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# Study the effect of organic promoters on thermodynamics behaviour for refrigerant gas clathrate hydrate.

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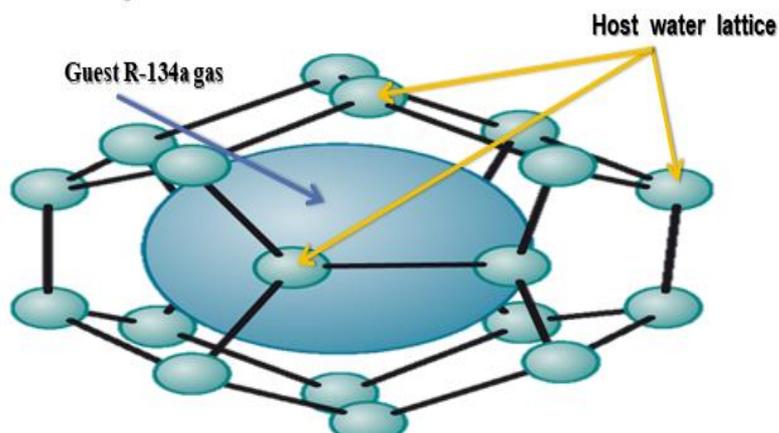
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**Abstract.** The present work consists of an experimental and theoretical investigation dealing with hydrate formation for the binary system (water+ refrigerant gas) and ternary systems (water+ refrigerant gas+ promoter) at constant initial conditions (pressure and temperature). Isochoric method (constant volume) search was used in current study to measure the formation data (pressure, temperature) for hydrate. Refrigerant R134a gas and different organic promoters such as benzene and cyclohexane were used in this study. For ternary systems at the different concentrations of promoters shifted hydrate formation data when benzene and cyclohexane decrease pressure and increasing temperature. Many objective functions were obtained from kinetic models such as the amount of gas consumed ( $\Delta n$ ), the growth rate ( $r(t)$ ), and conversion of the water to hydrate. The gas consumed ( $\Delta n$ ) of the binary system increased lead to increase in hydrate formation, also the hydrate growth rate ( $r(t)$ ) and increase water conversion to hydrate. The gas consumed in the presence of cyclohexane was higher than at using benzene as a promoter. The experimental results show that the presence of different promoters in the ternary systems have an effect on thermodynamic promotion of refrigerant hydrates formation. The promotion effect increased with increasing the concentration of promoter in the select range. Also, the results manifested that benzene and cyclohexane had a clear effect in reducing the pressure and raising the temperature of the hydrate formation. The storage capacity was investigated. It has been noticed that the existence of the promoters in the hydrate formation system led to a slight increase in the storage capacity with maximum value about (78.66) V/V.

## 1. Introduction

A clathrate is a complex molecule formed by the contact between gas and water at high pressure and low temperatures. The cavities within hydrate formation are formed by the hydrogen bonds which occupied by the gas molecules that are the guest molecules as shown in (Figure.1) [1].





**Figure 1.** Clathrate hydrate structure

For many years, clathrate hydrates were considered as harmful in oil and gas industry because of their annoying tendency to plug the pipelines [2]. In recent years and as a result of policies to reduce environmental pollution, they entered other fields where the research included: water desalination, separation processes [3]. After the positive aspects of clathrate hydrate technology, enhancing the hydrate formation is one of the main objectives of gas hydrate technology.

The slow formation of hydrates and energy costs involving the formation of hydrates at low temperature and high pressure are considered industrial impediments. Promoters should be used to rapidly form hydrates under the same operating pressure and temperature [4].

Organic component (cyclopentane, cyclohexane, benzene, acetone, etc.) can reduce the required hydrate formation pressure that is considered as a thermodynamic promoter [5]. For the specific case of gas in the cavities, it has been suggested that the enhanced hydrogen bonding and increase their number could be due to the physical tension on the water lattice caused by the relatively gas molecule present in the cavities [6].

The hydrate formation enhancement is not easy to achieve because of the hydrate formation layer volume depends on factors such as promoter choice, guest choice, initial pressure, temperature and concentration of promoter [7].

The main purpose is to study the phenomena of hydrate formation of refrigerant R134a for the ternary system (water +R134a + promoter) for different types of the promoter (Cyclohexane and Benzene) at different concentrations.

## 2. Experimental

### 2.1 Materials

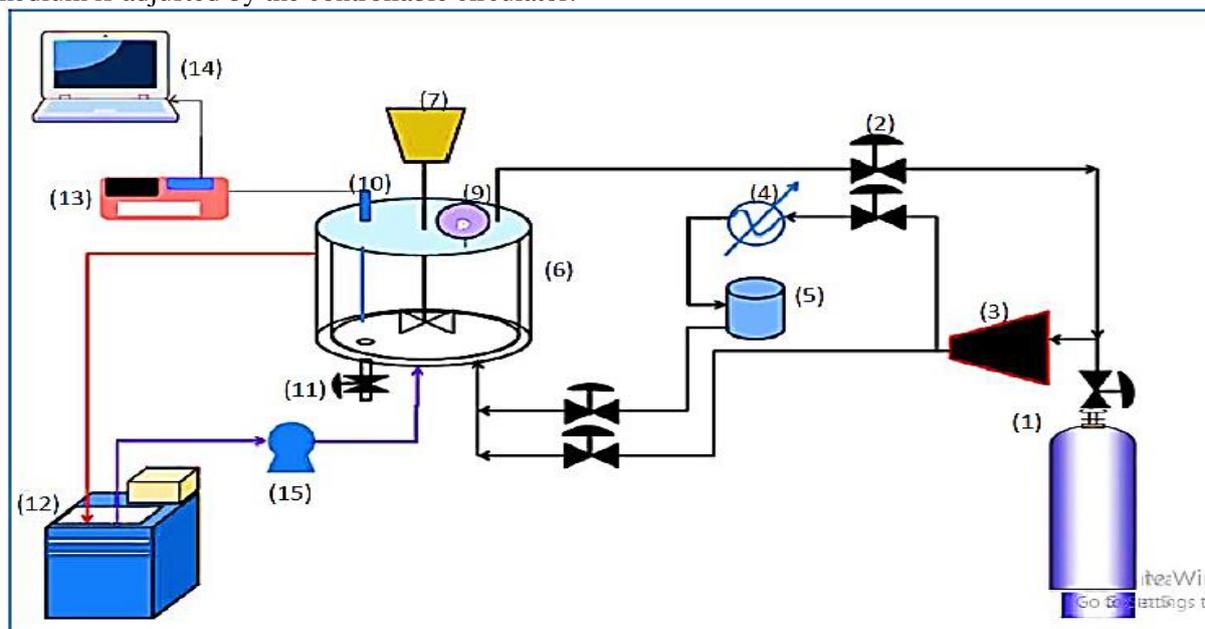
Refrigerant gas (R-134a) with a high purity equal to 99% was utilized to form a hydrate with distilled water. In experiments, promoters were used were Benzene and Cyclohexane that were immiscible with water.

