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Thermodynamic Study of Hot Potassium Carbonate Solution Using Aspen Plus

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***Abstract*—**This paper presents a study on the thermodynamics and transport properties of hot potassium carbonate aqueous system (HPC) using electrolyte non-random two liquid, (ELECNRTL) model. The operation conditions are varied to determine the system liquid phase stability range at the standard and critical conditions. A case study involving 30 wt% K_2CO_3, H_2O standard system at pressure of 1 bar and temperature range from 280.15 to 366.15 K has been studied. The estimated solubility index, viscosity, water activity, and density which obtained from the simulation showed a good agreement with the experimental work. Furthermore, the saturation temperature of the solution has been estimated.

***Keywords*—**Viscosity, Saturation index, Activity coefficient, Density.

I. INTRODUCTION

THE hot potassium carbonate process developed by Benson and Field (1970) [1] has since become an important technology used for CO_2 removal from natural gas streams using the chemical absorption method. The chemical solvent normally contains (20-40) wt% potassium carbonate, (1-3) wt% DEA activator and (0.4-0.7) wt%V_2O_5 corrosion inhibitor. The normal operation conditions of CO_2 absorption process is; pressure range (1- 2 atm) and temperature range (70-140) ^{0}C based on the unit design [1].

Benfield solvent has a number of advantages which are support the system process compared with amine system and the other methods. These advantages can be conclude as; the absorption can occur at high temperature making the regeneration process more efficient and economical and potassium carbonate solvent is a low cost, low toxic and less prone degradation effects that are commonly found with MEA at high temperatures, presence of oxygen and the other gases [2]. Benfield solvent also has a large capacity for CO_2 [3], and it is more manageable by many of separation and/or cost effectiveness in the presence SO_2 [4].

The disadvantages of HPC solvent can be presented as; the carbon steel corrosion problem which is a cause by potassium carbonate solution [5], and the precipitation of the solvent in form of fouling and crystals accumulations in Benfield reboilers system and pipeline. In a typical Benfield process, the two reboilers have been found prove too blockage due to formation of solid crystals. Laboratory analysis of the solutions taken from the two reboilers reported the content of 30-60 wt% potassium carbonate on dry basis.

The work was aimed to study the thermodynamic properties of 30 wt% potassium carbonate solution and determine the precipitation conditions.

The thermodynamic study of HPC solution describes the electrolyte system for explaining the effects of operation conditions on the electrolyte thermodynamics, chemical, and physical properties such as; heat capacity, activity coefficient, saturation index, viscosity and solution density and the other thermodynamics [6]. This leads to investigate the electrolyte phase equilibrium at vary operation conditions of pressure, temperature and solvent concentration. Aspen Plus simulator (Version 12.4) is used for modeling electrolyte systems. This related to the electrolyte data, reaction chemistry and the accurate electrolyte models which are build in Aspen database [7]. The calculations of thermodynamics and physical properties of K_2CO_3 aqueous electrolyte in the vapor-liquid phase equilibrium based on two models; Redlich-Kown model for vapor-liquid equilibrium between water and carbon dioxide, and Electrolyte Nonrandom Tow-Liquid (ELECNRTL) for modeling activity coefficient [7, 8, 9]. This work focuses on the investigation of thermodynamic behavior of HPC system at different operation conditions by changing the effective parameters such as temperature, pressure and solutes concentration. Fig. 1 shows the electrolyte system simulation algorithm using Aspen Plus electrolyte template.

II. REACTION CHEMISTRY

The chemical composition of Benfield solution is described as ionic species generated from the reaction of solid hydration as well as water dissociation, and detailed equations of the stoichometry and the equilibrium reaction for the absorption of CO_2 in aqueous carbonate solution are given below [9]:

Dissociation reactions:

$$K_2CO_3 \leftrightarrow 2K^+ + CO_3^{2-} \qquad (1)$$

$$KHCO_3 \leftrightarrow K^+ + HCO_3^- \qquad (2)$$

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Hydrolysis of dissolved CO2 to (H_3O^+) and bicarbonate ions (HCO_3^-):

$$CO_2 + 2H_2O \leftrightarrow HO^- + HCO_3^- \tag{3}$$

The dissociation of (HCO_3^-) to (H_3O^+) and (CO_3^{2-}):

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \tag{4}$$

The ionization of water to hydronium (H_3O^+) and hydroxide (OH^-) ions:

$$2H_2O \leftrightarrow HO_3^+ + OH^- \tag{5}$$

Salt dissociation reaction of carbonate and bicarbonate:

$$K_2CO_{3(S)} \leftrightarrow 2K^+ + CO_3^{2-} \tag{6}$$

$$KHCO_{3(S)} \leftrightarrow K^+ + HCO_3^- \tag{7}$$

The chemical absorption equilibrium reaction[1]:

