

301. Prediction of pseudo-retrograde hydrate phenomenon for ternary systems Ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) and Ethane (C₂H₆) + i-butane (i-C₄H₁₀) + water (H₂O) in hydrate-forming region

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Abstract

Gibbs energy minimization method is used to calculate the phase equilibria of ternary ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) and ethane (C₂H₆) + i-butane (i-C₄H₁₀) + water (H₂O) systems. CSMGem prediction software is used for flash calculations. Various concentrations of ethane were used for the evaluation of (L_w-V-H) phase equilibrium of two pure gases. It is commonly termed as the dissociation of H cant happened by increment of pressure but in case of ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) systems at 277.9K, flash calculations showed that *hydrate* may dissociate and this phenomena termed as pseudo-retrograde *hydrate* behavior may exist but this is not necessary in all cases. In case of ethane (C₂H₆) + i-butane (i-C₄H₁₀) + water (H₂O) system no pseudo-retrograde behavior was predicted by considerably increasing pressure at various temperatures 275K, 278K and 280K. Phase diagram for ethane + propane + water and ethane + i-butane + water systems were plotted for pressure as a function of mole fractions of ethane. Predictions of ternary mixtures equilibria for aqueous (vapor-liquid equilibria) systems reveal satisfactory predictions for ternary mixtures. This study will contribute to solve the problems of petroleum products during exploration and its production in offshore and onshore condition.

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1. Introduction

Clathrate or also known as gas *hydrates* belong to the group of physical crystal like compounds. Water is the major part of crystal structure forming component in cavity of gas *hydrate* formation. Water molecules can form a hydrogen bonding network, with defined cages or known as cavities, in which gas serves as guest and water serves as host molecule to form *hydrate*. Until more than 100 types of important *hydrate*-formers have been recognized and reported by Jens et al., [1]. Among them are NG components such as CH₄ *hydrates* (or gas *hydrates*, etc.) are water based solid crystals look like ice like structure in which very small tiny non-polar molecules (typically gases), polar molecules, low molecular weight gases or volatile liquids are trapped inside the "cages", known as cavities in the crystalline structure of H₂ joined water molecules at particular temperature and pressure condition. Presently structure I (sI), structure II (sII) and structure H (sH) are well established and studied. *Hydrate* structure sI and sII can be formed with addition of a single guest component while structure H requires minimum two different guest molecules (large and small) to form sH *hydrate*. Most components of natural gas mixtures are (CH₄, C₂H₆, C₃H₈, CO₂, N₂ and H₂S etc.) can form gas *hydrates*. The recent development on the use of clathrate *hydrates* in industrial process requires knowledge in the phase behaviour of *hydrate* forming system. Phase behaviour of simple hydrate systems have been thoroughly investigated mostly based on hydrocarbons and carbon dioxide system. In *hydrate* phase behaviour, pseudo-retrograde *hydrate* behaviour in which by increasing pressure solid phase dissociates and form liquid phase this phenomena occurs in *hydrate* forming region. Still reported data on these phenomena is not sufficient in current literature to see the phase behaviour of single, binary and multi component systems. This article talk about the predicted results for hydrate phase behaviour for the gas mixture of ethane (C₂H₆) + i-butane (i-C₄H₁₀) + water (H₂O) at specific temperature and pressures conditions. *Hydrate* formation conditions were predicted. Sabil et al., [2] has reported the experimental evidences in his research work occurrence of pseudo-retrograde behaviour of CO₂ and tetrahydrofuran system. Ballard et al., [3] has assumed that pseudo-retrograde may appear, but this is not restricted only for system having binary components those having structure I (sI) and structure II (sII) *hydrate* formers are present and having very low pressure. The research work is streamlined to find more evidences on the occurrence of pseudo-retrograde *hydrate* behaviour in mixed *hydrate* systems especially in natural gas components and CO₂ based systems to validate the Ballard et al., [3] hypothesis.

