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Original Paper

The development of high-performance kinetic hydrate inhibitors by introducing N-vinyl caprolactam and vinyl ether homopolymers into PVCap

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ABSTRACT

Low dosage kinetic hydrate inhibitors (KHIs) are a kind of alternative chemical additives to prevent gas hydrate formation in oil & gas production wells and transportation pipelines. In this work, a series of KHIs were experimentally synthesized with N-vinyl caprolactam (N-VCap) and vinyl ether including vinyl ether, vinyl n-butyl ether, vinyl isobutyl ether, triethylene glycol divinyl ether, with the mole ratio ranging from 9:1 to 5:5. The inhibition performance of new-synthesized KHIs on the formation process of methane hydrate were examined and compared with that of commercial N-vinyl caprolactam PVCap. Several ethylenediamine reagents were used as synergists and tested to improve the inhibition capacity of new-synthesized KHIs. The experimental results demonstrate that the introduction of ether groups on PVCap improves the performance of hydrate inhibitors. PVCap-VNBE (N-VCap: vinyl n-butyl ether = 5:5) shows the best inhibition performance for methane hydrate, which could extend the TVO to 1251 min under 6 K subcooling. N,N′-dimethylethylenediamine shows the best synergistic effect for PVCap-VNBE (5:5), and extends the TVO by 2.75 times at 7 K subcooling. Additionally, the relationship between hydrate inhibition performance and interfacial tension of newly-synthesized KHIs under high pressure were studied. It shows that the lower interfacial tension of KHIs would result in longer onset time, exhibiting better inhibition performance.

1. Introduction

Gas hydrates are ice-like crystalline compounds in which guest molecules like methane and ethane are trapped in the polyhedral water cavities (Aminnaji et al., 2023; Sloan, 2003; Zhao et al., 2017). When the elevated pressure accompanied by declined temperature, gas hydrates trend to form in gas and oil transportation flowlines in deep ocean and cold climate area, which may lead to the blockage of the pipeline (Liu et al., 2022; Wang et al., 2021a, 2021b). Therefore, preventing hydrates formation has always been the focus of the oil and gas industry.

Normally various means including pipe heating, depressurization, water removal and chemical inhibition were employed to prevent gas hydrate formation in gas and oil industry (Khurana et al., 2017; Li et al., 2020; Sun and Kang, 2016). The ideal way to avoid gas hydrate obstruction is to keep temperature and pressure out of the hydrate stable zone, but this is typically expensive, especially for long-distance lines (Ke and Kelland, 2016; Nakane et al., 2021). On the other hand, when dealing with gas and oil transportation, it always contains some water due to the process characteristics and it's also hard and expensive to totally remove the water phase. Among all the methods that mentioned, injecting chemical inhibitors is simpler and easier to implement (Altamash et al., 2017; Aminnaji et al., 2017; Ke and Chen, 2019; Ree et al., 2019). In traditional way, two types of hydrate inhibitors are utilized for industrial applications, thermodynamic hydrate inhibitors (THIs) and kinetic hydrate inhibitors (KHIs) (Dubey et al., 2023; Mohsenzade et al., 2021; Wang et al., 2019; Zou et al., 2023, 2024). THIs, such as methanol, ethanol, monoethylene glycol (MEG), sodium chloride (NaCl) etc. tend to shift the hydrate phase

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equilibrium curve to lower temperatures and higher pressures with a high concentration (typically 10–40 wt% of the water content) (Del Villano and Kelland, 2010; Wang et al., 2023b). Considering both economic and environmental reasons, KHIs are widely used to relieve these problems. KHIs are water-soluble polymers such as poly(N-vinylcaprolactam) (PVCap) and poly(N-vinylpyrrolidone) (PVP) which delay gas hydrate nucleation and slow down the hydrate growth rate with a low concentration (typically less than 1.0 wt% of the water present) (Cheng et al., 2023a; Kelland, 2006).

According to the published literatures related to KHIs experiments, short polymer chains with a high surface-to-volume ratio can disturb the water structure more effectively than long polymer chains (Long et al., 2019). Meanwhile, chemical modification is also an effective way to enhance the inhibition performance of KHIs. Such as, the PVCap was modified by adding tert-butyl acrylate to synthesize a new polymerization mixture, which achieved better inhibition performance (Huang et al., 2022). For KHIs, polymers with 3–6 carbons in the alkyl groups especially with cyclic groups have good KHI performance (Qin et al., 2015). Zhang and Kelland (2021) found a class of polymaleamides as KHI, which the inhibition performance was enhanced significantly than PVCap and can be compatible with high salinity brines. Li et al. (2017) explained the inhibition mechanism of PVP-A and PVP-E, which were synthesized by introducing a butyl ester group and a butyl ether group into PVP molecules, respectively, from the aspect of molecular simulation. Additionally, the performance of the polymers with longer alkyl groups can be improved as long as they maintain the water solubility. By the way, it is reported that KHI molecules may adsorb onto the gas-liquid interface by hydrogen bonding between water molecules and ether group (Long et al., 2022). Therefore, vinyl ether group with similar hydrophobic groups grafted on VCap or VP may be potential in hydrate inhibition field. Qin et al. (2015) synthesized new KHIs by introducing t-butyl group and phenyl group into PVP molecules to promote the inhibition ability. Ajiro et al. (2010) reported a series of poly(N-alkyl-N-vinylacetamide)s polymers with alkyl side groups since the polymers with the larger isopentyl or isobutyl groups performed best in both equipments. When alkylimidazolium groups were added to PVCap copolymers, the cloud points rose and the hydrate inhibition growth performance was comparable to that of PVCap (Rebolledo-Libreros et al., 2017). Huang et al. (2022) grafted tert-butyl acrylate group on PVCap molecules, which made the maximum tolerable degree of subcooling for sII hydrate more than 12 K. However, the effect of the number of carbon and oxygen atoms in ester group, and the effect of mole ratio on inhibition performance of KHIs were not clear. Meanwhile, adding some additives into KHIs as synergists is also an alternative way to promote the inhibition ability (Cheng et al., 2021, 2023b; Wang et al., 2023a). The most popular and familiar synergists are quaternary ammonium salts, glycol ether compounds, and polyethylene oxide (PEO) (Chen et al., 2010). Additionally, some THIs (monoethylene glycol, alcohols), ionic liquids also showed remarkable synergic effect (Ke and Chen, 2019; Kelland et al., 2023). However, the relationship between KHIs and synergists is very complex and still unclear until now. One possibility is that the KHI molecules are adsorbed by the surface of the aqueous phase, and thus affect the gas/liquid interfacial property (Zhang and Kelland, 2020; Zhang et al., 2020). So, one way to investigate the KHI adsorption behavior is to focus on the interfacial property between KHI and aqueous phase (Wan and Liang, 2021). Since water molecules dominant on both the aqueous phase and hydrate surfaces, we can infer information about the adsorption behavior of KHI molecules on the surfaces of hydrate nuclei by examining the gas/liquid interfacial characteristics. Schmidt et al. (2007) concluded that most of the interfacial tension data with hydrate formation conditions in the literature have been measured at temperature higher than 296 K. While for the cases with surfactants, Sun et al. (2004) and Watanabe et al. (2005) reported the interfacial tension of methane + water with sodium dodecyl sulfate (SDS) near the hydrate formation conditions. The interfacial tension of methane/aqueous VC-713 solution was determined by Peng et al. (2009) between 274.2 and 282.2 K in temperature and 0.1–20 MPa in pressure. Liu et al. (2009) used Inhibex 301 and Inhibex 501 to quantify the interfacial tension between methane and water in the range of 274.2–282.2 K and 0.1–20.2 MPa. Qin et al. (2016) investigated the kinetic inhibition mechanism with gas/liquid interfacial tension in different dosages of kinetic additives. But it is worthy verifying whether the rule is valid for newly synthesized polymers and synergists.