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3 \tag{8}$$

III. ELECTROLYTE NON-RANDOM TWO LIQUID MODEL DESCRIPTION

The electrolyte NRTL model is more applicable compared with the other models such as Pitzer model, this because the NRTL model include the general temperature dependence of ion interaction parameters and also the model is conveniently embedded in Aspen Plus software with built-in parameter estimation facility. Farther more, the NRTL model able to estimate the properties of medium and high concentration aqueous solutions [10]. The thermodynamic calculation of electrolyte system using NRTL model mainly depends on the ionic force between the individual ionic species. The force changes with the number and the type of the species as well as with the distance between species. Electrolyte NRTL databank contains the non-randomness factors (GMELCN), the energy parameters of (GMELCC, GMELCD and GMELCE) for several molecule-electrolyte and electrolyte-electrolyte pairs, see Table I. The details of the methodology and the equations and the calculations are discussed below[7]:

A. Temperature Dependency of the Dielectric Constant of Solvent is Defined by [7]:

$$\varepsilon_B(T) = A_B + B_B\left(\frac{1}{T} - \frac{1}{C_B}\right) \tag{9}$$

B. The Temperature Dependency Relations of Electrolyte NRTL Parameters are [7]:

Molecule-molecule binary parameters:

$$\tau_{BB'} = A_{BB'} + \frac{B_{BB'}}{T} + F_{BB'}\ln(T) + G_{BB'}T \tag{10}$$

Electrolyte-molecule pair parameters:

$$\tau_{ca,B} = C_{ca,B} + \frac{D_{ca,B}}{T} + E_{ca,B'}\left[\frac{\left(T^{ref} - T\right)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right] \tag{11}$$

$$\tau_{B,ca} = C_{B,ca} + \frac{D_{B,ca}}{T} + E_{B,ca}\left[\frac{\left(T^{ref} - T\right)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right] \tag{12}$$

Electrolyte-electrolyte pair parameters:

$$\tau_{c'a,c''a} = C_{c'a,c''a} + \frac{D_{c'a,c''a}}{T} + E_{c'a,c''a}\left[\frac{\left(T^{ref} - T\right)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right] \tag{13}$$

$$\tau_{ca',ca''} = C_{ca',ca''} + \frac{D_{ca',ca''}}{T} + E_{ca',ca''}\left[\frac{\left(T^{ref} - T\right)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right] \tag{14}$$

C. Activity Coefficient Model Electrolyte System

The electrolyte nonrandom two liquid is a versatile model for activity coefficient. Using binary and pair parameters, the model can represented aqueous electrolyte system as well as mixed solvent and also can; calculate the activity coefficient and mean activity coefficient($\gamma\pm$) for ionic species and molecular species in aqueous electrolyte system [11].

$$\gamma\pm = \left(\gamma_+^{\,x}\gamma_-^{\,y}\right)^{\frac{1}{(x+y)}} \tag{15}$$

The activity coefficient equation for molecular component is given by [7]:

$$\begin{aligned}\ln\gamma_B^{lc} = {} & \frac{\sum_j X_j G_{jB}\tau_{jB}}{\sum_k X_k G_{kB}} + \\ & \sum_{B'}\left(\frac{X_{B'}G_{BB'}}{\sum_k X_k G_{kB'}}\right)\left(\tau_{BB'} - \frac{\sum_k X_k G_{kB'}\tau_{kB'}}{\sum_k X_k G_{kB'}}\right) + \\ & \sum_c\sum_{a'}\frac{X_a}{\sum_{a''}X_{a''}}\frac{X_c G_{Bc,a'c}}{\sum_k X_k G_{kc,a'c'}}\left(\tau_{Bc,a'c} - \frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}}\right) + \\ & \sum_c\sum_{a'}\frac{X_{c'}}{\sum_{c''}X_{c''}}\frac{X_a G_{Ba,c'a}}{\sum_k X_k G_{ka,c'a}}\left(\tau_{Bc,c'a} - \frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}}\right)\end{aligned} \tag{16}$$