### 2.2 Apparatus

(Figure.2) shows the experimental schematic diagram used in this study. The most important part in the system is the glass cell with a total volume of 1500 cm<sup>3</sup> which consist of the internal diameter of 14 cm and a height of 14.5 cm, the cell was equipped with a magnetic stirrer that used in this experiment and it mainly modified electric stirrer which consists of two shafts, the first shaft connected to electric motor from top and to the other end attached to the magnet. The second shaft contains a magnet (corresponding to the magnet at the first shaft), which is inside a closed chamber to ensure no leakage, the second end of the second shaft is extended to the inside of the cell and at the end of the blender. This

process is done to ensure that there is no leakage of gas. A thermocouple with a division scale of 0.1 K and a digital pressure gauge with a division scale of 0.00005 bar were used to measure the temperature and pressure.

The cell connected to the system through pipes and controlled by a valve for gas injection, water input, and drain. The cell surrounded by transparency plastic vessel as heat jacket to maintain the temperature inside the cell, moreover cooling water was supplied from chiller type Julabo F10-VC which was which contains a cooling medium made of ethylene glycol/water. The temperature of the medium is adjusted by the controllable circulator.



**Figure 2.** (1) gas cylinder; (2) needle valve; (3) gas compressor; (4) condenser; (5) accumulator of gas; (6) Experimental cell; (7) magnetic stirrer; (8) water pump; (9) digital pressure gauges; (10) temperature sensor; (11) drain valve; (12) chiller; (13) interface system; (14) computer.

### 2.3. Experimental method

The constant volume (isochoric) system search strategy was utilized to investigate hydrate formation in this study. At the start, distilled water was used to wash the cell then it is washed with acetone to flush the cell. Washed water with acetone was drainage. The cell was emptied to vacuum pressure by the compressor for a time of 30 min to guarantee that there were no traces of contamination.

Before starting the experiment, the cell is examined in terms of venting using air at a pressure of 10 bar and using foam solution sprayed on the cell, joints, and valves and on the basis of which it is sure that there is no leakage that can be treated. Repeating this procedure periodically every 10 minutes during the experiment to make sure there is no leakage.

The air is evacuated from the cell by using the compressor then 200 ml (13% vol of the cell) of water solution mixture was fed to the cell. A specific measure of R-134a was acquainted of the cell (86% vol of the cell) with achieving the coveted pressure of 0.45 MPa (4.5 bar) at a temperature of 313.15 K (10 °C).

The mixer was rotated at 250 rpm after the gas that is pressurized to the cell is completed. The pressure of cell reduced consistently because of hydrate formation until the point where achieving the steady state condition.

The stirring speed is set at 250 rpm and initial temperature and pressure at 10 °C and 10 bar respectively with selecting Benzene and cyclohexane at different concentrations (0, 2.5, 5.0, 7.5 and 10.0) Vol%.

Hydrates are separated by water discharge (non-converted to hydrates) by the pressure inside the cell and thus the hydrate is extracted.

### 3. Mathematical Model

#### 3.1 Gas Consumed

The moles of the hydrate former consumed throughout the formation of hydrate are obtained by applying the real gas law as follows:

$$\Delta n_H = n_{g,0} - n_{g,t} = \left( \frac{PV}{ZRT} \right)_0 - \left( \frac{PV}{ZRT} \right)_t \quad (1)$$

The "0" Subscripts refer to the initial conditions where "t" refers to conditions at time, t, of the system, P pressure and T temperature at the phase equilibrium state, R was the universal gas constant, and Z was the gas compressibility determined by the Pitzer's correlation [8]:

$$Z = 1 + B^0 \frac{Pr}{Tr} + \omega B^1 \frac{Pr}{Tr} \quad (2)$$

Where 
$$B^0 = 0.083 - \frac{0.442}{T_r^{1.6}} \quad (3)$$

And 
$$B^1 = 0.139 - \frac{0.442}{T_r^{4.2}} \quad (4)$$

The hydrate number (number of water molecules) is identified by the partial filling the large and small cavities. The simple hydrate number is calculated [1]:

$$M = \frac{136}{(8\theta_s + 16\theta_L)} \quad (5)$$

where  $\theta_s$  and  $\theta_L$  are the fractions of linking large and small cavities occupied by guest molecules respectively, as follows [1]:

$$\theta_i = \frac{(C_i \times f_i)}{1 + (C_i \times f_i)} \quad (6)$$

$C_i$  is the Langmuir constant for large cavities ( $C_L$ ) and small cavities ( $C_S$ ) for R134a hydrate. Where  $f_i$  is the fugacity of (R134a) gas which is calculated by the following equation:

$$f_G = \phi * P \quad (7)$$

Where,  $\phi$  is the coefficient of fugacity, equation (4-8) can be utilized to estimate  $\phi$  through Peng-Robinson equation [8];

$$\ln(\phi) = (z-1) - \ln(z-B) - \frac{A}{2\sqrt{2}B} \ln \left( \frac{z+(1+\sqrt{2})B}{z+(1-\sqrt{2})B} \right) \quad (8)$$

In which A and B are adjustable parameters for R134a gas.

The Langmuir constant of R-134a  $C_i$  is formulated as follows[9]:

$$C_i = \frac{A_i}{T} \exp\left(\frac{B_i}{T}\right) \quad (9)$$

where  $A_i$  and  $B_i$  are constants with values 0.00575 and 4908 for  $C_L$  and constants equal to zero  $C_s$  for (R134a) gas [10]. The gas hydrate volume is not like the aqueous solution volume, To estimate the volume of R134a gas hydrate inside a cell the next equation is used [11] :

$$V_t = V_{\text{cell}} - V_{S_0} + V_{R_{Wt}} - V_{Ht} \quad (10)$$

where  $V_{\text{cell}}$  is the cell volume with value equal 1500 cm<sup>3</sup>;  $V_{S_0}$  is the initial aqueous solution volume with value equal to 200 cm<sup>3</sup>;  $V_{Ht}$  is the produced hydrate's volume and  $V_{R_{Wt}}$  is the reacted water's volume that enters the structure of the hydrate structure which calculated by using the following equation [11]:

$$V_{R_{Wt}} = M \times \Delta n_H \times V_w^L \quad (11)$$

The hydrate molar volume,  $V_{Ht}$ , can be estimated by the next equation [11]:

$$V_{Ht} = M \times \Delta n_H \times V_w^{MT} \quad (12)$$

The gas hydrate molar volume can be assumed equal to the empty hydrate lattice molar volume.