To develop more efficient KHIs, and to investigate the kinetic inhibition mechanism with the synergic effect, a series of N-vinyl caprolactam (N-VCap) and vinyl ether including vinyl ethyl ether, vinyl n-butyl ether, vinyl isobutyl ether, triethylene glycol divinyl ether with different mole ratio were synthesized and named as PVCap-VEE, PVCap-VNBE, PVCap-VIBE, and PVCap-TGDE, respectively. The effect of mole ratio on methane hydrate formation was evaluated and compared with commercial KHI PVP, Inhibex 501 and PVCap. The results indicate that polymer with vinyl n-butyl ether group and the corresponding mole ratio of 5:5 achieves the best inhibition performance, and outperform above listed KHIs. Besides, several ethylenediamine reagents, N-ethylethylenediamine, N-(2-hydroxyethyl)ethylenediamine, N,N-dimethylethylenediamine, N,N,N′,N'-tetrakis(2-hydroxypropyl) ethylenediamine (EDTP), and N,N′-dimethylethylenediamine were tested as synergist with KHI PVCap-VNBE. The relationship of inhibition performance and gas/liquid interfacial tension with respect to different types of additives was investigated. The results are consistent with Qin's work which the performance of kinetic inhibition strongly depends on the interfacial tension (Qin et al., 2016). Based on this conclusion, the corresponding insights into the mechanism of inhibition ability can be an alternative way to discover more powerful KHIs to prevent blockage caused by hydrate formation.

2. Experimental methods

2.1. Materials

Hydrate kinetic inhibitors, PVCap, PVCap-VEE, PVCap-VNBE, PVCap-VIBE, PVCap-TGDE were all synthesized in our laboratory. The PVP and Inhibex 501 were purchased from Sigma-Aldrich and ISP (International Specialty Products) Inc. USA, respectively. Synergists N-ethylethylenediamine, N,N-dimethylethylenediamine, N,N,N′,N'-tetrakis(2-hydroxypropyl)ethylenediamine and N,N′-dimethylethylenediamine were supplied by Energy Chemical. Analytical pure ethanol, isopropanol, N-vinyl caprolactam and 2,2′-azobisisobutyronitrile (AIBN) were also purchased from Energy Chemical. Analytical grade pure CH_4 (99.99%) was supplied by the Beijing Haipu Gas Industry Corporation.

2.2. Synthesis method of KHIs

The KHIs were synthesized in a 100 mL three-neck round bottom flask, which were all the ramification of PVCap. Their molecular structures are shown in Fig. 1. For the synthesis of PVCap, N-VCap and initiator AIBN were mixed together in isopropanol at 353.15 K under nitrogen atmosphere for 12 h. Then the system was cooled down and a certain amount of ethanol was added to the flask. The diluted product was evaporated again to purify the product. This process was repeated three times. Afterwards, the product was dried at 333.15 K in a vacuum oven for 48 h until the