The activity coefficient equation for cations is given by[7] :

$$\frac{1}{z_c}\ln\gamma_c^{lc}=\sum_{a''}\frac{X_{a'}}{\sum_{a''}X_{a''}}\frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc',a'c'}}+\sum_{B'}\left(\frac{X_B G_{cB}}{\sum_k X_k G_{kB}}\right)\left(\tau_{cB}\frac{\sum_k X_k G_{kB}\tau_{kB}}{\sum_k X_k G_{kB}}\right)+\sum_a\sum_{c'}\frac{X_{c'}}{\sum_{c''}X_{c''}}\frac{X_c G_{ca,a'c}}{\sum_k X_k G_{ka',c'a}}\left(\tau_{ca,c'a}-\frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}}\right) \quad (17)$$

The activity coefficient equation for anions is given by [7]:

$$\frac{1}{z_a}\ln\gamma_a^{lc}=\sum_{c''}\frac{X_{c'}}{\sum_{c''}X_{c''}}\frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka',c'a'}}+\sum_{B}\left(\frac{X_B G_{cB}}{\sum_k X_k G_{kB}}\right)\left(\tau_{cB}\frac{\sum_k X_k G_{kB}\tau_{kB}}{\sum_k X_k G_{kB}}\right)+\sum_a\sum_{c'}\frac{X_{c'}}{\sum_{c''}X_{c''}}\frac{X_c G_{ca,a'c}}{\sum_k X_k G_{ka',c'a}}\left(\tau_{ca,c'a}-\frac{\sum_k X_k G_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}}\right) \quad (18)$$

D. Saturation Index (SI) Model

The solubility index SI is a useful property for analysis of crystallization. In electrolyte solutions, if SI of the salt is greater than 1, then the salt exists as a solid. If SI < 1, then the salt has not reached the saturation point and will be in the liquid phase. The solubility index defined by; activity product of the salt divided by its solubility product [6] and [12];

$$SI=\frac{\sum_{i=1}^{NC} a_i^{v_{ij}}}{K_j} \quad (19)$$

$$SI=\frac{a_k^{k}\, a_A^{\infty}\, a_w^{n}}{K_{k_k} A_a H_2O} \quad (20)$$

$$K=e^{\left(-\frac{\Delta G^0}{RT}\right)}=e^{\left(\sum \ln a_i^{v_i}\right)} \quad (21)$$

IV. RESULTS AND DISCUSSION

The thermodynamic study of 30 wt% carbonate solution focused on the estimation of the solution viscosity, saturation index, density, and water activity at a fixed concentration, and pressure (1 bar) for temperature range between (280.15-370.15 K) based on the boiling point and freezing temperatures that was presented in Kohl [1]. The literature data of the solution viscosity determined the freezing temperature at 283.15 K and the boiling temperature at 366.48 K. As shown in Figure (2), the simulation viscosity values recorded the largest deviation at temperature 362.15 K with error percent of -1.1 % from the experimental data, this related to the evaporation of electrolyte solvent which caused by the boiling temperature. Fig. 3 shows the saturation index values at the similar conditions. The freezing temperature has been estimated at 287.15 K with temperature error of +1.4 % from the experimental data. Fig. 4 shows the estimated values of solution density and Table II presents the specific gravity error percentage compared with the experimental values which collected from Kohl [1]. Fig. 5 shows the effect of temperature on the water activity coefficient for 30 wt% carbonate solution. The error percentage has been found at the range of (-9.991% to -0.7042%) between temperatures of (30 to 100) ^{0}C respectively, these calculations presents in Table III. Table IV presents the results of thermodynamic properties at the estimated boiling and freezing temperatures.

