

Natural gas hydrate promotion capabilities of toluene sulfonic acid isomers

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The purpose of this study was to investigate the natural gas hydrate promotion capabilities of the hydrotrope Toluene Sulfonic Acid (TSA) isomers as an additive. The capabilities of TSA isomers were measured with different concentrations. The optimum additive concentration for hydrate formation was determined for the given pressure, temperature, mixing condition, and cooling time. The natural gas hydrate promotability of *para*-TSA was found to be 20% and 35% more than *meta*-TSA and *ortho*-TSA respectively at the optimum concentration. Beyond the optimum TSA concentration, the hydrate formation declined as the ice formation reduced the overall gas-to-water volume ratio in the hydrates

Keywords: natural gas hydrate, hydrotrope, toluene sulfonic acid.

INTRODUCTION

One of the research interests on natural gas in a commercial perspective is using of hydrates as a media for storage and transport. The idea of using hydrates as a gas storage medium existed since early 1940s¹ when its self-preservation, which allows hydrate to remain metastable at atmospheric pressure and a few degrees below the ice point. However, recently, natural gas hydrate has drawn much attention as a new means for natural gas storage and as an alternate for safe transport².

Hydrates have unique gas storage properties, as they can contain 180 volumes (standard temperature, pressure) of natural gas per volume of hydrate³ and could be stored at 258 K under atmospheric pressure for 15 days, retaining almost all the gas⁴. Storage of natural gas in the form of clathrate hydrates is of interest since hydrates can be produced under moderate conditions and can be stored at a typical temperature of 273 K under reasonable pressures of 1–2 MPa^{5,6}. In contrast, the conditions for conventional natural gas storage technologies are extreme, for example, the pressure of 20 MPa for compressed natural gas and temperature of 113 K for liquefied natural gas⁷. As well as in transport, it showed a big cost saving of 24% for the transport of natural gas in hydrates compared to liquefied natural gas⁸.

Not only, storage capacity appealing for industrial use of natural gas, as well as the process is appealing for safety reasons, slow release of natural gas from hydrates in case of storage tank rupture; flammable gases essentially encased in ice and relatively low storage pressures.

However, industrial applications of hydrate storage processes have been hindered by three problems, which affect the ability and economy of process scale up: slow formation rates, separating and packing hydrate particles for storage, and unreacted interstitial water as a large percentage of the hydrate mass.

Hydrates do not form immediately when water and natural gas are in contact at hydrate forming conditions. This process is occurring in three consecutive steps. Labile clusters form immediately (labile clusters) on dissolution of gas in water; they agglomerate by sharing faces, thus increasing disorder (agglomeration). The size of the cluster agglomerate reaches a critical value, growth begins (primary nucleation and growth)⁹.

Gas dissolution, formation of nuclei and growth of the new nucleus are mainly affected by pressure and temperature conditions of the system. In addition, agitating water increases the water–gas interfacial area and improves hydrate formation. Energy costs from stirring increase as slurry thickens. In fact, thickening slurry of the stirred may limit the hydrate mass in the water to as low as 5%^{10,11}.

The surfactants molecules help minimize mass transfer and kinetic difficulties during hydrate formation¹². This mechanism is applicable not only through surfactants but with ultrasonic waves¹³. When surfactants are added to a hydrate forming, the induction time (the period necessary for the appearance of the very first hydrate cluster of supernucleus size) required for hydrate formation decreases, and the hydrate formation rate increases^{14,15}. During the last two decades, several studies have been reported showing a significantly increased hydrate formation rate with adding surfactant molecules^{16–19}. The economics of synthetic natural gas hydrates as storage and transport medium critically depends on the gas volume stored per volume of hydrates. The purpose of the current study is to use a fundamental procedure to determine the peak concentration of the hydrotrope, Toluene Sulfonic Acid (TSA) isomers, for maximizing hydrate formation.

EXPERIMENTAL METHOD

Materials Used

The experiment materials in this work are listed in Table 1. The additives were weighted with the accuracy of ± 0.01 g on an electronic balance. Distilled water was used in all experiments. The composition of the natural gas is presented in Table 2.