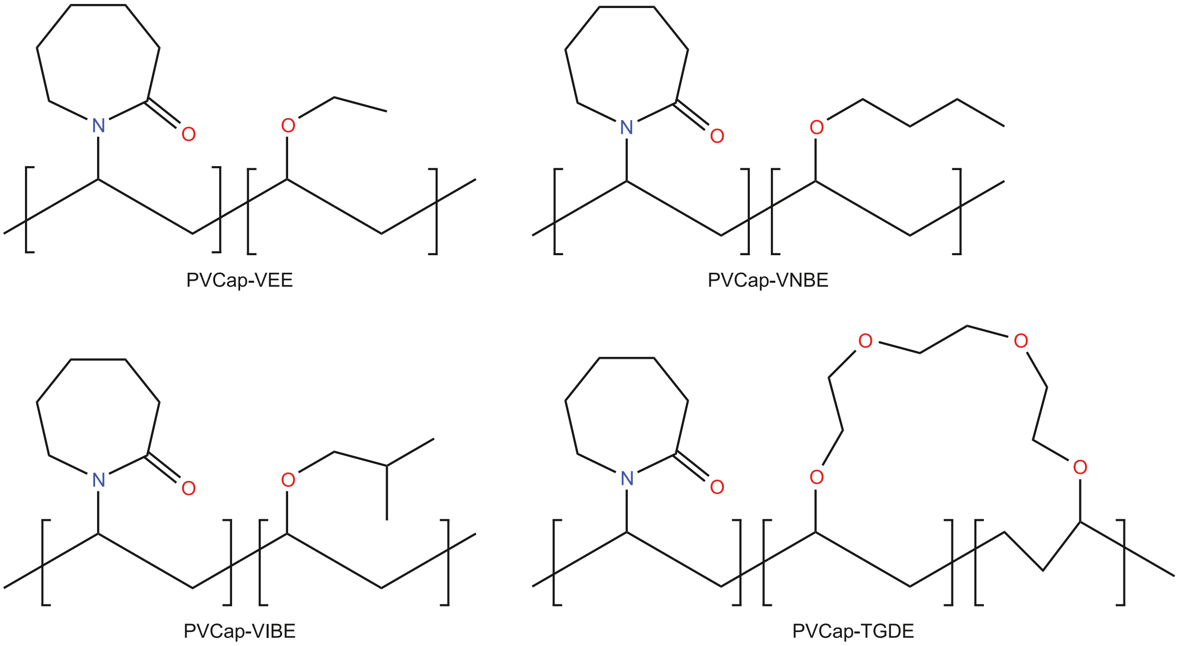


Fig. 1. Molecular structure of KHIs.

weight did not change. The way to synthesize other KHIs was similar to that of PVCap, except that certain corresponding ligand was put into the solvent. The Fourier Transform Infrared Resonance (FTIR) spectroscopy was recorded on Bruker Tensor II to further ascertain the structure of the polymerization.

2.3. Hydrate inhibition performance test

The experimental apparatus for testing the performance of KHIs in this work is shown in Fig. 2. The experiment was conducted in an apparent high-pressure sapphire cell that has a diameter of 2.54 cm, with an effective volume of 59 cm^3. The maximum working pressure of this cell is 40 MPa. As the formation and dissociation process of gas hydrates can be directly visual throughout the window, this instrument is useful in evaluating the hydrate inhibitors and has been used in our prior work (Cheng et al., 2021; Huang et al., 2022; Qin et al., 2015). The air bath with a viewable window was used to control the temperature of the cell. There is a magnetic stirrer inside the cell. The uncertainty of temperature is 0.1 K by Pt-100 resistance and the uncertainty of

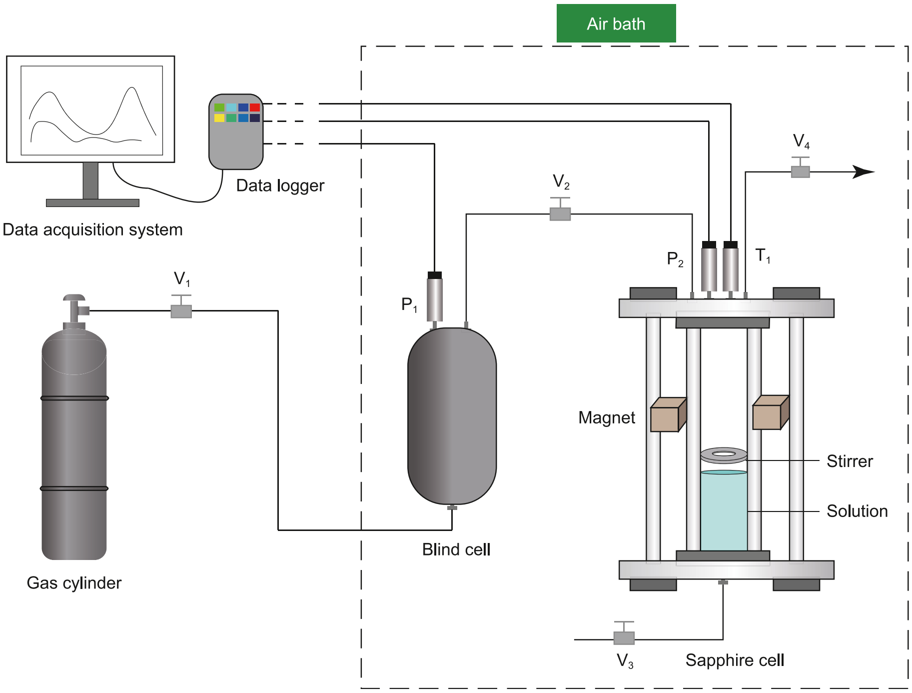


Fig. 2. Schematic diagram of experimental apparatus for kinetic inhibition test.

pressure is 0.001 MPa by pressure transducer.

The transparent sapphire cell was thoroughly cleaned with ethanol three times prior to the experiments to get rid of any possible containments. Then the nitrogen was used to purge the cell to guarantee the cell was fully cleaned and dried. In this study, the inhibition performance of KHIs were tested using the isothermal approach. Before the system was evacuated, the temperature of air bath was set to desired value. About 10 g aqueous solution containing inhibitor was added to the sapphire cell, the blind cell was charged with hydrate-forming gas to 10 MPa. The methane gas was injected into the cell from the blind cell until the desired pressure was reached after the stirrer was turned off and the temperature of cell stayed steady. The stirrer was then restarted at a steady pace. Monitor and Control Generated System (MCGS) was used to record the changes of pressure and other internal phenomena throughout the entire experimental run. The time interval between the end of gas injection and the onset of hydrate formation was defined as the induction time for hydrate formation. Two kinds of onset times for hydrate formation abbreviated as "TVO" and "TPD" were employed to record the time of hydrate formation in different status. The former was the time when hydrate crystals could be initially observed by naked eyes and the latter was the time when the obvious and continuous dropping of system pressure began. Here an example of PVCap-VNBE (9:1) solution is listed in Fig. 3 to illustrate the TVO and TPD.

The interfacial tension was measured by a JEFRI pendant-drop high pressure equipment manufactured by D.B. Robinson Corporation, as shown in Fig. 4. Three Eurotherm temperature controllers with 0.10 K inaccuracy were used to regulate the experimental temperature. All the pressure gauges were calibrated using a standard RUSKA pressure gauge with a 0.25% inaccuracy prior to each test.