Klauda and Sandler illustrated that the  $v_W^{MT}$  is the volume occupied by empty hydrate lattice (in K temperature and m<sup>3</sup>/kmol) as a function of temperature and pressure by the following equation [12]:

$$v_W^{MT} = (17.13 + 2.249 \times 10^{-5} \times T + 2.013 \times 10^{-6} \times T^2 \times \frac{10^{-30} N_A}{136} - 8.006 \times 10^{-9} \times P + 5.448 \times 10^{-12} \times P^2) \quad (13)$$

T and P are the temperature and pressure given in K and MPa units, respectively.

### 3.2 The Growth Rate of Hydrate Formation

The growth rate of hydrate formation is presented by using the following equation [11]:

$$r(t) = -\frac{1}{n_{w_0}} \frac{dn_R}{dt} \Big|_{t_i} = -\frac{1}{n_{w_0}} \frac{\Delta n_R}{\Delta t} \Big|_{t_i} = \frac{(n_{R134a,i-1} - n_{R134a,i+1})}{(t_{i+1} - t_{i-1}) * n_{w_0}} \quad (14)$$

$n_{R134a,i-1}$  And  $n_{R134a,i+1}$  present moles of R134a gas which is hydrate former at  $t_{i-1}$  and  $t_{i+1}$  respectively.  $n_{w_0}$  is the initial number of moles of water.

### 3.3 Water to Hydrate Conversion

The water is converts to hydrate for each mole of water feed can be estimated by relation the following [13]:

$$\text{The Water conversion} = \frac{M \times \Delta n}{n_{w_0}} \times 100\% \quad (15)$$

### 3.4 The Storage Capacity (SC)

The storage capacity is a volume of gas stored in per volume of hydrate which is calculate by following equation [13]:

$$SC = \frac{V_{STP}}{V_{Ht}} = \frac{\Delta n \times \left(\frac{R \times T_{STP}}{P_{STP}}\right)}{V_{Ht}} \quad (16)$$

where subscript STP stands for the standard conditions and  $V_{Ht}$  is the gas hydrate volume at the end, which is calculated by Eq. (12). (Figure.3) shows the algorithm of the previous calculation for calculating the gas consumed ( $\Delta n$ ), hydrate growth rate ( $r(t)$ ), conversion of water to hydrate, and storage capacity of R-134a gas.

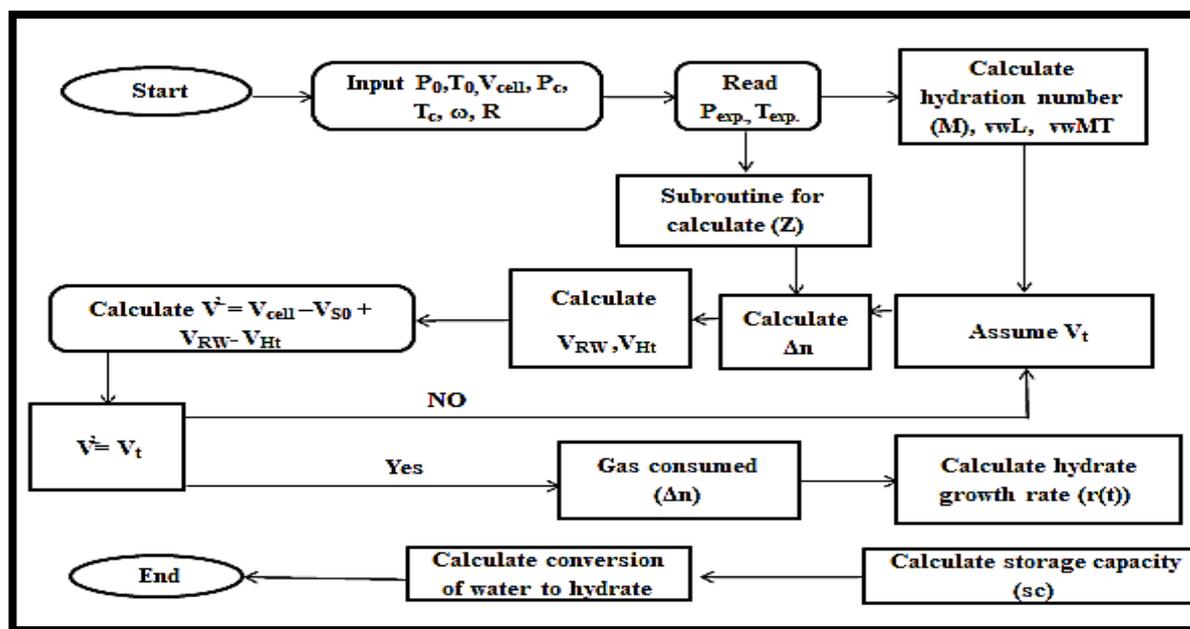


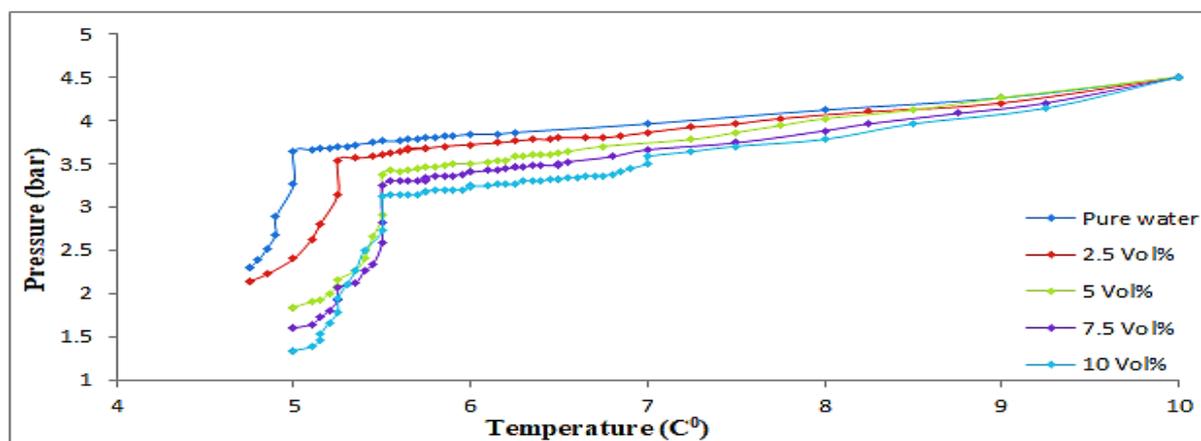
Figure 3. The suggested algorithm to calculations.

