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Anti-agglomeration of natural gas hydrates in liquid condensate and crude oil at constant pressure conditions



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HIGHLIGHTS

• Anti-agglomeration in a wide water-cut range in real petroleum fluids is demonstrated.

• The effect of CO₂ in the petroleum fluid on anti-agglomeration is compensated by LiOH.

• The high gas volume to liquid volume (oil and water) ratio is demonstrated to require higher dosage of anti-agglomerant.

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ABSTRACT

An effective anti-agglomerant (AA) can reduce capillary force between hydrate particles to prevent them from sticking together, therefore preventing the blockage in pipelines. In recent studies, we have reported an AA formulation which shows high effectiveness at low dosage in methane/natural gas hydrates over the entire water-cut range. All our past work, however, was conducted in a closed rocking cell system with *n*-octane as the hydrocarbon liquid phase. In this work, we investigate the effectiveness of an improved formulation in various systems at constant high pressure (~100 bar natural gas) and high cooling rate (-8 °C/h) over the water-cut range of 30–80%. Condensate liquid and crude oil are used as the hydrocarbon liquid phase. Because of the impact of the acidic gases in natural gas, a small amount of lithium hydroxide is included in the new formulation. Lithium hydroxide is more efficient than sodium hydroxide which was used in our previous studies. The dosage is reduced by ~40% by mass. We demonstrate the effectiveness of improved AA formulation in an extensive set of measurements. The effect of salinity on the AA effectiveness is also investigated. It is found that increasing salinity can decrease the dosage of base chemical in the formulation significantly.

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1. Introduction

Gas hydrates, also known as clathrate hydrates, are ice-like crystalline solids which are formed by host water molecules around small guest gas molecules, such as methane, ethane, propane, carbon dioxide, nitrogen and hydrogen sulfide, at relatively low temperature and elevated pressure conditions [1–3]. Formation of gas hydrates is a severe operational problem in gas and oil production and transportation. Gas hydrates deposit on pipe walls and agglomerate to form large plugs, which may result in

blockages in pipelines and cause serious safety and environmental consequences.

Besides expensive and sometimes ineffective engineering means, such as removal of water prior to pipeline transportation and maintaining the pressure and temperature conditions outside the hydrate formation region, gas hydrate risks can be also reduced/eliminated by injecting hydrate inhibitors into pipelines [4]. There are three kinds of hydrate inhibitors available for gas and oil industries to manage gas hydrate risks. Thermodynamic inhibitors (TIs), such as methanol, ethylene glycol and triethylene glycol, can shift the equilibrium hydrate formation to a lower temperature and a higher pressure condition. However, in order to be effective, these traditional hydrate inhibitors have to be injected up to 100% of the weight of water. It is also known that TIs are not environmentally friendly [5]. Kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs), which are known as low dosage hydrate inhibitors (LDHIs), become more attractive in offshore





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gas and oil production and transportation. LDHIs are dosed at a concentration of up to 3.0 wt.% based on the aqueous phase. KHIs are usually water-soluble polymers, which can significantly decrease the gas hydrate formation rate and allow to produce/-transport gas or/and oil fluid in a certain period of time [2]. The main drawback of KHIs is that they lose the effectiveness when the subcooling is over ~12 °C [4].

Unlike KHIs, AAs are effective at high subcooling. AAs may not slow down the hydrate growth, but they can prevent hydrate particles from sticking together to form large hydrate pieces, therefore holding back the blockage in pipelines. Quaternary ammonium salts (QAs), which were first developed by Shell in early 1990s, are the most well-known AAs [6]. Chua and Kelland have reported systematic study of gas hydrate anti-agglomerant performance of single-tail quaternary tributylammonium bromides at 33% watercut (ratio of aqueous phase to total liquid phase, volume basis) [7]. Besides OAs, successful anti-agglomerant performance of commercial additives and new AAs have been published by several research groups [8–13]. However, most of AAs are only effective at low water-cut (e.g., less than 30%). Gao reported a proprietary Champion Technologies AA product, which can be effective at high water-cut (up to 80%) with 4 wt.% NaCl and 15 wt.% methanol or 7 + wt.% NaCl [4].