2. Methodology

The prediction of phase equilibria is performed by flash calculations taking 30% overall gas composition and 70% in excess water. The predictions of phase equilibria points were calculated in respect of ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) at 277.9K. Similar prediction method was also used by Ballard et al., in 2001[3]. For Ethane (C₂H₆) + i-butane (i-C₄H₁₀) + water (H₂O) system were studied with three different temperatures 275K, 278K and 280K with various gas compositions taken in mole fractions and studied to see the effect of concentration on phase equilibria. The pressure of the system is increased at a selected value keeping iso-thermal condition until *hydrate* solids are detected through flash calculations. The pressure is slowly increased by 1atm until the *hydrate* solid is completely eliminated from the system. A series of these equilibrium points were produced for selected equilibrium lines. By measuring a series of these equilibrium lines, the phase behaviour of the system is constructed in Excel sheet using equilibrium points at various mole fractions of Ethane (C₂H₆) + i-butane (i-C₄H₁₀) + water (H₂O) system.

A flash calculation based method is also reported by Bishnoi and Gupta [4] based on Gibbs energy minimization is adopted in this work. This prediction can report the phases present at various gas mole fractions, temperature, and pressure conditions. This prediction method is used to for the determination of the number of phases present due to changing the pressure. Applying flash calculations the possible phases comprise V, L_w, L_{hc}, structure I *hydrate*, and structure II *hydrate*. SRK Eos [5] is used to model the fugacities in (V, L_{hc}, and L_w)

$$\ln \frac{f_i}{y_{ip}} = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{B} \times \left(\frac{2 \sum i_y i_a i_k}{a} - \frac{bk}{b} \right) \ln \left(\frac{Z + B}{Z} \right) \quad (1)$$

A famous Krichevsky–Kasarnovsky [6] equation is plasticized to find out the solubility of hydrocarbons in the L_w phase. Van der Waals and Platteeuw theory [7] used to calculate the “*f*” fugacity of water in *hydrate* phase. This main equation can foretell the chemical potential of water in *hydrate* structure; where in the μ_w^β shows the chemical potential of water, in empty *hydrate* structure, V_m shows the number of cages of type m/water molecule is present in the *hydrate* phase.

$$\mu_w^H = \mu_w^\beta + RT \sum m V_m \ln(1 - \sum j \theta_{jm}) \quad (2)$$

Structure and θ_{jm} is used to calculate the Jth occupancy of guest molecule in the mth *hydrate* cage. This fractional occupancy can be written as,

$$\theta_{Jm} = \frac{C_{Jm} f_{Jm}}{1 + \sum_k C_{km} f_{km}} \quad (3)$$

Where, f_{Jm} and C_{Jm} shows the fugacity and Langmuir constant of component J present in m cage. The constant value depending on temperature and can be described as the interaction parameters in between the gas molecule and the H₂O can be assessed by arrogating a circular structure with correct proportion potential can be written as,

$$C_{Jm} = \frac{4\pi}{kT} \int_0^{R_m - a_J} \exp \left[-\frac{\omega_{Jm}(r)}{kT} \right] r^2 dr \quad (4)$$

Where $\omega_{Jm}(r)$ used to calculate the cell potential of gas molecule J in cavity m and a_J stand for the spherically inner radius of J and R_m value stands for the radius of cavity m. In this work, the Kihara cell potential parameters [8] can be applied for the calculation of water-gas effect upon one another in every cavity. The H₂O chemical potential in L_w phase is obtained by Marshall et al.,[9] and after some time it was simplified by another researcher Holder et al.,[10] and Menten et al.,[11] and his co-workers which can be simply defined as in (Eq.(5)),

$$\mu_w^L = \mu_w^\beta - \Delta\mu_w^0 + T \int_{T_0}^T \left(\frac{\Delta h_w}{T^2} \right) dT - \int_0^P \Delta V_w dp + RT \ln(\alpha_w) \quad (5)$$

Where, $\Delta\mu_w^0$ shows the variation in the chemical potential of H_2O in the unoccupied *hydrate* structure and pure L_w at a (273.15 K) and absolute zero pressure, Δh_w and ΔV_w are presented. α_w shows the activity of water. To obtain the fugacity of water in *hydrate* phase, Eqs. (1) and (4) can be applied. *Hydrate* fugacity depending on the chemical potential of water in liquid water phase mentioned in Eq. (5).

$$f_w^H = f_w^L \exp\left(\frac{\mu_w^H - \mu_w^L}{RT}\right) \quad (6)$$

All predictions have been taken in the presence of excess water due to liquid water phase.

3. Results and Discussion

Table 1. Predicated CSMGem values for the system ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) at 274K.