## 4. Result and discussion

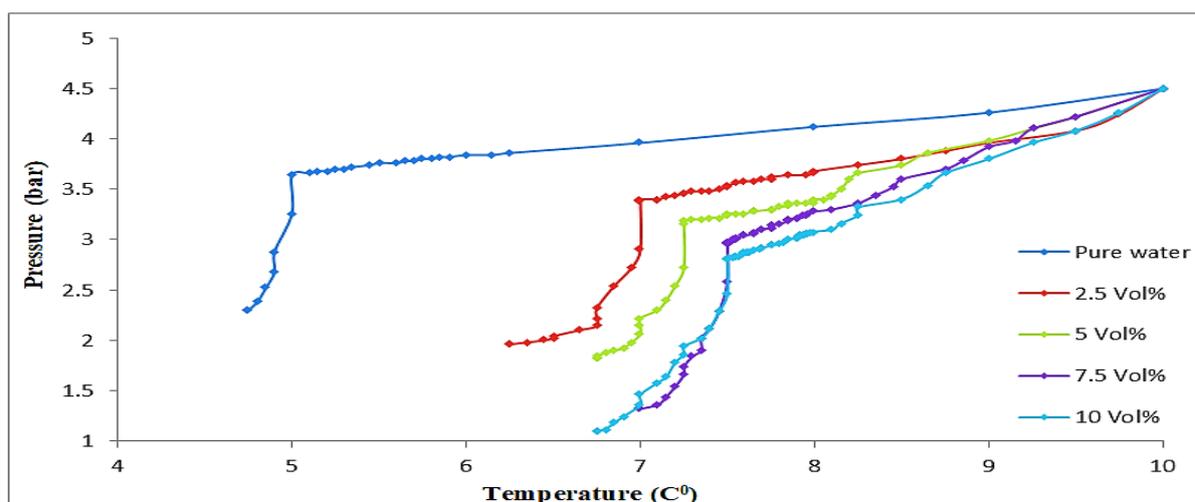
### 4.1 Thermodynamic Behavior study

Thermodynamic behavior of clathrate hydrate formation was a function of pressure and temperature with time for refrigerant gas type R-134a with different promoters concentrations. Isochoric search method is used in this study. The measurements of the hydrate phase equilibrium for the pure water and different promoters with refrigerant gas were performed through three phases: hydrate (H), liquid water ( $L_w$ ) and vapor.

The addition of benzene and cyclohexane as an insoluble hydrocarbon component in water can also lead to a decrease in pressure and an increase in temperature as described by [13,14]. The highest effect of benzene and cyclohexane is achieved at concentration 10 Vol% and this effect is gradually reduced due the concentration that is increase as shown in (Figure.4) and (Figure.5).



**Figure.4** Effect of different Benzene concentrations on the pressure and temperature path during formation of R-134a hydrate.



**Figure.5** Effect of different Cyclohexane concentrations on pressure and temperature path during formation of R-134a hydrate.

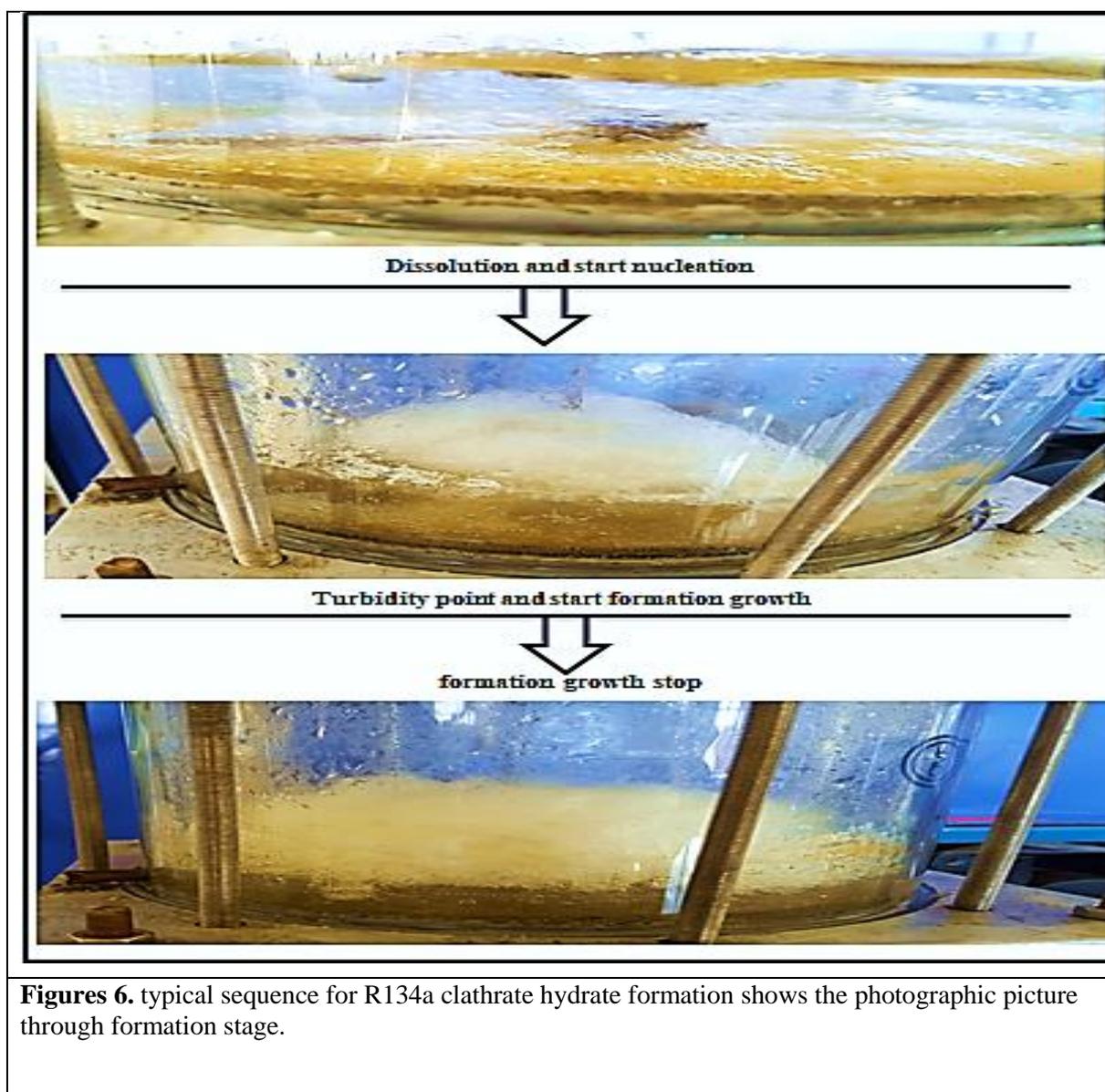
Cyclohexene has a significant effect on the conditions of formation of hydrate gas, which is greater than in benzene in reducing pressure and raising the temperature as described by [6].