Recently, our research group has reported the performance of a new AA synthetized by Lubrizol Corporation. We have demonstrated the effectiveness of newly developed AA formulation in methane hydrate over the entire water-cut range in the closed system by a sapphire rocking cell instrument, and proposed a new mechanism different from the well-known water-in-oil emulsion theory [14]. However, it is found that the AA loses effectiveness in natural gas which contains appreciable amounts of acidic gases, such as CO₂ and H₂S. To address the problem, we introduced NaOH to the new formulation to neutralize the effect of CO_2 [15]. We have reported hydrate powder formation in the antiagglomeration of natural gas hydrates at high water-cut and high hydrate volume fractions [16]. The measurement of hydrate particle sizes by the focus beam reflectance measurement has been conducted. It is found that our AA formulation can reduce hydrate particle size significantly and eliminates large particles in an autoclave reactor [17].

All our published work was conducted in a closed system with *n*-octane as the oil phase, which may be simpler than the real situation in the gas and oil production. In this work, we investigate the effectiveness of our improved AA formulation in more challenging conditions which may be close to the conditions of offshore explorations in deeper and colder waters [18]. Experiments are conducted under constant high pressure (~100 bar natural gas) and high cooling rate $(-8 \circ C/h)$ over the water-cut range of 30-80% in a rocking cell instrument. Condensate liquid and crude oil are used as the hydrocarbon liquid phase for the first time in the tests with the new AA, and deionized (DI) water and brine (NaCl in the range of 20,000-80,000 TDS (total dissolved solids)) as the aqueous phase. Because of the effect of acidic gases in natural gas on the AA performance [15], mainly CO₂ in this study, a small amount of LiOH is included in the new formulation. By using LiOH in this work, instead of NaOH which we have used in the past [15], the dosage of base chemical in the formulation is reduced

by \sim 40% (mass basis). The new formulation is applied in various gas/brine/hydrocarbon liquid systems, and the effectiveness is judged by visual observations and the ball running time in rocking cells. We demonstrate the effectiveness of the improved AA formulation in the various testing systems. We also find that the increase in salt concentration in the aqueous phase can increase AA performance.

2. Experimental section

2.1. Materials

The AA used in this study is synthetized by Lubrizol Corporation. It contains 80-89% cocamidopropyl dimethylamine (C₁₇H₃₆N₂O), known as the effective component, 5–10% glycerin, small amount of free amine and water. Fig. 1 shows the chemical structure of cocamidopropyl dimethylamine. Condensate liquid (OS312464) and crude oil (OS312462) used as oil phases in the tests are supplied by Lubrizol Corporation. Condensate liquid has density of 0.726 g/ml and viscosity of 0.85 cP at 25 °C; it is slightly acidic. pH decreases from 7.2 to 6.9 when 2 mL of condensate liquid is added into 10 mL DI water. The density and viscosity of crude oil are 0.814 g/ml and 5.9 cP at 25 °C, respectively. Crude oil is more acidic than condensate liquid. pH decreases from 7.2 to 6.0 when 2 mL crude oil is added into 10 mL DI water. The composition of synthetic natural gas (Praxair Distribution Inc.) used in this study is shown in Table 1. Salinity of aqueous phase is controlled by adding NaCl (99.5%, Sigma-Aldrich). Base chemicals, such as NaOH (98.5%, Acros Organics) and LiOH (98%, Acros Organics), are used to improve the performance of AA.

2.2. Experimental set-up

The experiments are conducted in a high pressure sapphire rocking cell equipment (PSL Systemtechnik, Germany) shown in Fig. 2 [14–16]. Each cell has a volume of 20 mL equipped with a stainless steel ball and two sensor positions which record the ball running time. The diameter of the running ball is around 0.4 in., and the inner diameter of cell is around 0.5 in. When the cells are rocking, the balls provide agitation. In each test, the cells are filled with various amounts of aqueous solution, condensate liquid/crude oil and natural gas. The water bath is filled before the cells, which contain liquids, are pressurized with natural gas to the desired pressure of around 100 bar. During the tests, additional gas is added into the cells from time to time to keep the pressure in the range of 95–105 bar. The rocking frequency is set to 15 times/ min at an angle of \sim 45°. The bath temperature, cell pressure and ball running time are recorded during the experiments. Fig. 3 shows an example of the bath temperature and cell pressure profiles.