Table 1. Materials used in this study

Component	Purity [%]	Supplier
<i>para</i> -TSA	98.5	Sigma-Aldrich
<i>meta</i> -TAS	98	Merck
<i>ortho</i> -TAS	98	Merck
Water	Distilled	–

Apparatus

Stainless steel sulfur combustion reactor with capacity of 424 cm³ and maximum pressure of 20 MPa was used

Table 2. Composition of the natural gas mixture used in this study

Component	Mol [%]
Methane	71.5
Ethane	11.0
Propane	6.5
n-Butane	1.9
iso-Butane	0.9
n-Pentane	0.4
iso-Pentane	0.4
Carbon Dioxide	4.0
Nitrogen	1.8
Hydrogen Sulfide	1.6
Total	100

for this experiment²⁰. The cell was 6 cm in internal diameter and 15 cm in height. Through a branched fitting a resistance temperature detector probe (RTD), placed on the top of the cell; allowing temperature measurement during the process. As well as a pressure transducer calibrated from 0–11 MPa was mounted on the branch fitting. The pressure relief valve was set to relieve at 11 MPa and was fitted on one end of the branch fitting.

Two internal diameter viewing tubes extended into the cell through two Female Nominal Pipe Thread (FNPT) ports. The short one allowed light input from a 150 W source sent by a fiber optics light guide; the long one enabled observing hydrate formation through a camera probe inserted in it. Both viewing tubes were sealed at one end with transparent sapphire windows pressure checked at 11 MPa.

The cell contents was mixed with a magnetic stirrer (9.5×38 mm magnetic stir bar) at the speed of 250 rpm. A cooling bath which could able to maintain the temperature with the accuracy of ± 0.01 K from the set point was also used. A gas booster system was used to compress the gases to the pressures required in this research^{21, 22}. The RTDs, pressure transducers and gas volume meter were all connected to a data acquisition system, which was inserted into the expansion slots of a computer. The schematic diagram of the experimental set-up is shown in Figure 1.

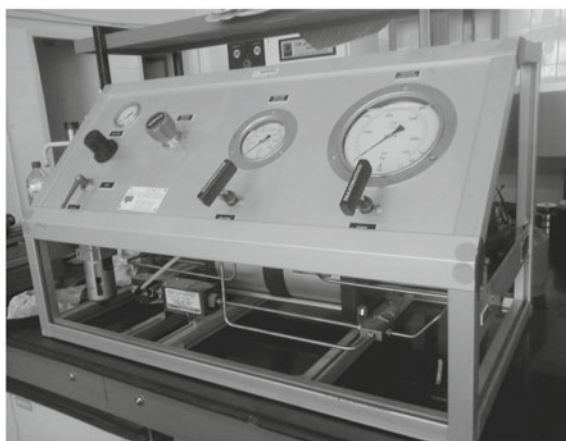
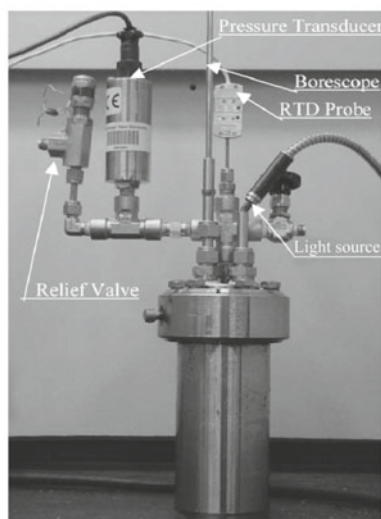
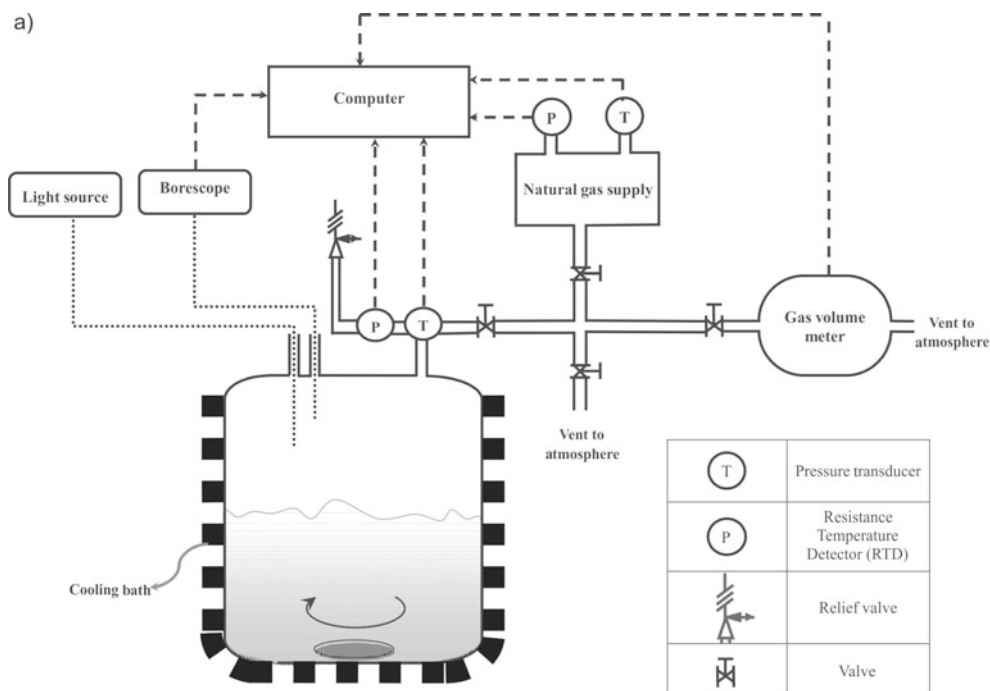