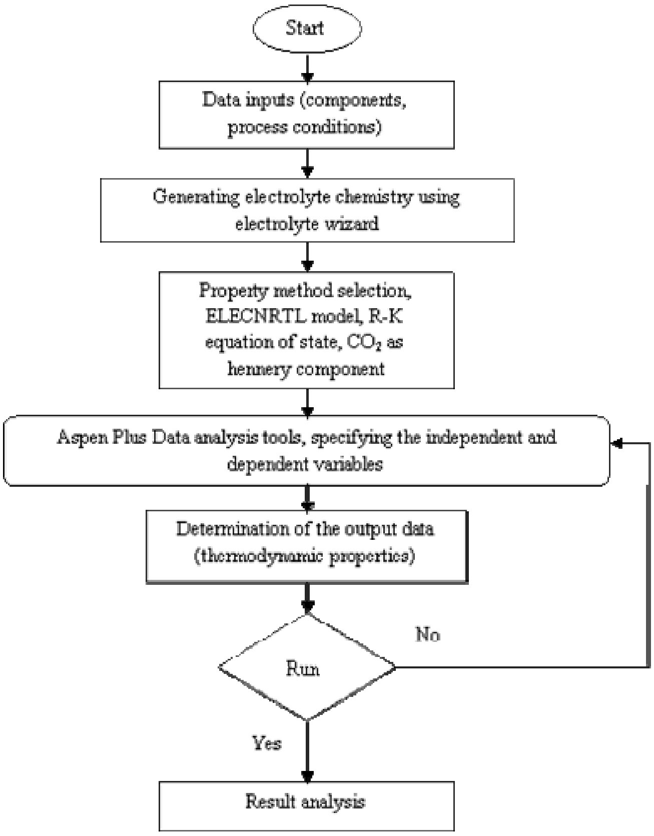

Fig. 1 Electrolyte system Simulation algorithm

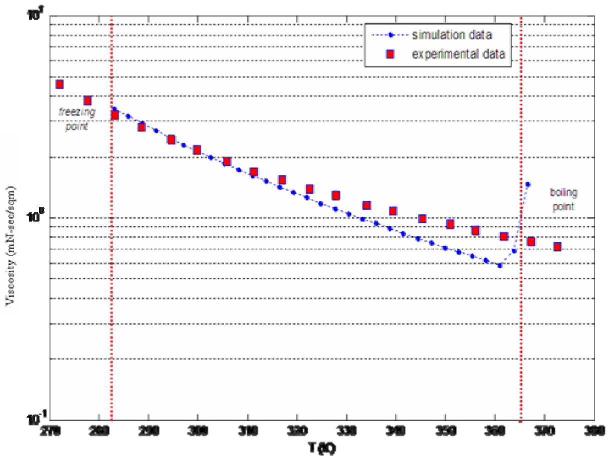

Fig. 2 Viscosity of 30% K_2CO_3 solution compared with experimental data, Kohl [1]

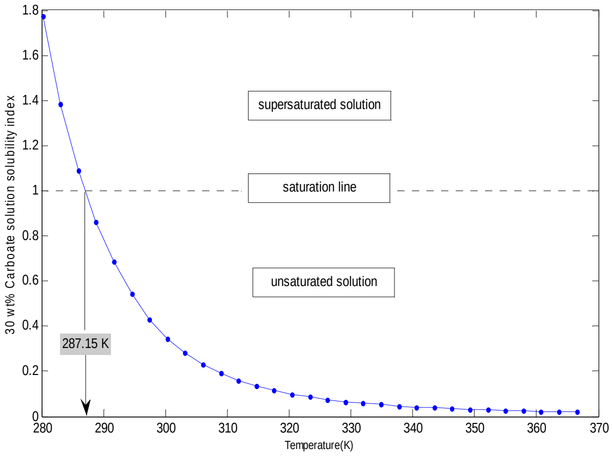

Fig. 3 Saturation index of 30 wt% K_2CO_3 standard solution

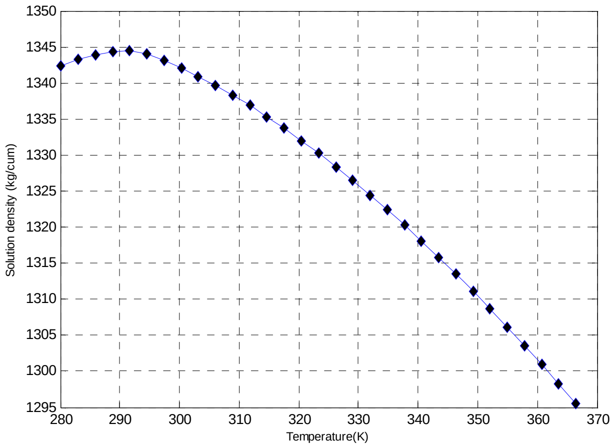

Fig. 4 Water activity of 30 wt% K_2CO_3 standard solution

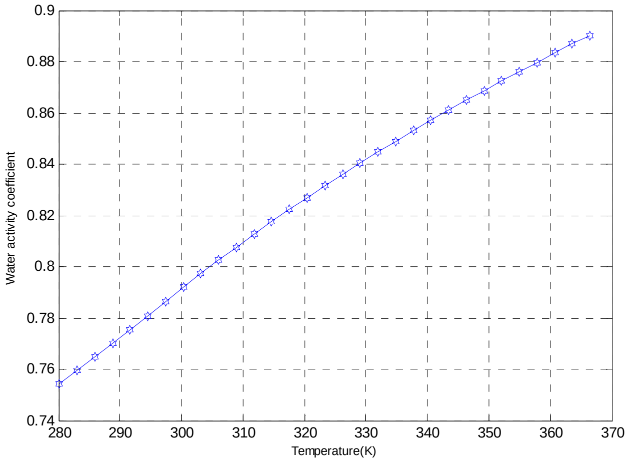

Fig. 5 Water activity coefficient of 30 wt% K_2CO_3 standard solution

TABLE I
THE ELECTROLYTE PAIR PARAMETER VALUES (ASPEN PLUS)