The pendant-drop cell, together with all the lines and connections, were soaked in ethanol and then washed with petroleum ether prior to each experiment. Then nitrogen was employed to dry the entire system to make sure it was clean. Then the system was evacuated. Methane gas was put into one of the sample cylinders, and aqueous solution was put into the other one. Methane gas was slowly charged into the pendant-drop cell until the desired pressure was reached. When the system got to thermal equilibrium status, one drop of the required solution was injected into the pendant-drop cell through the central injection needle by a JEFRI pump, and the size of droplet was managed to keep stable for roughly 5 min at the experimental pressure. Then the profile of the liquid drop was magnified and recorded by a microscope and computer through a video camera. The aforementioned steps could be repeated to get the interfacial tension data at various pressure and temperature.

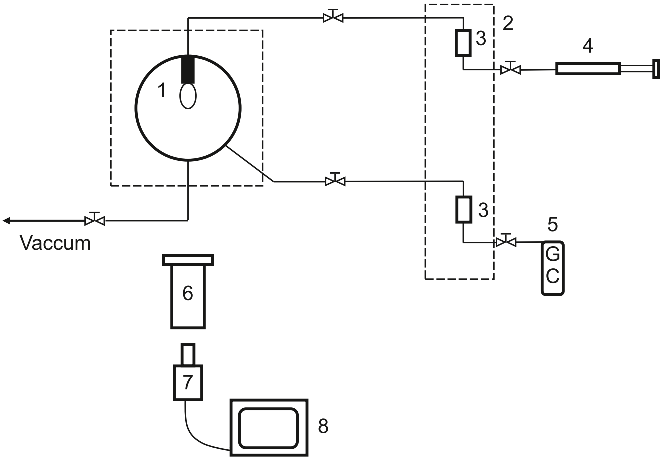


Fig. 4. Schematic diagram of the experimental apparatus for interfacial tension measurement: 1-Pendant drop cell, 2-Thermostat, 3-Sample cylinder, 4-JEFRI pump, 5-Gas cylinder, 6-Microscope, 7-Video camera, 8-Computer.

3. Results and discussion

3.1. Characterization of the KHIs

The FTRI spectra was used to characterize the structure and functional groups of the KHIs synthesized with different mole ratio of N-VCap and vinyl ethers from 9:1 to 1:1. As shown in Fig. 5, the absence of C=C–H, =CH–, and C=C absorption peaks around 912, 993, 1682, and 3010 cm^{-1} on the infrared absorption spectra indicated that the VCap monomer has been successfully polymerized into PVCap. To verify the conclusion, we found the bending

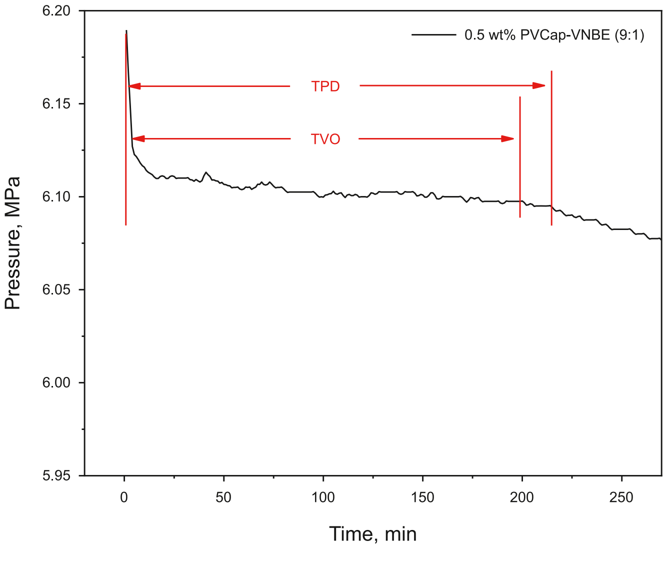


Fig. 3. The pressure-time curve of 0.5 wt% PVCap-VNBE (9:1) solution under 6 K subcooling (6.2 MPa, 273.65 K).

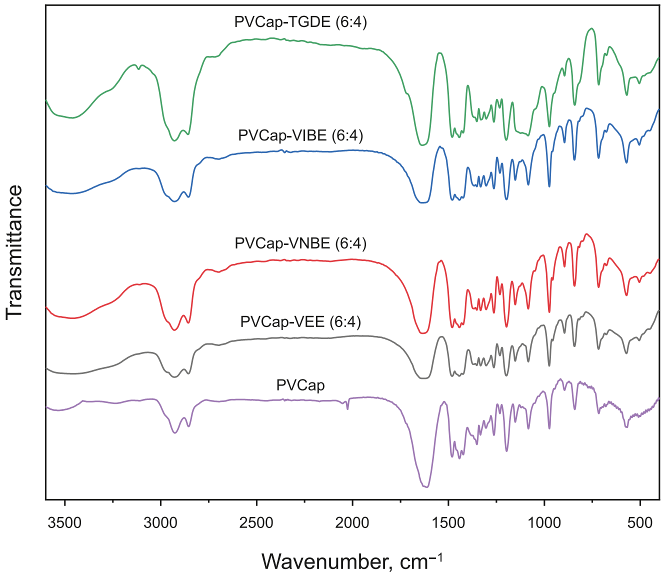


Fig. 5. The FTIR spectra of polymers with a mole ratio 6:4 of N-VCap and vinyl ethers.

vibrational absorption peaks of $-CH_2$ and $-CH_3$ were at 1465 and 1380 cm^{-1}. The peaks around 2876 and 2853 cm^{-1} are the saturated C−H symmetric and antisymmetric stretching vibration absorption peaks, respectively. The peaks at 1617 and 1430 cm^{-1} are the absorption peak of −C=O and C−N stretching vibration in PVCap molecular. The structures of other synthesized KHIs are similar to that of PVCap. In Fig. 5, the FTIR spectra of polymers, which a mole ratio of N-VCap and vinyl ethers is 6:4, were listed. For example, the difference of structure between PVCap and PVCap-VNBE (6:4) is that there is no obvious absorption peak around 1225~1200 cm^{-1}, which indicates that vinyl ether was no longer present in the sample. The peaks at 1150 cm^{-1} represents the strong absorption peak of C−O−C, which indicates that the vinyl ether is successfully polymerized with VCap, and converts into aliphatic ether. Besides, the FTIR spectra of polymers with other mole ratio of N-VCap and vinyl ethers are similar with the diagram listed in Fig. 5.