Figure 1. a) Schematic diagram of the experimental apparatus b) Hydrate formation reactor vessel c) Gas pressure booster

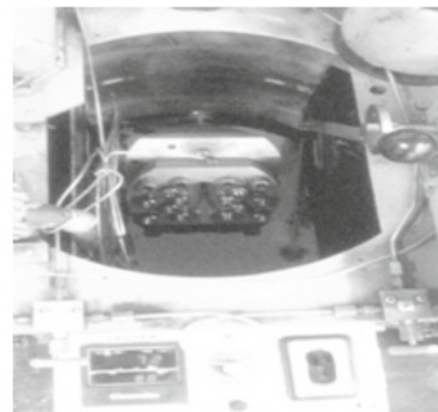
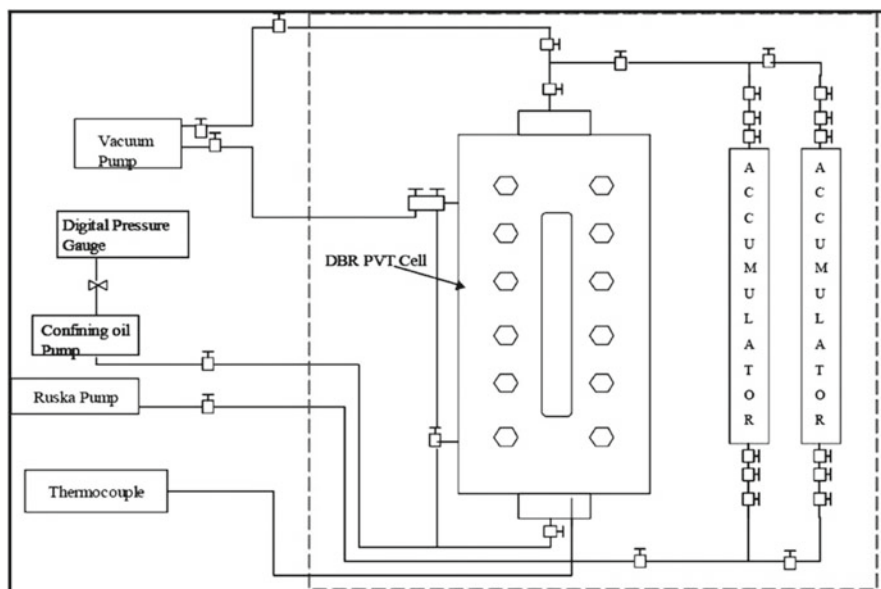


Figure 2. A schematic of experimental setup for PVT and hydrate formation experiments