Mole fraction	Lw -V	Lw-sII-V	Lw-sI-V	Lw-sII
	P(atm)	P(atm)	P(atm)	P(atm)
0.1	2.595	2.133		2.514
0.2	2.780	2.175		4.891
0.3	2.889	2.360		6.672
0.4	3.400	3.410		
0.5	4.372	3.460		
0.6	5.267	3.815		
0.7	6.609	5.410		
0.8	5.267	7.406	6.410	
0.9	4.521	6.730	5.257	

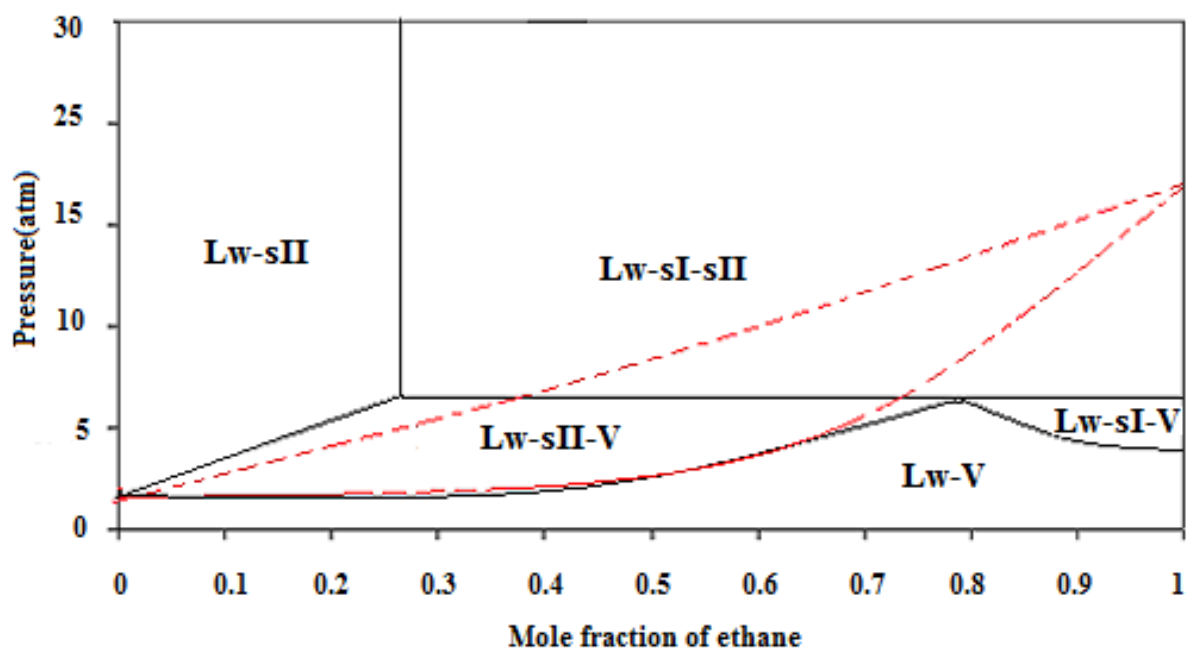


Fig.1. Pressure as a function of mole fraction for ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) system at 274 K.

Fig.1 Shows the *hydrate* formation phase diagram when ethane (C₂H₆) + propane (C₃H₈) are added together at 274K. Here ethane behaves like an inhibitor for sII *hydrate* because of occupancy in large cavity of sII. Propane (C₃H₈) can serve as an inhibitor to sI *hydrate* formation when it added in ethane (C₂H₆) + water (H₂O) system. Nevertheless propane may not enter in the sI cages because the fugacity of ethane is much lower when the Propane C₃H₈ is subjected, subvert the sI *hydrate*. Holder [12] reported the inhibiting effect as an “antifreezing” agent. The P v.s mole fraction for ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) system is mentioned in Fig. 2. From (0.0-0.5) mole fraction of ethane (C₂H₆) sII *hydrate* is predicted. If the pressure is increased up to 9.5 atm, from (0.23-0.5) mole fraction of ethane, sII *hydrate* is predicted to dissociate and to form three phase L_w-V-L_{hc} equilibrium line. The point at which the *hydrate* dissociates is predicted through flash calculation is termed as pseudo-retrograde pressure at constant temperature. It can be defined as the changing of a solid phase to liquid phase by increasing the considerable pressure keeping low temperature conditions.