3.2. The inhibition performance of synthesized KHIs

Several methane hydrate formation experiments were conducted to assess the inhibition performance of the synthesized KHIs and commercial KHIs, such as PVCap, PVP and Inhibex 501. The subcooling is defined as the difference between the phase equilibrium temperature of gas hydrate corresponding to experimental pressure, and the experimental temperature. The subcooling was set to 6 K in this work, which the corresponding pressure and temperature was about 6.2 MPa and 275.65 K, respectively. The phase equilibrium temperature of gas hydrate was calculated by Chen-Guo model (Chen and Guo, 1998). The experimental results are shown in Fig. 6 and Table 1. The dosage of KHIs was set to 0.5 % (weight percentage, abbreviated as wt%).

According to Table 1, among the commercial KHIs, PVP has the worst hydrate inhibition performance. The gap between TVO and TPD is too small to be distinguished because of the fast growth rate of hydrates. PVCap has the best inhibition performance among the commercial inhibitors. Compared to the induction time for hydrate formation in the presence of commercial inhibitors like PVCap in the literature, the difference is very small in this work (Huang et al., 2022; Long et al., 2019). It shows that increasing the size of the amide ring increases the inhibition performance of KHIs. Based on the experimental results, it is evident that the addition of ether group improves the performance of PVCap to some extent. Hydrogen bonds could be formed between the oxygen atoms in ether or alcohol ether groups and hydrogen atoms in water molecule. According to the perturbation-inhibition mechanism hypothesis, this hydrogen bonding would perturb the hydrogen bonding between water molecules, thus inhibiting hydrate nucleation by perturbing water molecules to form cage structures during the hydrate crystal nucleation stage.

PVCap-VIBE and PVCap-VNBE show better inhibition performance when the ratio of N-VCap to vinyl ethers varied from 9:1 to 5:5. When the corresponding mole ratio is 5:5, PVCap-VNBE exhibits the best performance and TVO reaches 1251 min, while TPD comes to 1494 min. The hydrate formation process of PVCap-VNBE is shown in Fig. 7. Fig. 7(a) shows the morphology of the KHI solution after the experiment started 5 min. It can be seen that the inhibitor is completely dissolved in water and there are some bubbles produced by stirring on the wall. The solution is clear and not turbid. Fig. 7(b) shows that after 1251 min, white crystals started to appear above the gas-liquid interface adhering to the wall, which is the sign of hydrate formation. The corresponding part is marked by red circle. Fig. 7(c) and (d) show the process of hydrate crystals starting to grow until massive hydrates were formed, respectively. When the ratio is 6:4, PVCap-VIBE shows the best inhibition performance with 727 min for TVO, which is about 240 min longer than PVCap-VNBE with the same ratio. It indicates that the presence of heterostructures contributes to the inhibition properties. The inhibition performance of the copolymers is lower when the percentage of vinyl ether groups are relatively low. In general, N-VCap copolymers with longer alkyl chains and vinyl butyl ether have stronger inhibition performance, which could be enhanced when the proportion of vinyl butyl ether increases.

3.3. Performance of synergist

In industrial applications, KHIs are usually used in conjunction with synergists, which could further enhance the inhibition performance of KHIs. In terms of molecular structure, ethylenediamine reagents contain two nitrogen atoms, which leads to the appearance of hydrogen bond easily. Meanwhile, in order to investigate the effects of carbon chain length, heterostructure, steric hindrance, different functional groups on the synergistic effect, 1.0 wt% of each synergists, N-ethylethylenediamine, N-(2-hydroxyethyl) ethylenediamine, N,N-dimethylethylenediamine, EDTP, N,N′-dimethylethylenediamine with PVCap-VNBE were selected for the inhibition evaluation experiments. The experiments were conducted at the subcooling of 7 K (274.64 K, 6.17 MPa). The corresponding experiment results are listed in Table 2.

According to the experimental results, at 7 K subcooling, all synergists except N-(2-hydroxyethyl)ethylenediamine would prolong the time of hydrate formation, which demonstrates the synergistic effects with PVCap-VNBE (5:5). N,N′-dimethylethylenediamine is the most effective synergist, exhibiting 2.75-fold increment in TVO comparing to the blank experiment. In contrast to N-ethylethylenediamine and N,N-dimethylethylenediamine, N,N′-dimethylethylenediamine demonstrates superior inhibition performance. This suggests that the more methyl groups bound to the N atom, the longer the chain length, and the more branched the chain, the greater the ability to cover the hydrate lattice range and inhibit hydrate formation. Moreover, N,N-dimethylethylenediamine has a large steric-hinerance effect, which could form an overlapping electron cloud exhibiting repulsive action, leading to a decrease in its activity, making its synergistic ability lower than that of N,N′-dimethylethylenediamine. Compared with N-(2-hydroxyethyl)ethylenediamine, EDTP shows better inhibition ability. In terms of structure, EDTP has three more hydroxyl functional groups than N-(2-hydroxyethyl)ethylenediamine. Additionally, the site at which a hydrogen bond forms between the inhibitor and the water molecule increases as the number of hydroxyl functional groups increase. This disrupts the regular structure of hydrate and thus enhances the inhibition ability of KHIs.

3.4. Interfacial tension measurements

To clarify the mechanism of KHIs and synergists, we investigated the onset time of gas hydrates with 1.0 wt% kinetic additives (0.5 wt% PVCap-VNBE + synergist), and corresponding interfacial tensions of the gas/liquid systems under high pressure.