At the beginning of each experiment, the testing cells are rocked at 20 °C for half an hour to reach equilibrium. The approximate equilibrium hydrate formation temperature based on hydrate dissociation in the tests is about 1-2 °C below the starting temperature. Then the water bath is cooled from 20 °C down to 4 °C at a cooling rate of -8 °C/h, while the cells are being



Fig. 1. Chemical structure of the effective component in the anti-agglomerant.

rocked. They are then kept at 4 °C up to 24 h before the temperature ramps back to the initial temperature. After each experiment, the pH of aqueous phase is measured by Oakton Waterproof pHTestr 30 (Eutech Instruments)/pH paper (Hydrion, range of 1–12).

Gao has reported Green Canyon gas hydrate (containing 87.2 mol% methane, 7.6 mol% ethane, 3.1 mol% propane and small

 Table 1

 Composition of the synthetic natural gas used in this work.

Component	Concentration (mol%)
Methane	79.294
Ethane	10.8
Propane	4.59
Butane	1.10
Isobutane	0.606
<i>n</i> -Pentane	0.200
Isopentane	0.200
Nitrogen	1.81
Carbon dioxide	1.40



Fig. 2. Schematic diagram of sapphire rocking cell equipment for gas hydrate tests.



Fig. 3. Typical batch temperature and cell pressure profiles of an open system test.

amount of other gases) phase diagrams for different salinities. With 4 wt.% NaCl, the hydrate equilibrium temperature for 100 bar Green Canyon gas is around 18.8 °C. Once the salt concentration increases to 7 wt.%, the hydrate equilibrium temperature decreases to 17.2 °C [4]. Compared with Green Canyon gas, the synthetic natural gas used in this study is richer in ethane and propane (Table 1), and may have a higher hydrate equilibrium temperature but have not measured hydrate equilibrium temperature. The effect of salt concentration on equilibrium hydrate formation temperature in our measurements is about the same as in Gao's work. Considering that we have performed our AA experiments at 4 °C, the thermodynamic effect from NaCl, and other additives does not change the hydrate driving force substantially.

3. Results and discussion

Effectiveness of AA at various testing conditions is judged by visual observations and ball running time. Sharp pressure drop in cell pressure profile indicates hydrate formation. In this work the natural gas is not continually injected to the rocking cells during the experiments. As a result the pressure in the cells slowly decreases because of the system temperature decrease before the start of hydrate formation. However, to keep the pressure constant we inject the gas intermittently. A long ball running time implies high viscosity of the slurry in the cell. Figs. 4 and 5 show the examples. Besides "No" and "Yes", "Yes^p" is also used to evaluate the AA performance. "No" means hard plug by hydrates. The ball is trapped by hydrates, and cannot move. "Yes" implies a clear pass. The ball can move freely in the hydrate slurry. "Yes^p" indicates possible pass with deposition of hydrate particles at the end of cell or on the wall. If a high shearing force is applied, the slurry can move without plugging the tube. In some experiments, we find that the steel ball is temporally trapped by the deposit of hydrate particles at the end of cell during cooling. Once the temperature reduces further, the deposit becomes loose and the ball can move again in the hydrate slurry. The formation of slurry demonstrates the repulsion between particles. At lower temperature, the adhesion between particles becomes weaker due to a thinner water film on the hydrate surface [19]. However, if hydrate volume fraction is high, there is not enough fluid to carry particles. The friction between particles may stop the ball.



Fig. 4. The cell pressure and ball running time profiles (test in red line: pass; test in blue line: fail). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Visual observation of AA effectiveness.