Table.2. Predicated CSMGem values for the system ethane (C₂H₆) + propane (C₃H₈) + water (H₂O) at 277.9K.

Mole fraction	Lw -V	Lw -sII-V	Lw -sI-Lhc	Lw -sI-V
	P(atm)	P(atm)	P(atm)	P(atm)
0.1	4.910	5.205		
0.2	5.247	7.000	9.810	
0.3	5.355	9.500	10.216	
0.4	5.273	9.500	13.103	
0.5	8.734	9.500	13.100	
0.6	13.236		13.100	
0.7	14.110		13.100	13.100
0.8	12.137		13.100	10.000
0.9	9.642		13.100	9.45

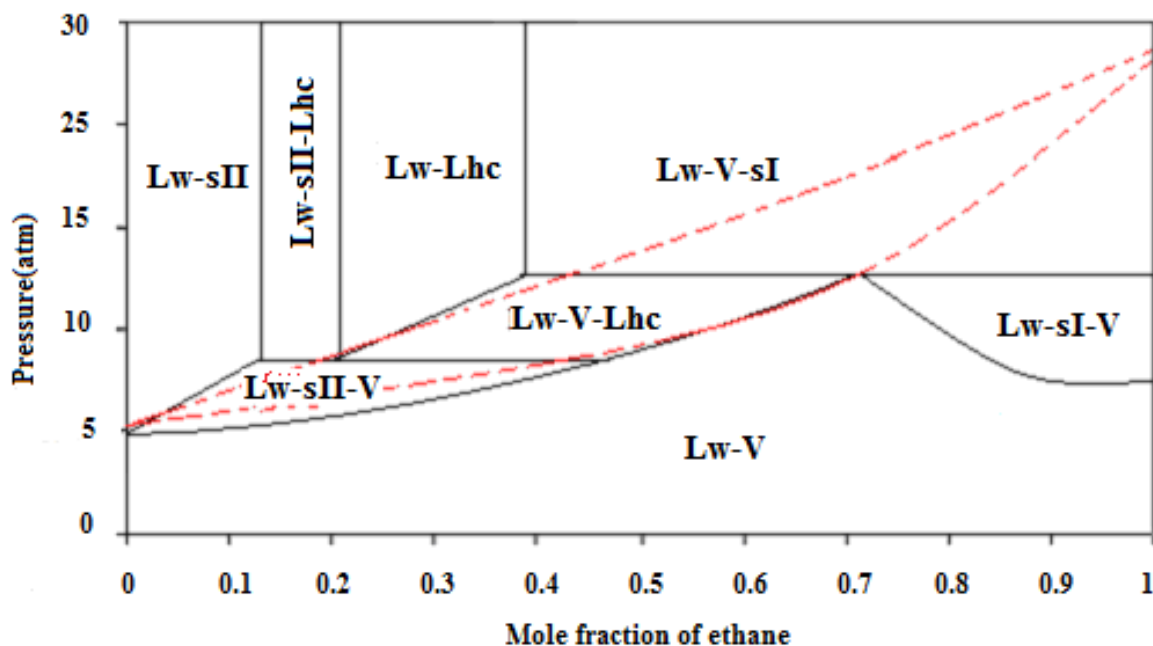


Fig.2. Pressure vs. mole fraction for the system ethane (C_2H_6) + propane (C_3H_8) + water (H_2O) at 277.9K.

Pseudo-retrograde behaviour can be obtained by vapour liquid equilibria of ethane (C_2H_6) + propane (C_3H_8) + water (H_2O) system at 277.9 K. The dotted line shows in Fig.2 is L_w-V-L_{hc} phase envelope. The $L_w-sII-V$ phase area crossing from the L_w-V-L_{hc} area and meeting at the quadruple point at (9.5 atm) pressure. In terms of Gibbs phase rule, prediction shows that there is one degree of freedom (three components and four phases) are formed at 277.9 K. This point creates a four-phase line, $L_w-sII-V-L_{hc}$. If the considerable pressure is increased, one of the phases may disappear. In this situation, the predicted results show that sII phase dissociates with increasing pressure and L_w-V-L_{hc} appears which shows uncertainty because upon pressurization *hydrate* phase has to remain. The validity of the predicted results of Fig.2 reported in literature similar data taken by Ballard et al.,[3], Holder and Hand [13] for ethane (C_2H_6) + propane (C_3H_8) + water (H_2O) shows pseudo-retrograde behaviour upon pressurization.