Experimental Procedure

Natural gas dew points and hydrate formation curve

A High-Pressure High-Temperature (HPHT) the visual laboratory cell (Figure 2)²³ has been used to study the natural gas properties and the condition in which hydrates form. The HPHT cell has a 100 MPa maximum working pressure, from 266 to 422 K working temperature and a 100 cm³ total volume. The cell also has a transparent glass cylinder which allows the fluid to be observed. After dew point pressure tests, to perform the hydrate experiments, the high-pressure visual cell was thoroughly cleaned and evacuated before being filled with the sample. Then, the hydrocarbon fluid was introduced to the cell and meanwhile, to fix the pressure and temperature, the piston's position moved accordingly. A high pressure pump was then used to inject water into the cell. The visual capacity of the cell, allows the correct determination of the hydrate formations' conditions. During the experiment, the pressure was kept constant and the temperature was cooled down to pinpoint the conditions in which hydrate form with an acceptable accuracy.

Hydrate promotion capability

The liquid mixture (approximately 200 cm³ in each experiment of water + TSA isomers) was introduced in the cell and placed into a temperature bath set, about 5 K above the expected three-phase (H-L_w-V) equilibrium temperature.

Air was removed from the cell by a vacuum pump and natural gas purging²⁴. Subsequently, the cylinder was pressurized to the test pressure. The temperature was then gradually decreased and enough time was given to the system to reach equilibrium condition²⁵.

The cylinder was then depressurized to ambient pressure, one at a time, to remove the excess gas, formed during the process. The depressurizing procedure was carried out at maximum speed to minimize the hydrate dissociation and also to ensure the removal of the excess gas. Dissociating procedure was done using the isochoric temperature cycle method²⁶.

The cylinder temperature was gradually increased and set at 300 K for 10 min being connected to the gas volume meter while the gas pressure was just above atmospheric pressure. The gas released from the hydrates displaced the gas from the cylinder. Inaccuracies in gas volume measurement, due to the dissolved gas in water, were ignored during the measurements of gas volume²⁷. The gaseous volume is measured from the meter considered as the standard gas volume.

RESULTS AND DISCUSSION

Figure 3 shows the experimental dew points and the hydrate formation curve as well as predicted phase envelop, critical point (results of GERG-2008²⁸), and the pure water hydrate formation (result of Ameripour and Barrufet correlation²⁹) for the natural gas of given composition and test points.

Instead of using the method of volume of gas stored in a unit volume of hydrate which was proposed by Makogon³⁰, hydrate capacity was measured by the gas-to-water volume ratio in the formed hydrate³¹ which

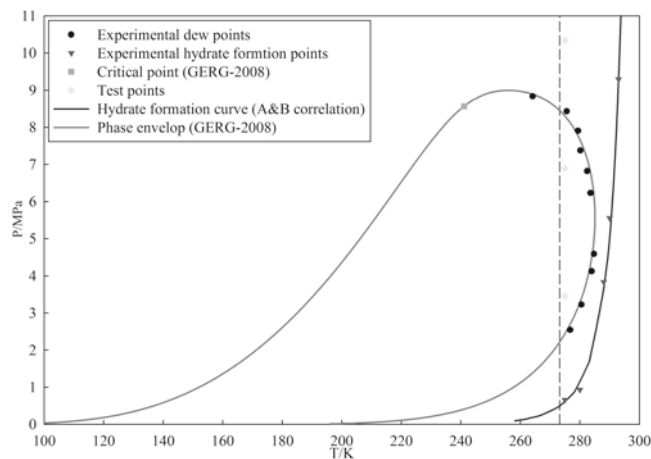


Figure 3. Experimental and predicted phase envelop, critical point [results of GERG-2008 (Kunz and Wagner, 2012)], and pure water hydrate formation curve [result of Ameripour and Barrufet correlation (Ameripour and Barrufet, 2009)] for the natural gas of given composition and test points

is more realistic. The tests carried on distilled water yielded small amount of gas even at higher pressures, as ice formation preceded hydrate formation.