In general, the addition of hydrocarbon components (benzene, and cyclohexane) to the solution leads to a decrease in pressure. By comparing benzene, and cyclohexane, cyclohexane was thermodynamically most stable hydrate promoter.

#### 4.2 Gas Hydrate Formation Visual Observations

The experiments were done in the isochoric pressure method. After the addition of water, the gas is injected (until it reaches the required pressure while ensuring the initial temperature stability). In the dissolution stage, The temperature decreases slowly and is accompanied by the dissolving of the gas in the water until it reaches a low dissolving stage and the pressure stabilizes in the nucleation stage. After the end of the nucleation stage and reaching the point of turbidity that recognized in the cell. The turbidity point was a significant sign for hydrate nucleation that is accompanied by formation.

The hydrate appeared in the form of a light layer and are accompanied by a significant reduction in pressure. The hydrate layer thickness is increasing and it grown gradually until it reaches a stage where the pressure drop as described by [6]. Hydrate formation was visually observed through the cell side as the (Figure.6).



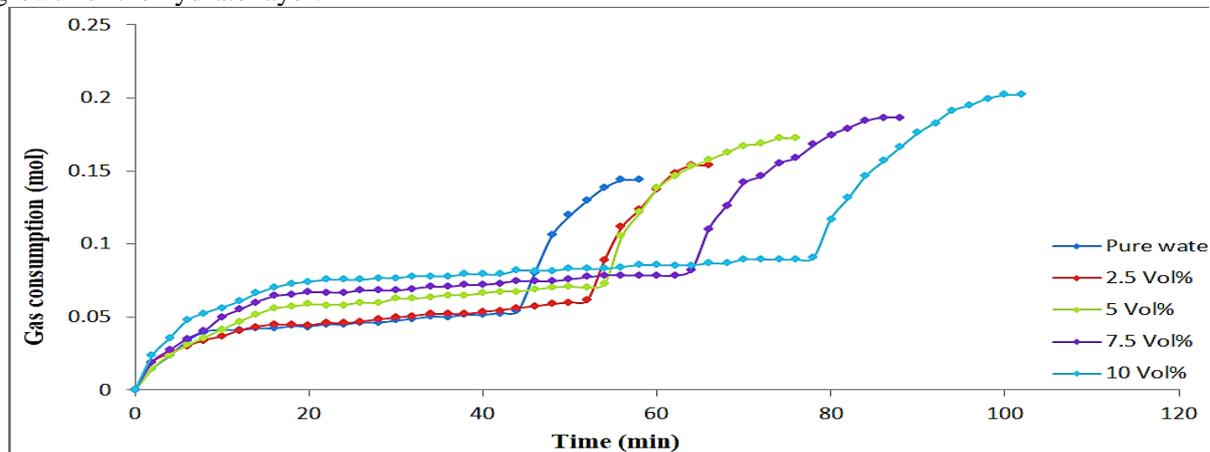
### 4.3 Kinetic Model Results

The suggested model mentioned in section 4 was used to show the result of the experimental and obtain the gas consumed, formation rate and other parameters of gas hydrate ternary system.

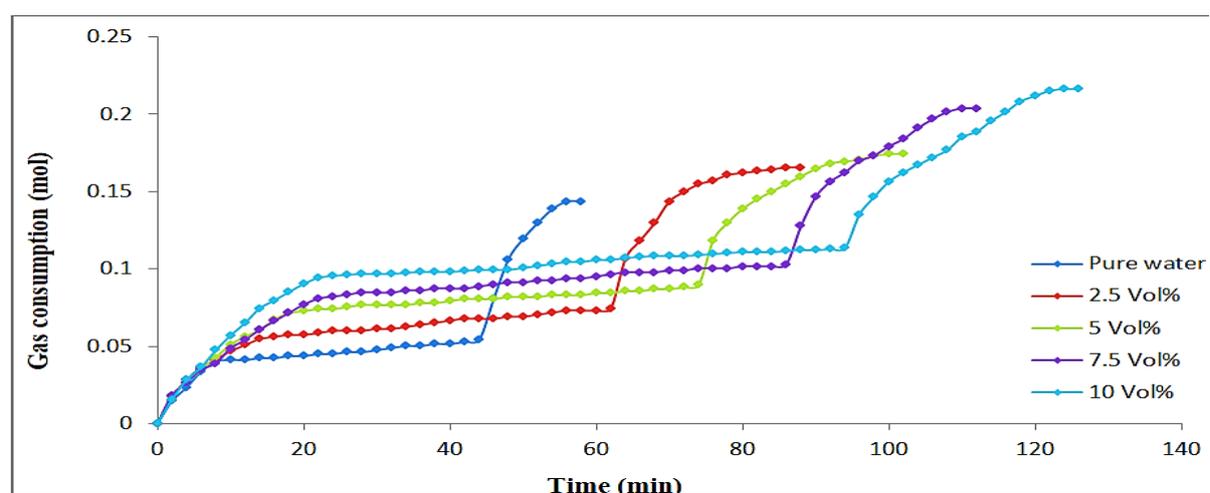
#### 4.3.1 Gas consumption

The gas feed is 0.2760 mole from eq.(1), the gas consumption was calculated at various concentrations of different promoters through the gas hydrate formation for water + R134a + promoter system. The effect of benzene and cyclohexane on gas consumption in the experiments are shown in (Figure.7) and (Figure.8) The gas consumed was increased slowly at the initial time and the moles of gas consumed increase with a drop in the pressure increase and temperature inside the cell due to the

growth of the hydrate layer. The gas consumed was increased slowly at the initial time and the moles of gas consumed increase with a drop pressure increase and the temperature inside the cell due to the growth of the hydrate layer.