Table 3. Predicted CSMGem values for the system ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) at 275K.

Mole fraction	L_w-V	$L_w-sII-V$	L_w-sI-L_{hc}	$V-L_{hc-sI}$	$L_w-L_{hc}-V$
	P(atm)	P(atm)	P(atm)	P(atm)	P(atm)
0.1	1.782	2.580	1.740		
0.2	2.004	2.082	5.424		
0.3	2.289	2.445	7.294		19.978
0.4	2.663		7.294		19.650
0.5	3.155		7.294		9.819
0.6	3.869		7.294	7.500	
0.7	4.993		7.294	10.357	
0.8	7.310		7.289	14.032	

0.9

6.510

14.492

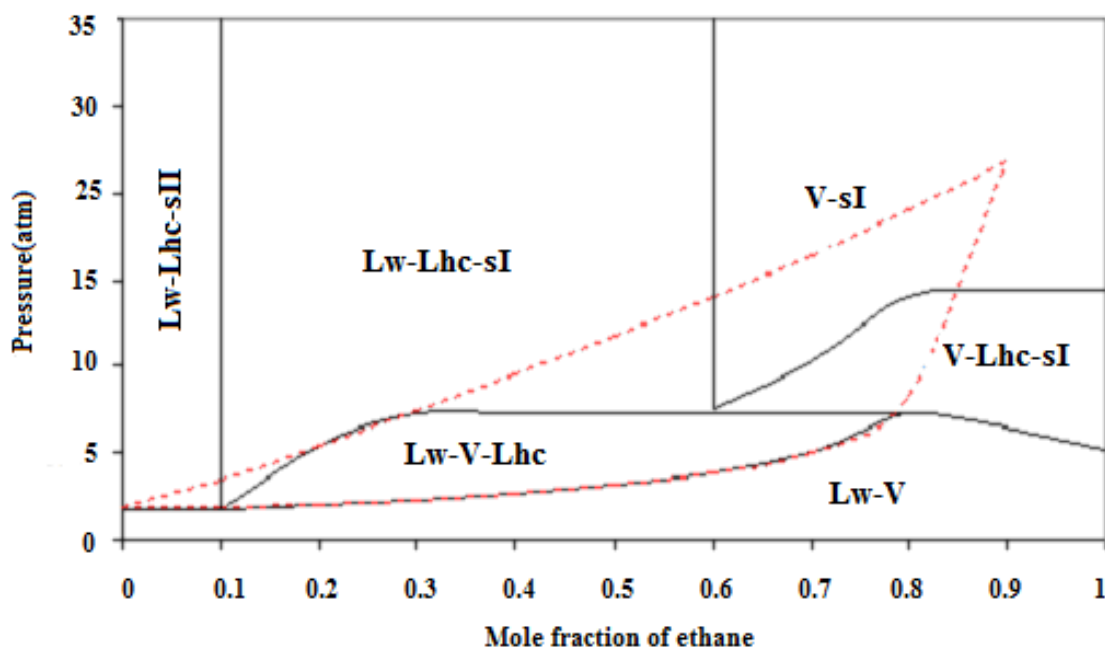


Fig.3. Pressure vs. mole fraction for the system Ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) at 275K

By considering all data Fig.3 is plotted between pressure and mole fractions of Ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system at 275K and 35 atm. Behaviour of ethane is observed using CSMGem simulation software by flash at various pressure and range mole fractions. Predicted results show that sII hydrate of ethane is predicted at 0.1 mole fraction and found stable after considerable increase in pressure, it is observed that it may not dissociate, where sI is formed at 0.6 mole fraction of ethane by same manner by increasing the considerable pressure the prediction shows that sI do not dissociate. Calculation are taken at 30% overall gas composition in presence of excess water. Phase behaviour is observed by the amount of V-L_w equilibrium condition for ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system. Prediction shows that no dissociation is observed in both structures sI and similarly in sII by increasing the considerable pressure, in the light of these observations no evidence of pseudo-retrograde behaviour is predicated in ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system using CSMGem.

Table .4. Predicted CSMGem values for the system Ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) at 278K.