Firstly, the interfacial tension versus pressure of 0.5 wt% typical commercial KHIs, i.e., PVP, PVCap, Inhibex 501 and PVCap-VNBE in methane gas was conducted. As shown in Fig. 8(a), the interfacial tension between high-pressure methane gas and the commercial KHIs solutions system decreases with increasing pressure at 281.15 K, and the corresponding order was H_2O > PVP > Inhibex 501> PVCap. In Fig. 8(b), as pressure increases, the interfacial tension of 0.5 wt% PVCap-VNBE solution also gradually declines. When the pressure is constant, the order of interfacial tension is PVCap-VNBE (9:1) > PVCap-VNBE (7:3) > PVCap-VNBE (6:4) > PVCap-

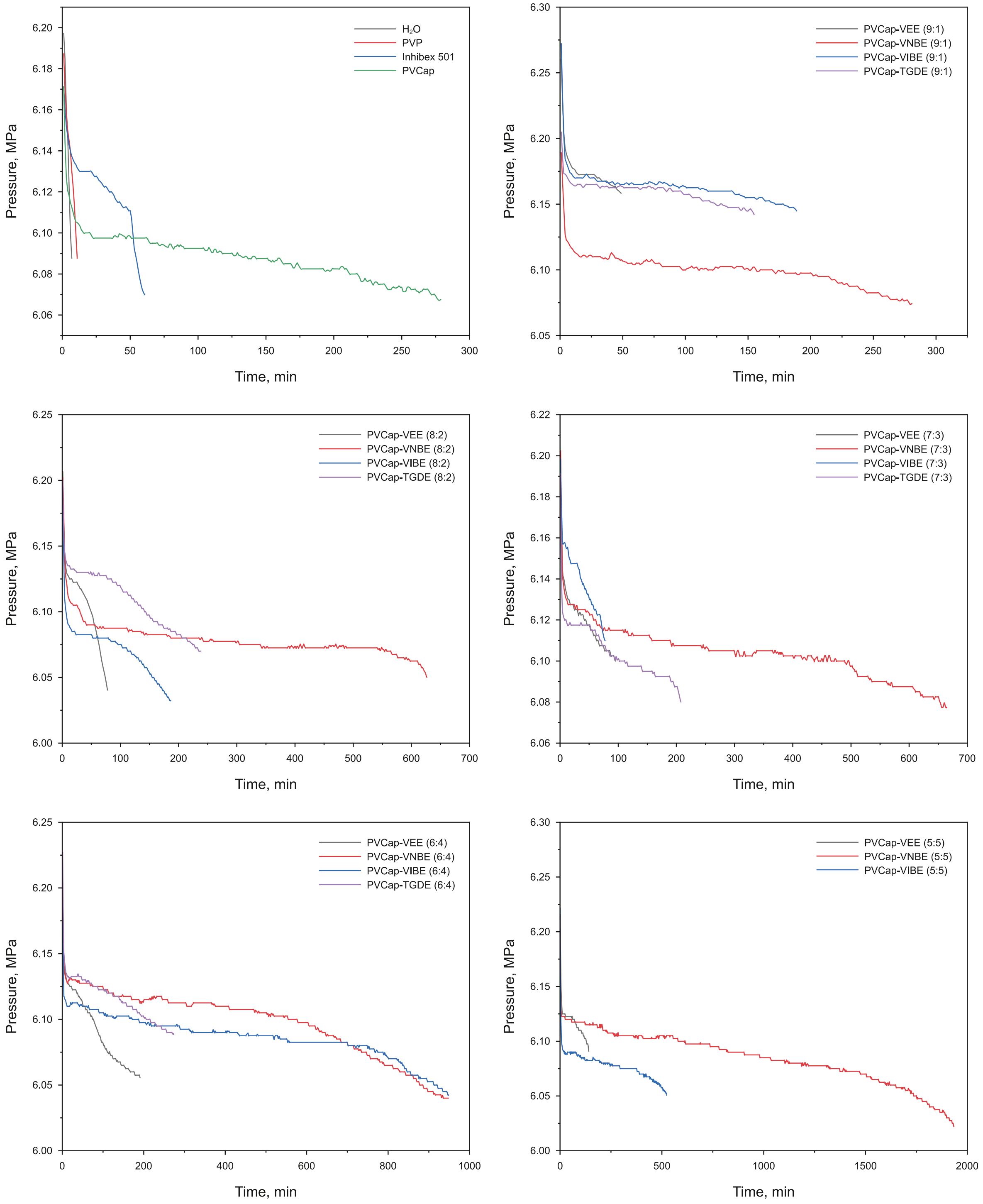


Fig. 6. Pressure-time curve of methane hydrate formation process with various KHIs at 6 K subcooling.

VIBE (6:4) > PVCap-VNBE (5:5). It demonstrates that when pressure increases, the interfacial tension decreases. When under the same pressure and temperature, the better inhibition performance KHIs solution has lower interfacial tension.

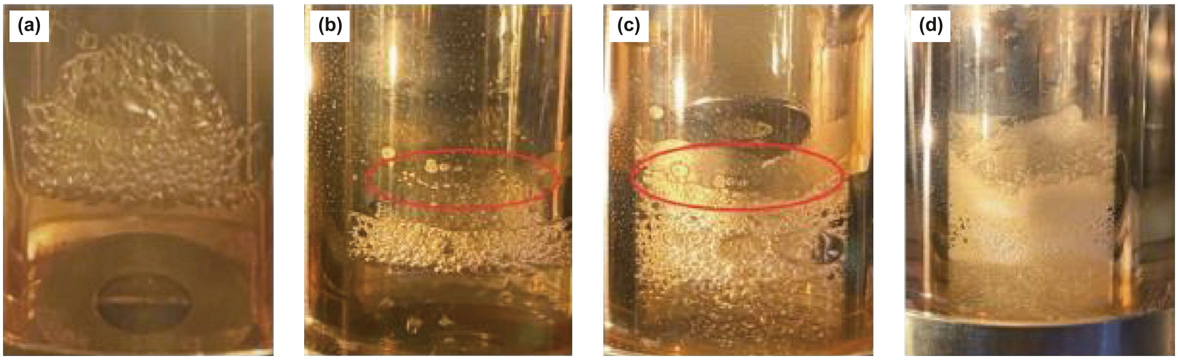
The comparison between TVO of hydrate formation process and the interfacial tension for KHIs + synergists system is shown in Fig. 9. It shows that the TVO and interfacial tension behave the conversely variation tendency. Among the tested KHIs, the PVCap-VNBE (5:5) containing system achieved the highest TVO and lowest interfacial tension, and exhibited the best inhibition performance. In Fig. 10, the trends were broadly similar, which interfacial tension and inhibit ability are negatively correlated.

Meanwhile, the interfacial tension between different concentrations of PVCap-VNBE (5:5) solution and methane gas was measured at 281.15 K and 3.0 MPa, respectively. The results are shown in Fig. 11. It indicates that the interfacial tension firstly decreases and finally tends to be stabilized with the increase of KHI concentration. It can be concluded from the fitting curve that the

Table 1
The onset time of hydrate formation process under the subcooling of 6 K.