**Figure 7.** The effect of benzene on R134a gas consumed versus time during the hydrate formation process for the pure water + refrigerant gas R-134a system.



**Figure 8.** The effect of cyclohexane on R134a gas consumed versus time during the hydrate formation process for the pure water + refrigerant gas R-134a system.

As shown in the plots, with the increase in concentration, the consumed gas raised with time because the promoter concentration has in effect on the number of water cages increase due to the effects of promoter in the solution.

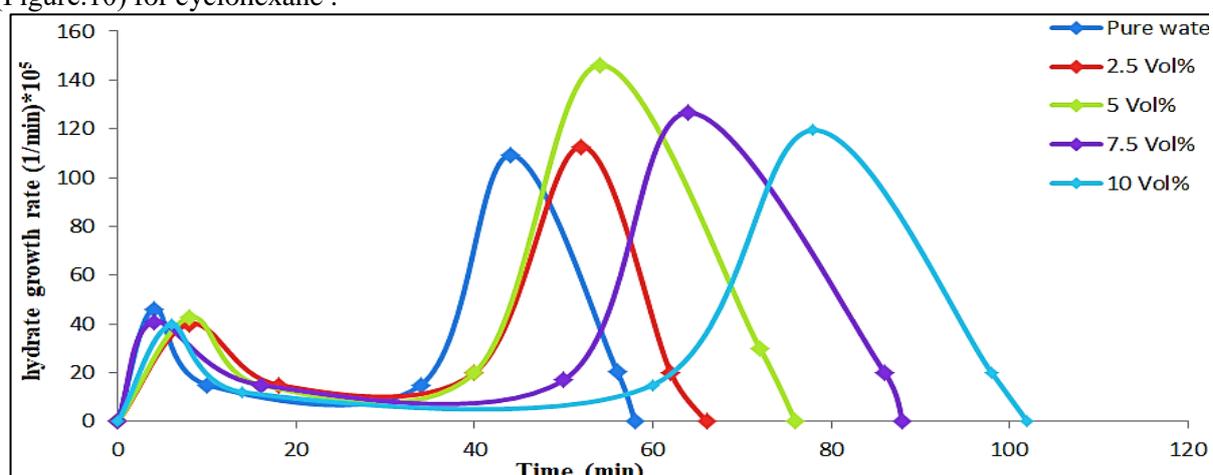
This result indicates that there is a higher driving force represented by the difference in the fugacity of gas phase that depended on pressure of formation of gas hydrate when concentrations is increased. During hydrate formation, the gas consumed enhancing with various concentrations of different promoters and gas consumed higher than in binary system as obtained by [15].

### 4.3.2 Growth rate of R134a hydrate formation

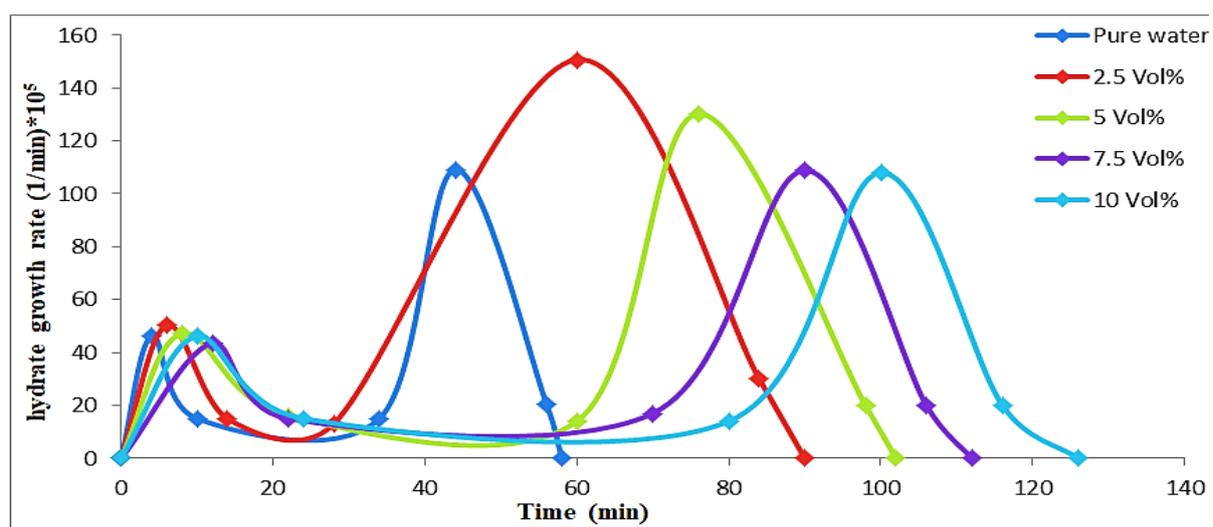
The rate of hydrate is mostly expressed as the molecules of R134a that are converted to hydrate. The growth rate during the growth period depended on various concentrations of promoters with constant initial pressure. The different promoters have a different influence on the growth of hydrate.

The growth rate in the binary and ternary system first increases gradually during the dissolving gas stage and then becomes semi-stable during the nucleation stage where the particles of hydrates begin to grow gradually until it reaches the formation point and start hydrate growth with an increase in pressure drop.

This is followed by a rapid decline in the value of the growth of hydrate rate and then return to rise again as a result of the dissolving of a new quantity of gas to replace that went to the top. The growth of hydrate equal zero due to stop hydrate formation that represented in (Figure.9) for benzene and (Figure.10) for cyclohexane .



**Figure 9.** The R134a hydrate growth rate for a ternary system of Benzene with different concentration against time.



**Figure 10.** The R134a hydrate growth rate for a ternary system of Cyclohexane with different concentration against time

As mentioned previously, the highest consumption of gas is achieved with the highest concentrations at 10 vol.% However, in calculating the hydrate growth rate, the value of the gas consumed will be divided by the time it takes to grow and the growth rate is inversely proportional to the time taken that shown in **Table.1**.