Figure 4, 5 and 6 show the hydrate promotion capabilities of TSA isomers at three different test points. As it is obvious in these figures the natural gas hydrate storage capacity increases by increasing the pressure as well as the increase in hydrotrope concentration regarding the

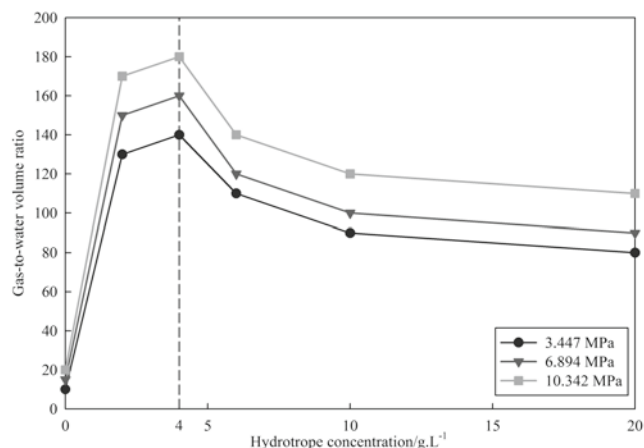


Figure 4. Effect of *para*-TSA concentration as a promoter on hydrate storage capacity (T/275 K)

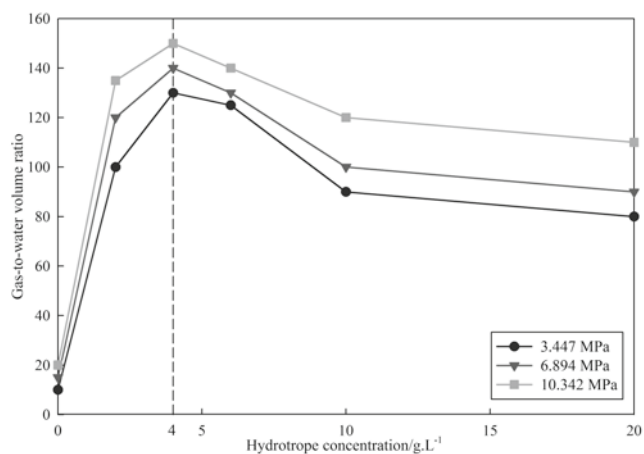


Figure 5. Effect of *meta*-TSA concentration as a promoter on hydrate storage capacity (T/275 K)

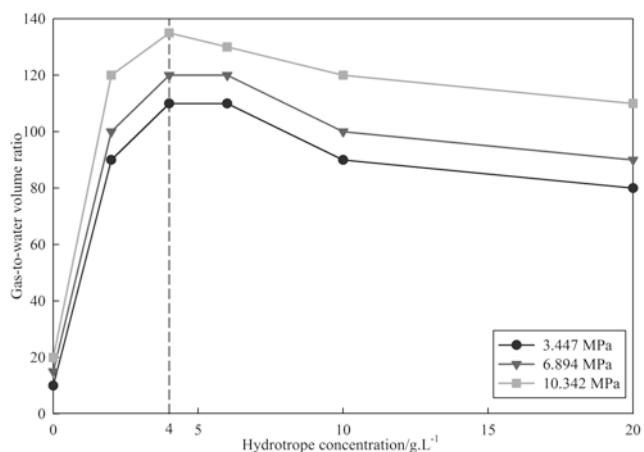


Figure 6. Effect of *ortho*-TSA concentration as a promoter on hydrate storage capacity (T/275 K)

increase in gas-to-water volume ratio. For all of pressure and TSA isomers there is a sharp increasing for storage capacity in hydrotrope concentration of 2 g/L.

At lower concentration, the surface active molecules are mainly present in the gas water contact and mainly affect the interface properties of the water rather than bulk properties of the solution, so the surface activity of such molecules increases the solubility of gas in water gas contact by higher magnitudes. This enables the hydrate to form in the interface more rapidly, giving shorter induction time. With regard to these figures the optimum additive concentration for hydrate formation at a given pressure, temperature, mixing condition, and the cooling times for all isomers were observed around 4 g/L that is the inhibitor effect of higher concentrations on hydrates observed by Rovetto et al.³².