3.1. Base effect

The pH affects the AA performance, and a base chemical is introduced into the formulation to neutralize the effect of acid gases (e.g. CO_2 in natural gas) in the system. CO_2 in the natural gas lowers the pH resulting in serious foaming without base chemical. Low pH also changes the surfactant interaction with hydrates [15]. The testing fluids in this work have two acid sources: CO_2 in the natural gas and acidic components in the condensate liquid and crude oil. It has been demonstrated that the addition of NaOH can solve the problem [15]. However, a high dosage (sometimes more than 4 wt.% NaOH) is required. In this study, the use of LiOH in place of NaOH is investigated in the AA/base/brine/hydrocarbon liquid/natural gas system. The base chemicals (e.g., NaOH and LiOH) in the formulation not only increase the AA performance, but also work as neutralizing inhibitors, a type of corrosion inhibitors. Neutralizing inhibitors can reduce corrosion rate by removing H^+ ions in the aqueous phase (well-known example is CO_2 corrosion in gas and oil pipelines) [20].

Both LiOH (M_W = 24 g/mol) and NaOH (M_W = 40 g/mol) are strong bases, but LiOH has much lower molecular weight. Theoretically, the required LiOH dosage (mass concentration) is only 60% of the dosage of NaOH. With NaOH, anti-agglomeration at 80% water-cut is seen at 4.0 wt.% of NaOH in the aqueous phase at constant pressure of 100 bar, -8 °C/h cooling rate and 0.5 wt.% of AA, and 4 wt.% of NaCl. Using LiOH instead of NaOH, only 2.5 wt.% of LiOH is required in the aqueous phase under the same conditions. These experimental results match theoretical value (2.5/4 = 0.625 \approx 60%). The test conditions and results with two base chemicals are shown in Table 2.

3.1.1. Liquid condensate tests

The experiment is designed to obtain the minimum working dosages of AA, NaCl and base chemical under various experimental conditions. Several experiments are conducted in duplication to confirm the reproducibility. In all duplicate tests we observed the same results for AA effectiveness as well as the effect of the base. We first investigate the effect of gas volume in the cell on minimum working dosages of AA, NaCl and base chemical. Table 3 shows the minimal dosages of AA and LiOH at different amounts of the aqueous and oil phase. There is significant change in the volume of the gas phase, from 10 (50 volume%) to 18 mL (90 volume%). The amount of total liquid(s) in the cell should be in the range of 2–10 mL for accurate measurements. Water-cut

and salinity are fixed at 80% and 4 wt.% NaCl, respectively. Higher volume of natural gas in the rocking cell requires higher concentrations of AA and LiOH in the aqueous phase. When the volume of natural gas is 10 mL (50 volume%) in the testing cell, it needs only 0.2 wt.% of AA and 1 wt.% of LiOH. When the volume of natural gas increases to 15 mL (75 volume%), the minimal required dosages of AA and LiOH are 0.5 wt.% and 2 wt.%, respectively. Once the volume of natural gas increases to 16.25 mL (81.25 volume%), it requires 0.5 wt.% of AA and 2.5 wt.% of LiOH to avoid plugging. With 90 volume% (18 mL) of natural gas, the require amounts are 0.5 wt.% of AA and 5 wt.% of LiOH. It seems that with high volume of natural gas in the rocking cell the anti-agglomeration becomes more challenging. However, considering the dosage of LiOH in mass instead of wt.%, the consumed amount of LiOH (wt.% × volume of aqueous phase) does not change much in different tests.

Table 4 shows the test conditions and results at different watercuts under the fixed total liquid volume. Salinity is 4 wt.% NaCl. When the volume of natural gas is fixed, lower water-cut requires higher concentrations of AA and/or base in the aqueous phase. For example, when the volume of natural gas is 15 mL, the system requires 0.5 wt.% of AA and 2 wt.% of LiOH at 80% water-cut. Once water-cut decrease to 30%, it needs 0.5 wt.% of AA and 4 wt.% of LiOH. However, the required amount of LiOH in mass decreases at 30% water-cut.