Ionic spices				*Energy parameters*		
Molecule i or electrolyte i		*Molecule j or electrolyte j*		*C*	*D*	*E*
H_2O		H_3O^+	HCO_3^-	8.045	0	0
H_3O^+	HCO_3^-		H_2O	-4.072	0	0
H_2O		H_3O^+	CO_3^{--}	8.045	0	0
H_3O^+	CO_3^{--}		H2O	-4.072	0	0
H_2O		H_3O^+	OH^-	8.045	0	0
H_3O^+	OH^-		H_2O	-4.072	0	0
H_2O		K^+	HCO_3^-	8.75	0	0
K^+	HCO_3^-		H_2O	-4.489	0	0
H_2O		K^+	CO_3^{--}	0.783373	0	0
K^+	$CO3^{--}$		H_2O	0.602788	-1173.12	-1173.12
H_2O		K^+	OH^-	7.840673	773.3601	773.3601
K^+	OH^-		H_2O	-4.2587	-305.651	-305.651

TABLE II
SPECIFIC GRAVITY ERROR PERCENTAGE

T ^{0}C	*SG, Kohl (1997)*	*SG, Aspen results*	*Error%*
70	1.30059	1.315777	1.17%
75	1.29472	1.311058	1.26%
80	1.29003	1.308609	1.44%
85	1.28416	1.300913	1.32%
90	1.27947	1.298235	1.49%
95	1.27361	1.295504	1.77%
100	1.269	1.290733	1.71%
105	1.26422	1.283649	1.58%

TABLE III
WATER ACTIVITY COEFFICIENT ERROR PERCENTAGE

T ^0C	*Walker* [13]	*Aspen results*	*Error %*
30	0.8855	0.797029	-9.991
40	0.8864	0.814698	-8.0891
50	0.8885	0.831038	-6.4673
60	0.891	0.846212	-5.0267
70	0.8948	0.860367	-3.8481
80	0.9001	0.873632	-2.9406
90	0.9037	0.88612	-1.9453
100	0.9043	0.897932	-0.7042

TABLE IV
THERMODYNAMIC PROPERTIES VALUES AT FREEZING AND BOILING TEMPERATURES

Property	*T_F 287.15 (K)*	*T_B 362.15 (K)*
Water activity coefficient	0.76449	0.887
Enthalpy(*KJ/Kg*)	-13585	-13417.52
Cp (*J/Kg-K*)	1873.37	2349.53
Density (*Kg/cum*)	1343.896	1298.913
Solubility index	1	0.02216
Solution pH	12.938	11.569

NOMENCLATURE

Symbol	*Quantity*
T^{ref}	Reference temperature, 298.15 [K]
T	Current temperature
$\gamma_{\pm}$	Mean activity coefficient
x	Number of anions
y	Number of cations
$\tau_{Ba,ca}$	$\tau_{aB} - \tau_{ca,B} + \tau_{B,ca}$
$\tau_{Bc,ac}$	$\tau_{cB} - \tau_{ca,B} + \tau_{B,ca}$
Xj	xj Cj (Cj=Zj for ions Cj = unity of molecule)
B	Solvent molecule
c	Cation
a	Anion
z_c	charge number of cation
z_a	charge number of anion
τ	binary energy interaction parameter
NC	number of the chemical species
a (i,k,A,w)	activity
A	Debjie Huckel parameter
n	mole number
w	water
K	solubility product
k	stoichiometric coefficient for cation
α	degree of dissociation
ΔG^0	Gibbs energy at standard conditions

V. CONCLUSION

The thermodynamic study of 30 wt% potassium carbonate was carried out to obtain the thermodynamic values of viscosity, saturation index, density and water activity. These properties are estimated at temperatures range between (280.15- 366.15) K and pressure of 1 bar. As compared with the experimental value, the estimated saturation index determined at temperature of 287.15K was found to be acceptable with error percentage of +1.4%. The deviation for the estimated specific gravity values gave an error percentage between 1.26% and 1.77%, and that of the water activity coefficient gave (-9.99%) at temperature 30^{0}C and (-0.71%) at temperature of 100^{0}C.

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