Mole fraction	L_w-V	L_w-V-L_{hc}	L_w-L_{hc}	$V-L_{hc}-sI$	$L_{hc}-sI$	$V-sI$	L_w-L_{hc}
	$P(atm)$	$P(atm)$	$P(atm)$	$P(atm)$	$P(atm)$	$P(atm)$	$P(atm)$
0.1	2.009	3.788	50.000		45.000		10.187
0.2	2.253	5.833	50.000		25.000		22.000
0.3	2.558	7.962	50.000		25.435		23.000
0.4	2.958	10.036			18.790		20.000
0.5	9.800	10.036		10.100			
0.6	7.699	10.036		12.000		45.000	
0.7	5.800	10.036		14.600		50.000	
0.8	5.600	10.036		17.492		54.000	
0.9	5.800			20.000		31.000	

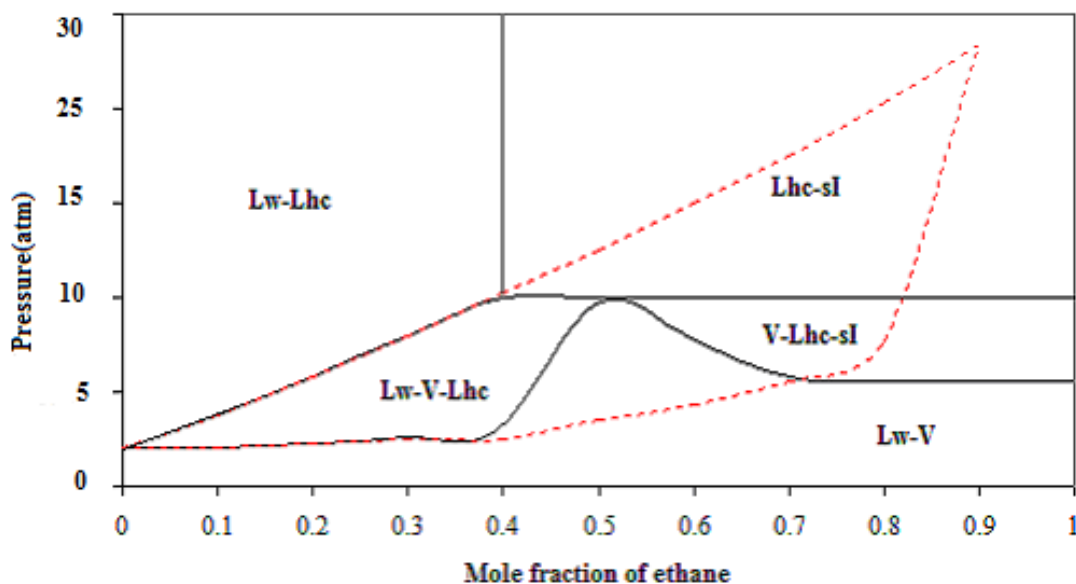


Fig.4. Pressure vs. mole fraction for the ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system at 278K

Pressure versus mole fractions of ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system at 278K is shown in Fig.4 overall gas composition is taken as 30% with excess water. Three phase *hydrate* equilibrium line $V-L_{hc}-sI$ is observed at 10 atm pressure. Phase behaviour of hydrocarbon at various pressure and mole fractions of ethane (C_2H_6) and i-butane ($i-C_4H_{10}$) is observed using Predication Software CSMGem is used by evaluation through flash calculation. Phase behaviour is observed by assessment of the $V-L_w$ equilibria of ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system. No dissociation is observed up to 25 atm and above pressures, so no pseudo-retrograde behaviour is predicated in ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system .

Table.5 Predicted CSMGem values for the system ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) at 280 K.

Mole fraction	L_w-V	L_w-V-L_{hc}	L_w-L_{hc}	$L_w-L_{hc}-sI$
	P(atm)	P(atm)	P(atm)	P(atm)
0.1	2.156	3.992	40.000	
0.2	2.414	6.118	40.000	
0.3	2.741	8.331	40.000	
0.4	3.169	10.634	40.000	
0.5	3.755	12.531		24.485
0.6	4.603	12.531		24.485
0.7	5.935	12.531		
0.8	8.320	12.531		
0.9	12.308	12.531		