Salt ions may decrease AA efficiency due to the competition of adsorption on hydrate particle surface between AA molecules and ions in our previous work [11]. On the other hand, salt has thermodynamic inhibiting effect by lowering the chemical potential of water [4,21-24]. Salt can change the bulk properties of aqueous phase. For example, around five water molecules occupy the inner hydration shell of the Na⁺ ion [25]. Once the water molecules orient themselves towards Na⁺ ions, they may not participate in hydrate formation. Cl⁻ ions can also affect water molecule's orientation in the aqueous phase [26]. Therefore, with salts, hydrate content in the mixture is lower. Lower hydrate content results in lower viscosity and lower plugging risk. Moreover, the addition of salt to the aqueous phase can decrease CO₂ solubility [27]. In this study, we observe that salts can lower the minimum dosage of base chemical in the AA/base/brine/hydrocarbon liquid/natural gas system. When the brine concentration is increased from 0 to 8 wt.%, the required LiOH dosage decreases from 3 wt.% to 2 wt.% at a fixed AA dosage of 0.5 wt.%. In these tests water-cut is 80%, and natural gas volume is 15 mL. Increasing salinity decreases CO₂ solubility,

Table 2

Results of condensate liquid with different base chemicals. $P = 100$ k	oar
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Aqueous (mL)	Condensate (mL)	Water-cut (%)	NaCl (wt.%)	AA (wt.%)	NaOH (wt.%)	Final pH	Effectiveness
3 3	0.75 0.75	80 80	4 4	0.5 0.5	3.5 4	11.1 11.4	No Yes ^p
Aqueous (mL)	Condensate (mL)	Water-cut (%)	NaCl (wt.%)	AA (wt.%)	LiOH (wt.%)	Final pH	Effectiveness

Table 3Results of condensate liquid at different gas volumes. P = 100 bar.

Aqueous (mL)	Condensate (mL)	Water-cut (%)	NaCl (wt.%)	AA (wt.%)	LiOH (wt.%)	Final pH	Effectiveness
8	2	80	4	0.2	1	10.3	Yes ^p
4	1	80	4	0.5	2	11.1	Yes ^p
3	0.75	80	4	0.5	2.5	11.5	Yes ^p
1.6	0.4	80	4	0.5	5	Over 12	Yes ^p

Table 4

Results of condensate liquid at different water-cuts. P = 100 bar.

Aqueous (mL)	Condensate (mL)	Water-cut (%)	NaCl (wt.%)	AA (wt.%)	LiOH (wt.%)	Final pH	Effectiveness
4	1	80	4	0.5	2	11.1	Yes ^p
1.5	3.5	30	4	0.5	4	Over 12	Yes ^p
1.6	0.4	80	4	0.5	5	Over 12	Yes ^p
1	1	50	4	0.5	5	Over 12	No
1	1	50	4	0.5	7	Over 12	No
1	1	50	4	1	6	Over 12	Yes ^p

Table 5

Results of condensate liquid at different salt concentrations. P = 100 bar.

Aqueous (mL)	Condensate (mL)	Water-cut (%)	NaCl (wt.%)	AA (wt.%)	LiOH (wt.%)	Final pH	Effectiveness
4	1	80	0	0.5	3	11.8	Yes ^p
4	1	80	2	0.5	2.5	11.6	Yes ^p
4	1	80	4	0.5	2	11.1	Yes ^p
4	1	80	8	0.5	2	10.4	Yes



Fig. 6. Proposed effect of natural surfactants in crude oil on decrease of AA effectiveness.

so less amount of base chemical is needed to neutralize the effect of acidic gas (CO_2) in the system at higher salinity. Table 5 shows the test conditions and results at different salinities.

3.2. Crude oil tests

Compared to condensate liquid, crude oil has generally higher viscosity, and it is more acidic. Crude oil also contains some natural surfactants, such as asphaltenes, which may compete with the AA at the surface of hydrate particles resulting in lowering the effectiveness of AA. Fig. 6 shows the possible effect of natural surfactants in crude oil on the AA performance. These properties make the anti-agglomeration in crude oil/natural gas system more challenging, and the system requires higher dosages of AA and base chemical. Unlike condensate liquid tests, the volume of aqueous solution is fixed at 10 mL in the crude oil tests. In oil production and transportation, the volume of high pressure gas phase in the pipelines is mostly less than 50 volume%.

Experiments are conducted at 80% and 30% water-cut. Tests were performed in the closed system (constant volume of natural gas) before moving to an open system (constant pressure of natural gas). The AA dosage is fixed at 1 wt.% in the aqueous phase in the open system tests. The constant pressure test conditions and results are shown in Table 6 (80% water-cut) and Table 7 (30% water-cut).