**Table.1.** The maximum hydrate growth rate for different promoters used in this study at different concentrations.

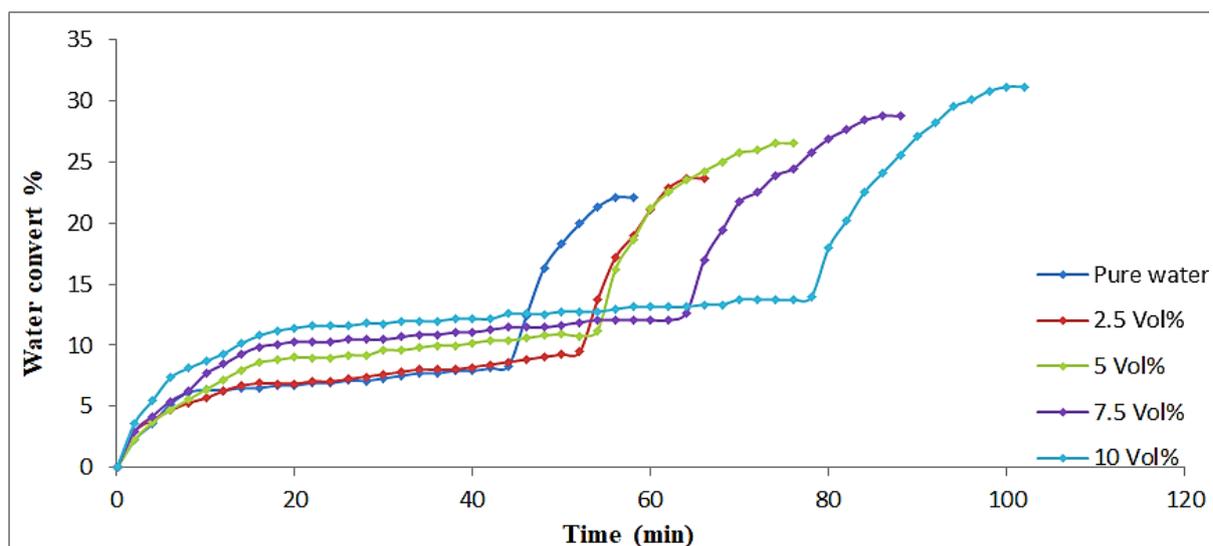
Promoters	Concentrations Vol.%	The growth of hydrate rate (1/min)*105
No promoter	-	109.2
Benzene	2.5	112.75
Benzene	5	146.07
Benzene	7.5	126.6
Benzene	10	119.42
Cyclohexane	2.5	150.73
Cyclohexane	5	130.23
Cyclohexane	7.5	108.82
Cyclohexane	10	107.9

The highest value is when the adding of benzene and lower than when adding cyclohexane because the drooping in pressure took a relatively long time that increases the driving force with time. It can be summarized that benzene gave the highest Growth rate at 5 vol.% and the lowest at 10 vol. %, cyclohexane gives the highest Growth rate at 2.5 vol.% and the lowest at 10 vol.%.

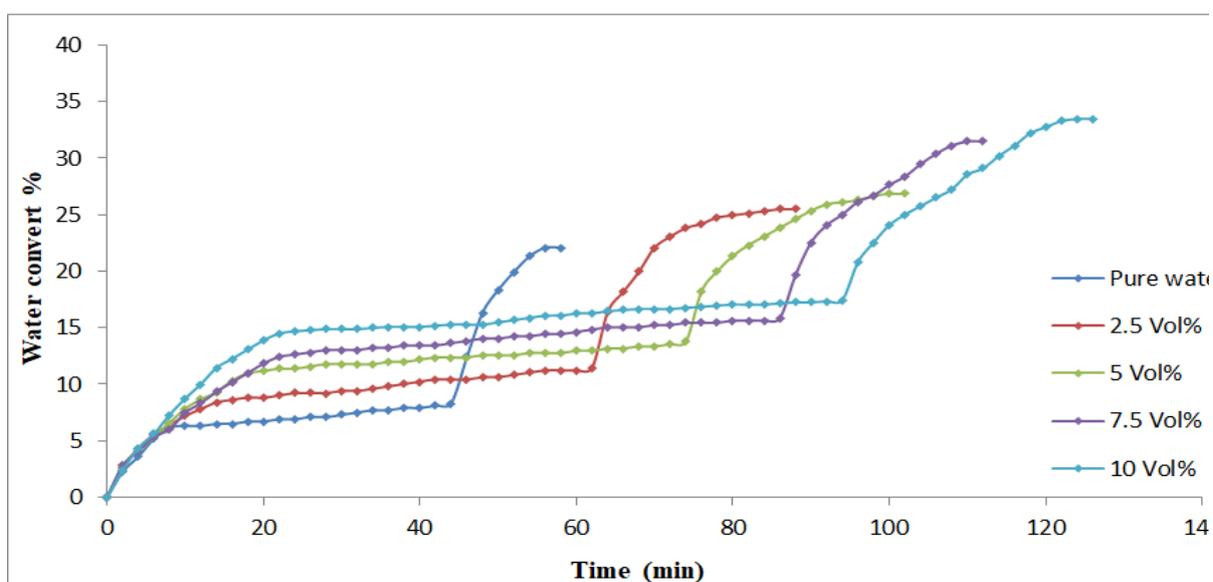
#### 4.3.3 The conversion of water to hydrate

The moles of water transform to hydrate during the hydrate growth process were calculated for the binary system and ternary system. For a different type of promoter, the water to hydrate conversion increase with increase the promoter concentration because of adding the promoter to solutions increase hydrate formation.

The ternary system in presence of promoters has the same behavior conversion of water to hydrate which was higher than the conversion of the binary system that is shown with benzene and cyclohexane in the (Figure.11) and (Figure.12).



**Figure 11.** Effect of Benzene on the water to hydrate conversion as a function of time for the ternary system.



**Figure 12.** Effect of Cyclohexane on the water to hydrate conversion as a function of time for the ternary system.

The water conversion increase because the higher pressure drop because depending on the pressures and driving forces those obtained by [7]. **Table.2** shows the maximum value of the water to hydrate conversion for a ternary system that was represented as a function of time for promoters at different concentrations for each type of promoter.