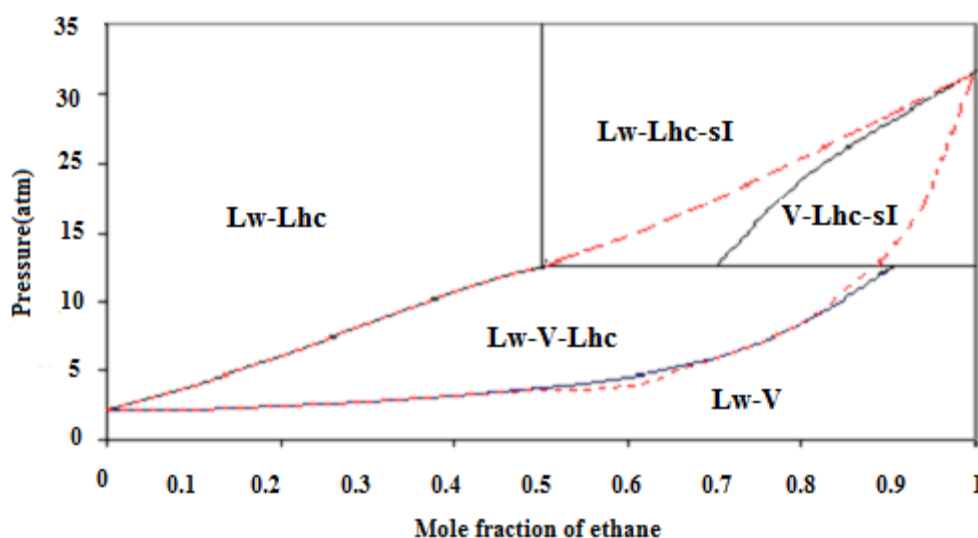


Fig.5. Pressure vs. mole fraction for the system ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) at 280K

Fig.5 is plotted between pressure and mole fraction of ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system at 280K and 30 atm for the system. Behaviour of hydrocarbon at various pressure and mole fractions of ethane is observed by using prediction software CSMGem through Flash calculation. Phase behaviour is observed for the $V-L_w$ equilibria of ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system. The L_w-V-L_{hc} phase area passes through and intersects the $V-L_{hc}-sI$ area. No dissociation is occurred in sI by further pressurization, so no pseudo-retrograde behaviour is predicted.

The overall gas composition is taken as 30% with excess water at various temperatures and pressure ranges by establishing the isothermal condition and Gibbs energy minimization *hydrates* equilibria are studied. The predicted values show that, for a range of temperature approximately 0.5 K, it is possible that *hydrate* may dissociate in case of *sII hydrate* of ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system by increasing considerable pressure. In case of Ethane (C_2H_6) + propane (C_3H_8) + water (H_2O) system, pseudo-retrograde behaviour may help in solving industrial related transportation problems. The three phase in fig: 4 & 5 $L_w-L_{hc}-sI$ and in fig: 3 two phase $V-sI$ are observed. It is found that Ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) system do not show pseudo retrograde behaviour of ternary system at the studied temperature and pressure conditions. Further efforts are needed to confirm the results by performing a series of experiments for the validity of pseudo-retrograde behaviour in different systems and also to verify the predicted results.

4. Conclusion

Pseudo-retrograde phenomena is predicted containing ethane (C_2H_6) + propane (C_3H_8) + water (H_2O) system at (9.5 atm) and 277.9K, similar results were also predicted by Ballard. In case of ethane (C_2H_6) + i-butane ($i-C_4H_{10}$) + water (H_2O) no Pseudo-retrograde phenomena is predicted. Existence of sI and sII *hydrates* has great importance in transmission of gas

pipelines Experimental results are required for validation of predicted results generated through CSMGem prediction software

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List of symbols appendix A

a	guest core radius
C	Langmuir constant
F	fugacity coefficient
h	enthalpy (J/mol K)
k	Boltzmann's constant (J/K)
P	pressure
r	integration variable
R	gas constant
T	temperature in (K)
v	volume in (cm ³ /mol)

Greek letters

μ	chemical potential (J/mol)
ν	number of hydrate cavities / water molecule
θ	occupancy of gas in the hydrate cavity
$\omega(\)$	cell potential
Δ	difference between H structure and water

Subscripts

0	properties at reference conditions
J	guest component
m	hydrate cavity
w	water

Superscripts

β	unoccupied hydrate phase
H	solid hydrate
Lw	liquid water
Lhc	liquid hydro carbon