Polymer	Concentration, wt%	Mole ratio (N-VCap: vinyl ether)	Pressure, MPa	Temperature, K	TVO, min	TPD, min
H_2O	\	\	6.197	275.77	1	2
PVP	0.5	\	6.187	275.58	6	7
Inhibex 501	0.5	\	6.172	275.71	21	23
PVCap	0.5	\	6.172	275.77	58	210
PVCap-VEE	0.5	9:1	6.260	275.77	18	25
PVCap-VNBE	0.5	9:1	6.185	275.75	199	214
PVCap-VIBE	0.5	9:1	6.270	275.73	78	138
PVCap-TGDE	0.5	9:1	6.207	275.64	92	98
PVCap-VEE	0.5	8:2	6.207	275.75	13	25
PVCap-VNBE	0.5	8:2	6.197	275.80	54	566
PVCap-VIBE	0.5	8:2	6.185	275.74	22	80
PVCap-TGDE	0.5	8:2	6.200	275.77	52	75
PVCap-VEE	0.5	7:3	6.190	275.67	11	40
PVCap-VNBE	0.5	7:3	6.200	275.66	389	492
PVCap-VIBE	0.5	7:3	6.192	275.77	19	29
PVCap-TGDE	0.5	7:3	6.192	275.70	48	52
PVCap-VEE	0.5	6:4	6.192	275.70	27	31
PVCap-VNBE	0.5	6:4	6.202	275.68	482	579
PVCap-VIBE	0.5	6:4	6.185	275.74	727	757
PVCap-TGDE	0.5	6:4	6.230	275.64	62	70
PVCap-VEE	0.5	5:5	6.200	275.70	35	59
PVCap-VNBE	0.5	5:5	6.222	275.68	1251	1494
PVCap-VIBE	0.5	5:5	6.227	275.63	345	379
PVCap-TGDE	0.5	5:5			[a]	[a]

[a] 0.5 wt% PVCap-TGDE (5:5) is not soluble in water.



T = 5 min T = 1251 min T = 1320 min T = 1494 min

Fig. 7. The morphology of PVCap-VNBE solution during hydrate formation process: **(a)** gas dissolved, **(b)** trace hydrate formation at the sapphire autoclave wall, **(c)** hydrate crystal growth, **(d)** massive hydrate formation.

Table 2
Average methane hydrate onset time of 0.5 wt% PVCap-VNBE (5:5) with 1.0 wt% ethylenediamine reagents at 7 K subcooling.

Synergist	Concentration, wt%	TVO, min	TPD, min
blank	0.5	94	232
N-ethylethylenediamine	1.0	148	152
N-(2-hydroxyethyl)ethylenediamine	1.0	46	128
N,N-dimethylethylenediamine	1.0	162	174
N,N′-dimethylethylenediamine	1.0	208	221
EDTP	1.0	258	303

critical micelle concentration (CMC) of PVCap-VNBE (5:5) is 0.57 wt %. When the concentration is below CMC, PVCap-VNBE (5:5) molecules are well dispersed in the solution to inhibit hydrate formation.

Qin et al. (2016) reported the use of Gibbs adsorption isotherm to investigate the influence of inhibitor concentration on the interfacial properties of solutions to explain the relationship between interfacial tension and inhibitor performance. It was found that the inhibitors containing both hydrophilic and lipophilic groups exhibited a concentration-dependent interfacial tension. The inhibitor synthesized in this study, PVCap-VNBE, belongs to the class of surfactants containing both hydrophilic and lipophilic groups, which enables it to orient and distribute well-organized at the gas-liquid interface. It is more effective in replacing the original interface and reducing the interfacial tension. Additionally, this type of distribution hinders the contact between water molecules and gas molecules to some extent. The atoms in ether groups, could form hydrogen bonds with water molecules, disrupting the hydrogen bonding between water molecules and inhibiting the formation of hydrate cages.

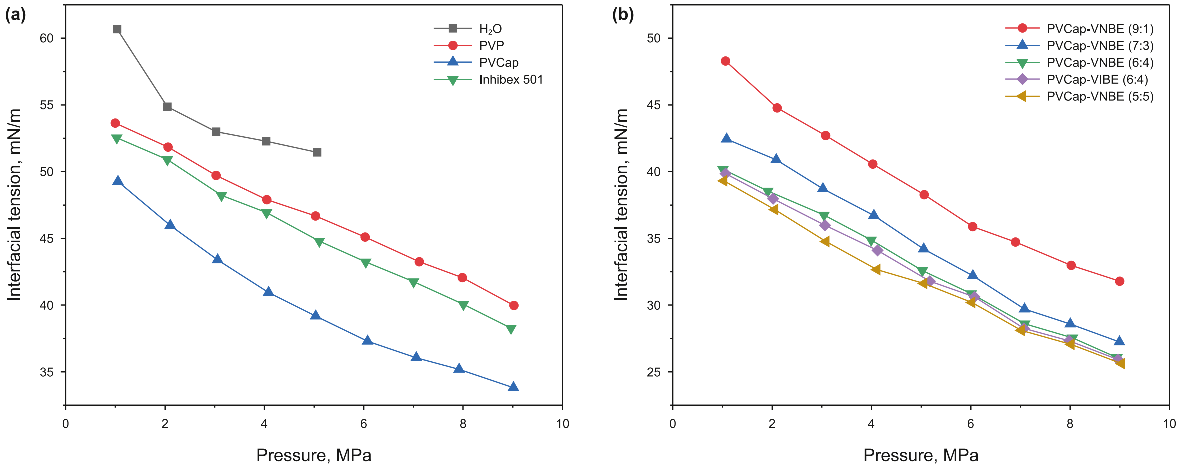


Fig. 8. The interfacial tension between KHIs-containing (0.5 wt%) aqueous solution and high-pressure methane gas under 281.15 K. **(a)** commercial KHIs, **(b)** PVCap-VNBE (mole ratio of N-VCap:Vinyl n-butyl ether ranges from 9:1 to 5:5).