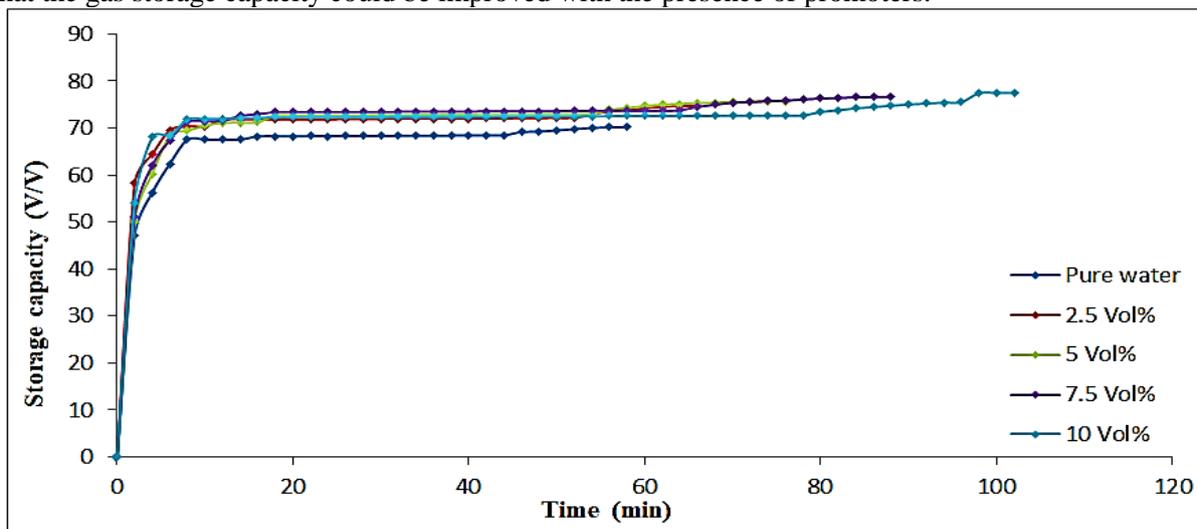
**Table.2** Maximum water conversion value for promoters at different concentrations.

Promoters	Concentrations	Water conversion%
No promoter	-	22.08
Benzene	2.5	23.63
Benzene	5	26.51
Benzene	7.5	28.75
Benzene	10	31.15
Cyclohexane	2.5	25.48
Cyclohexane	5	26.84
Cyclohexane	7.5	31.46
Cyclohexane	10	33.45

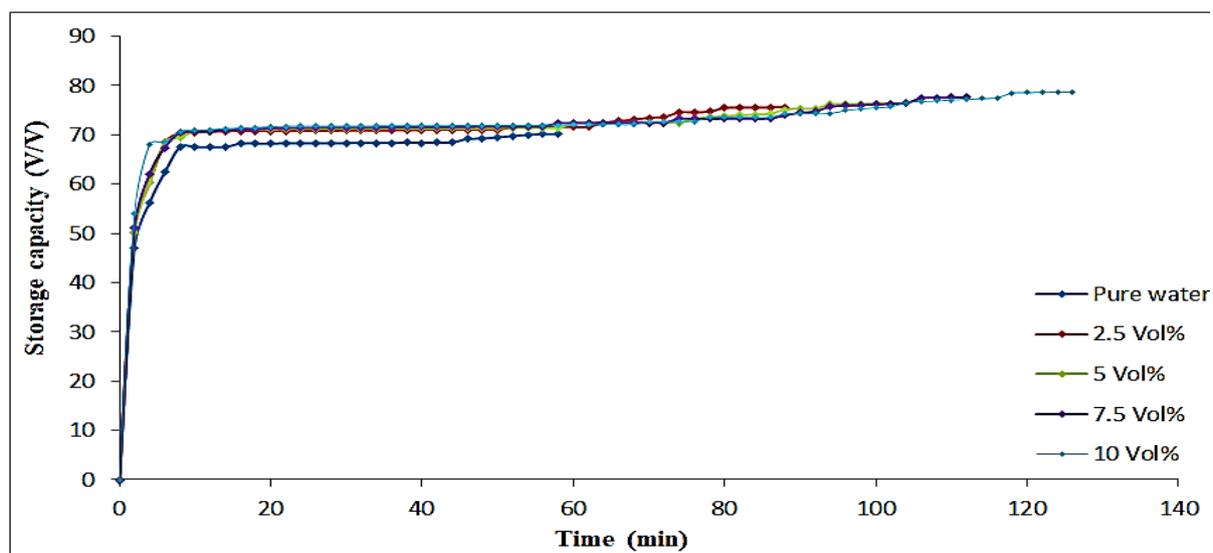
#### 4.3.4 The storage capacity

The storage capacity for the binary system consider as a function of time at the appropriate pressure and temperature. The promoters were added to improve the gas storage capacity in a quiescent system by increasing the pressure drop when adding to the water solution that leads to increases the final storage capacity of the gas hydrate compared to pure water.

Promoters increase the 134a solubility in water hydrates could be formed both at the interface between the gas and the liquid and in solutions. (Figure.13) for benzene and (Figure.14) for cyclohexane reveal that the gas storage capacity could be improved with the presence of promoters.



**Figure 13.** Effect of Benzene Storage Capacity during R134a hydrate growth at constant initial conditions (temperature and pressures).



**Figure 14.** Effect of Cyclohexane Storage Capacity during R134a hydrate growth at constant initial conditions (temperature and pressures).

The final storage capacity of R134a at different concentration of promoters is apparent in **Table.3**. To that end at each tested concentrations, the addition of promoter has effect on the final storage capacity of R134a hydrate. However, it is noticeable that the pressure drop is increased when adding the promoters to the water solution.

**Table.3** Final storage capacity value for different promoters used in this study with different concentrations.

Promoters	Concentrations (Vol.%)	Storage capacity (V/V)
No promoter	-	70.16
Benzene	2.5	74.66
Benzene	5	75.69
Benzene	7.5	76.59
Benzene	10	77.47
Cyclohexane	2.5	75.57
Cyclohexane	5	76.33
Cyclohexane	7.5	77.59
Cyclohexane	10	78.66

## 5. Conclusions

- R134a refrigerant gas was used to form hydrate in a binary system (water+ R134a) and ternary system (water +R134a+ promoter). Two types of the promoter were used in this study (Benzene and Cyclohexane) with different concentrations. The addition of a promoter to the system resulted in shift formation conditions data to high temperatures and low pressures.

- The results of the promoter on the consumed gas, rate of growth and water to hydrate conversion of was studied by kinetic hydrate formation depicted that when the concentration increased, the rate of hydrate formation or the moles of R134 consumed and the water conversion increased with increasing concentration. The promoter in the hydrate formation system slightly increases in the storage capacity with maximum value about (78.66) V/V.
- The best value achieved for R134 consumed is 0.2163 mol., the water conversion is 33.45% and storage capacity 78.66 V/V. All these values achieved with cyclohexane. The best value achieved for the growth rate of hydrate  $150 \times 10^{-5}$  1/min, with benzene.

### Acknowledgment

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