\text{solid}} = \mu_{\text{liquid}}$$

But for the real solution

$$\mu_{\text{solid}} = \mu_{\text{liquid}} + RT \ln \gamma x$$

$$\mu_{\text{solid}} - \mu_{\text{liquid}} = RT \ln \gamma x$$

$$\Delta G = RT \ln \gamma x$$

$$\left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_P = \left(\frac{\partial (R \ln \gamma x)}{\partial T} \right)_P$$

Hence Gibbs- Helmholtz equation is,

$$\left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_P = - \frac{\Delta H}{T^2} \quad (16)$$

Then

$$\left(\frac{\partial (R \ln \gamma x)}{\partial T} \right)_P = - \frac{\Delta H}{T^2}$$

$$\left(\frac{\partial (\ln \gamma x)}{\partial T} \right)_P = - \frac{\Delta H}{RT^2}$$

$$\ln \gamma x = \int_{T_0}^{T_f} \frac{\Delta H_F}{RT^2}$$

Assumed that ΔH_F is constant then eq. (16) will be,

$$\ln \gamma x = \frac{\Delta H_F}{R} \left[\frac{1}{T_f} - \frac{1}{T_0} \right]$$

$$T_f = \frac{1}{\frac{1}{T_0} - \frac{R \ln \gamma x}{\Delta H_F}} \quad (17)$$

3. Result and Discussion

Using water mole fraction phase equilibrium data for the aqueous solution Ethanol and Methanol at normal pressure, together with the thermodynamic derived model in order to calculate effective values for the freezing point temperature as a function of activity coefficients as well as used these to predict data the effective values of the average water enthalpy of fusion.

The other parameters required in the thermodynamic model were evaluated using the standard methods

described in [12]. Furthermore the derived model based on regular solution theory was used in the present work is given in [10]. Table (1) illustrates the results obtained from the experimental data as well as freezing point temperature experimental and theoretical and activity coefficient of water for the system Water/Ethanol, the average water enthalpy of fusion for this system was (3089.912 KJ/Kgmole). The prediction was good regards in the concentrations (0.99-0.86) the model predicts freezing point with less accuracy after that range.

The meaning of the statistical parameters ARD and RMS is:

ARD= average relative deviation

$$ARD = \frac{1}{n} \sum_{i=1}^n \frac{(T_f)_{\text{calc}} - (T_f)_{\text{exp}}}{1 - (T_f)_{\text{exp}}} \times 100 \quad (18)$$

RMS= root mean square

$$RMS = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{(T_f)_{\text{calc}} - (T_f)_{\text{exp}}}{1 - (T_f)_{\text{exp}}} \times 100 \right)^2} \quad (19)$$

The comparison between the experiential data and theoretical model gives average relative deviation (2.43) with root mean square (1.39).

Table 1. Shows the comparison of experimental data obtained from ref. [9], with theoretical data for the system Water/ Ethanol at normal pressure and average water enthalpy of fusion 3089.912 KJ/Kgmole.

$X_{\text{Water}}^{\text{exp.}}$	$T_{\text{Freezing}}^{\text{exp.}}$ (K)	Activity coeff. γ_{Water}	$T_{\text{Freezing}}^{\text{theo.}}$ (K)
0.99	272.15	1.0005	271.26
0.95	268.15	1.0111	265.81
0.93	265.65	1.0234	263.32
0.91	262.55	1.0361	261.71
0.88	257.15	1.0632	259.44
0.86	254.25	1.0799	258.45
0.80	244.45	1.1401	255.84
0.75	239.25	1.2014	253.22
0.67	232.15	1.3041	247.70
0.50	221.85	1.5119	226.52

Table (2) illustrates the results obtained from the experimental data as well as freezing point temperature experimental and theoretical and activity coefficient of water for the system Water/Methanol the average water enthalpy of fusion for this system was (4548.45 KJ/Kgmole). The prediction was good

in the concentration range was took. The comparison between the experiential data and theoretical model gives average relative deviation (0.91) with root mean square (0.84).

Table 2. This table shows the comparison of experimental data obtained from ref. [9], with theoretical data for the system Water/ Methanol at normal pressure.

$X_{\text{Water}}^{\text{exp.}}$	$T_{\text{Freezing}}^{\text{exp.}}$ (K)	Activity coeff. γ_{Water}	$T_{\text{Freezing}}^{\text{theo.}}$ (K)
0.98	270.95	1.0007	270.20
0.95	268.15	1.0032	267.12
0.93	264.85	1.0071	264.16
0.90	261.45	1.0126	261.14
0.87	257.55	1.0196	258.10
0.84	253.15	1.0280	254.91
0.81	248.15	1.0377	251.60
0.78	243.15	1.0485	248.01
0.74	237.55	1.0601	244.17

4. Conclusions

In the present work, we applied regular solution theory, that presented in [10] for estimating the activity coefficient which was used to predict the freezing point of the aqueous solutions Ethanol and Methanol. The freezing point temperature for real solution may be calculated from the activity coefficient and enthalpy of fusion with freezing point of pure solvent equation (17). This equation can be used for different freezing liquids, and provide approach prediction values.

5. References

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