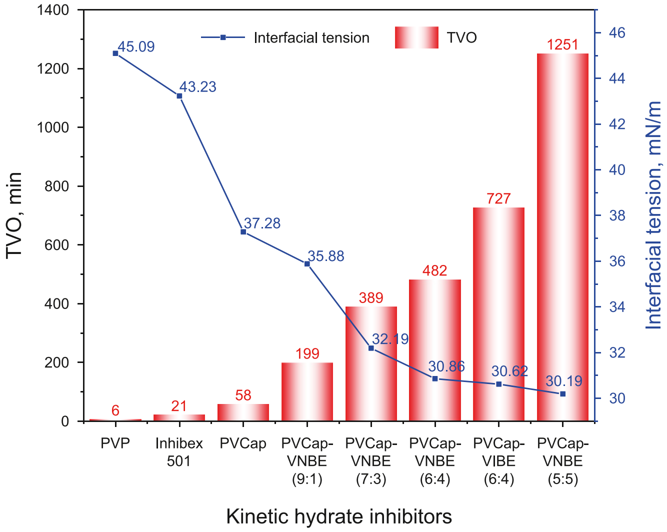


Fig. 9. The relationship between TVO and the interfacial tension of KHIs solution (PVCap-VNBE with different mole ratio).

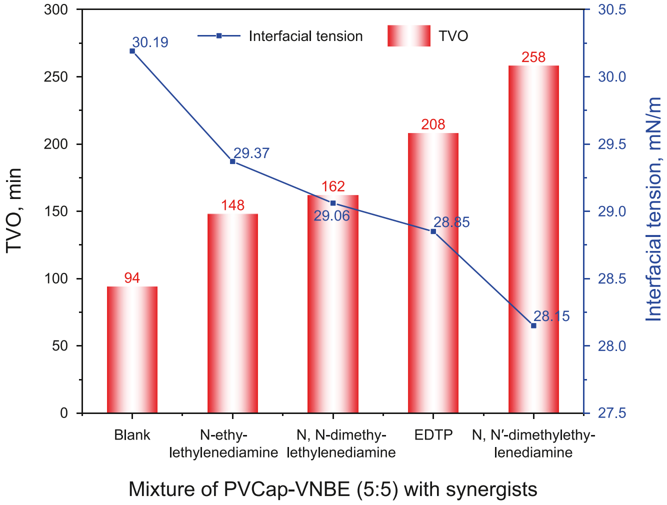


Fig. 10. The relationship between TVO and interfacial tension of PVCap-VNBE (5:5) + synergists aqueous solution.

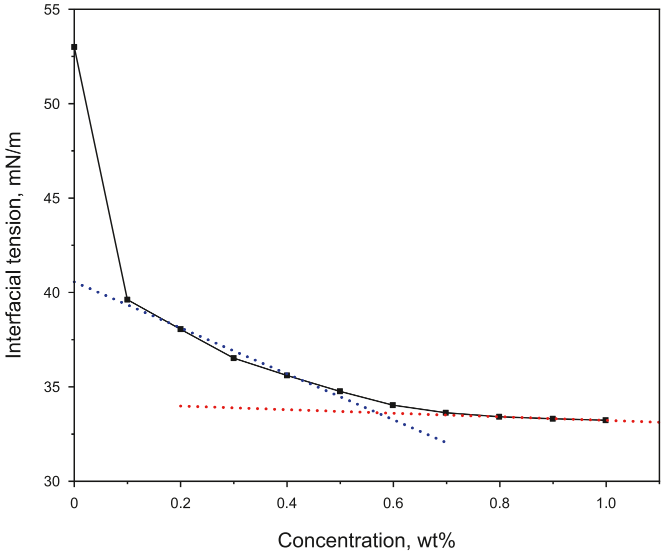


Fig. 11. The variation of the interfacial tension between high-pressure methane gas and PVCap-VNBE (5:5)-containing aqueous solutions with different KHIs concentration under 281.15 K and 3.0 MPa.

4. Conclusions

A series of KHIs were synthesized with N-VCap and vinyl ether groups, with the mole ratio of N-VCap and vinyl ether groups ranging from 9:1 to 5:5. The inhibition performance of newly-synthesized KHIs was evaluated by the formation kinetics of methane gas hydrate. Several ethylenediamine reagents were used as synergists, and the synthetical inhibition ability accompanied with KHIs were tested. Finally, the relationship of interfacial tension between KHIs-containing aqueous solutions and high-pressure methane gas was studied. The experimental results show that the introduction of ether groups on PVCap can significantly improve the inhibition performance of KHIs. When the polymers are soluble in water, the longer the alkyl chain is, and the more hydroxyl groups grafted on ether group, the stronger the inhibition performance of newly-synthesized KHIs will be. To some extent, the isomeric structure of the polymer increases the inhibition ability. When the subcooling at 6 K, PVCap-VNBE (5:5) shows the best inhibition performance for methane hydrate, which could enlarge the TVO to 1251 min. The synergistic effect of ethylenediamine reagents on PVCap-VNBE (5:5) was investigated. The chain length, functional group and structure of copolymer have certain influence on the inhibition capacity. N,N′-dimethylethylenediamine showed the best synergistic effect with PVCap-VNBE (5:5), extending the TVO by 2.75 times when the subcooling was at 7 K. The relationship between hydrate inhibition performance of newly-synthesized KHIs and interfacial tension was studied. It was found that the interfacial tensions would decrease with the increase of system pressure of methane gas. In addition, the KHIs aqueous solution with lower interfacial tension would result in better inhibition performance. Through extensive experiments, this work tried to modify the commercial KHI PVCap so as to further improve the inhibition performance and successfully develop a good performance KHIs and synergists, which would contribute to the development of new KHIs.

CRediT authorship contribution statement

Xing Huang: Writing – original draft. **Yi-Jian Zhu:** Methodology, Formal analysis. **Xiao-Hui Wang:** Writing – review & editing. **Ran Zhu:** Methodology. **Peng Xiao:** Methodology. **Wei-Xin Pang:** Methodology. **Chang-Yu Sun:** Validation, Formal analysis. **Guang-Jin Chen:** Supervision, Funding acquisition.

Declaration of competing interest

We declare no competing financial interest.

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