Figures 7, 8 and 9 show the hydrate storage capacities promotion of TSA isomers at a certain pressure. It is clear in these figures that the surface activity of *para*-TSA is 20% and 35% more than *meta*-TSA and *ortho*-TSA respectively for the concentrations of 4 g/L. The promoting effect of TSA isomers depends on their arrangement in the surface film of gas water contact and their ability to form a suitable base for nonpolar gas dissolution. As far as *para*-TSA can fill the water gas contact film therefore, nonpolar gas molecules such as methane and ethane can be dissolved in surface layer

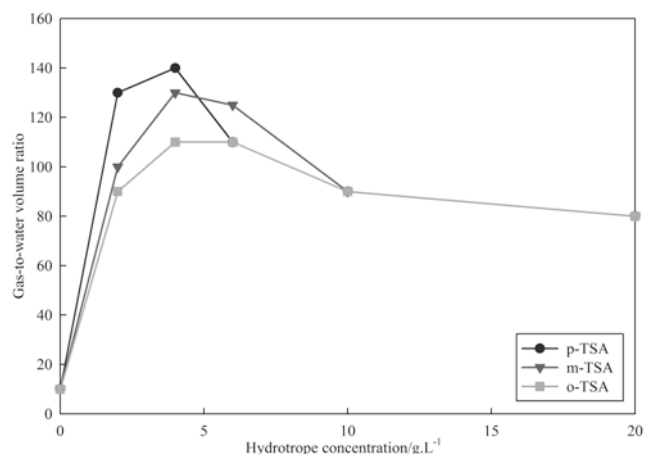


Figure 7. Effects of TSA isomers on the hydrate storage capacity (T/275 K; P/3.447 MPa).

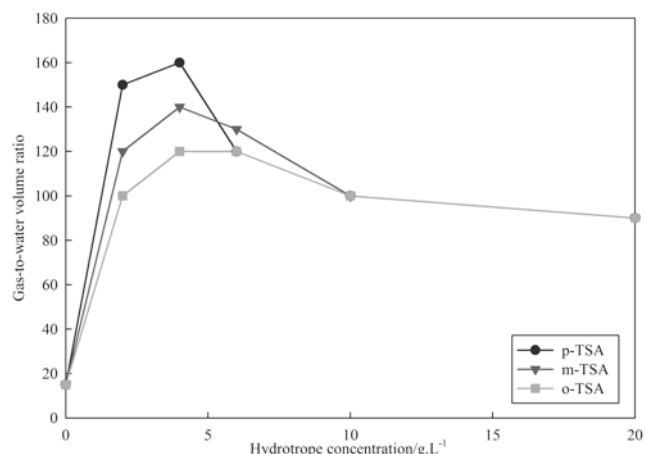


Figure 8. Effects of TSA isomers on the hydrate storage capacity (T/275 K; P/6.894 MPa)

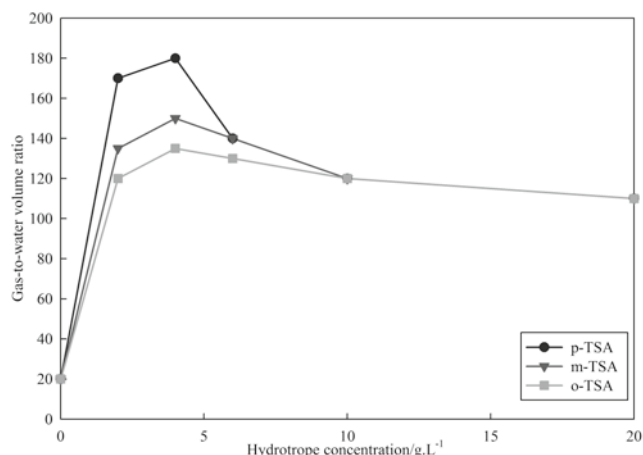


Figure 9. Effects of TSA isomers on the hydrate storage capacity (T/275 K; P/10.342 MPa)

as trapping in its network³³. Beyond the optimum TSA concentration, the hydrate storage capacity declines and by increasing its amount to 10 g/L its promotion capabilities is lower than 2 g/L.

CONCLUSIONS

Hydrate promotion capabilities of Toluene Sulfonic Acid (TSA) isomers as a hydrotrope additive was investigated. The optimum additive concentration for hydrate formation at a given pressure and temperature, mixing condition, and cooling times for all isomers was observed to be 4 g/L. Beyond the optimum TSA concentration, the hydrate formation declined as ice formation reduced the overall gas-to-water volume ratio in the hydrates. The surface activity of *para*-TSA at the optimum point was 20% and 35% more than *meta*-TSA and *ortho*-TSA respectively, thus it is suggested to be the best promoter.

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