Salts increase the effectiveness of AA in the crude oil tests, the same as in the condensate liquid tests. For example, in Table 6, with 8 wt.% of NaCl in the aqueous phase, crude oil/natural gas system only requires 1 wt.% of AA and 1 wt.% of LiOH; with 4 wt.% of NaCl in the aqueous phase, crude oil/natural gas system requires 1 wt.% of AA and 2.5 wt.% of LiOH; when NaCl concentration decrease to 2 wt.% in the aqueous phase, the system needs 1 wt.% of AA and 3 wt.% of LiOH; without salt in the aqueous phase, the system needs 1 wt.% of AA and 3.5 wt.% of LiOH. In the case of crude oil production and transportation, when water is coproduced with oil, generally the salinity is high. Salinity can be 15 wt.%, or

1	9	2	

Table 6		
Results of cru	ide oil at 80% wat	er-cut. <i>P</i> = 100 bar.

Aqueous (mL)	Crude oil (mL)	Water-cut (%)	NaCl (wt.%)	AA (wt.%)	LiOH (wt.%)	Final pH	Effectiveness
8	2	80	0	1	3.5	11.2	Yes ^p
8	2	80	0	1	4	11.5	Yes
8	2	80	2	1	3	11.0	Yes ^p
8	2	80	4	1	2.5	10.8	Yes ^p
8	2	80	4	1	3	11.0	Yes
8	2	80	8	1	1	10.1	Yes ^p

Table 7

Results of crude oil at 30% water-cut. P = 100 bar.

Aqueous (mL)	Crude oil (mL)	Water-cut (%)	NaCl (wt.%)	AA (wt.%)	LiOH (wt.%)	Final pH	Effectiveness
3	7	30	0	1	1.5	10.5	Yes ^p
3	7	30	0	1	2	10.7	Yes
3	7	30	2	1	1.5	10.0	Yes
3	7	30	4	1	1	9.6	Yes
3	7	30	8	1	1	9.1	Yes

higher; the combination of crude oil and brine may not require high concentration of LiOH.

At lower water-cut, the dosage of LiOH may decrease significantly compared to 80% water-cut case (Table 7), especially when salinity is low (less than 4 wt.% of NaCl). For example, at 30% water-cut with 4 wt.% of NaCl, the system only requires 1 wt.% of LiOH, on the other hand at 80% water-cut with 4 wt.% of NaCl, the system needs 2.5 wt.% of LiOH. With 2 wt.% of NaCl, the system only requires 1.5 wt.% of LiOH at 30% water-cut, however at 80% water-cut the system may need 3 wt.% of LiOH. Without salt, the system requires 1.5 wt.% of LiOH at 30% water-cut, however at 80% water-cut the system needs 3.5 wt.% of LiOH.

In the past, we have discussed that the final pH should be higher than 9 to avoid plugging in the closed system if gas phase contains acidic gases [15]. However, in the open system experiments with condensate liquid and crude oil, we find that the plugging may occur with a final pH higher than 9. When the volume fraction of natural gas is large and the volume fraction of the aqueous phase is small, in some cases the finale pH should be higher than 12 to prevent the blockage. The continuous injecting of the acidic gas (e.g., CO₂ in the natural gas) during the experiments requires higher concentration of base chemical to neutralize the system.

4. Conclusions

We have demonstrated the effectiveness of improved AA formulation in various AA/base/salt/condensate liquid or crude oil/natural gas systems. The following specific conclusions can be drawn from this work.

- 1. LiOH is more effective than NaOH as a base chemical in the new formulation. The reduction of concentration of base chemical is around 40% in mass, due to the difference in molecular weights.
- 2. Salt may have different effects on AA performance; thermodynamic inhibition and reduction of AA adsorption on hydrate surface. Another important effect of salt is that it can decrease CO_2 solubility in the aqueous phase. In this study, it is found that increasing salinity leads to significant decrease in dosage of base chemical in the formulation.
- 3. Higher volume of natural gas in the rocking cell (lower volume of the aqueous phase) requires higher concentrations of AA and base in the aqueous phase. The amounts of LiOH and AA required, however, are not increased in mass.

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