Preparation of CB[n] eutectic compounds for drilling fluid cooling and optimization of process conditions

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Abstract

In the process of deep shale gas horizontal well drilling, rotary guidance tools not only adjust the borehole trajectory, but also transmit downhole geological and engineering data transmission. These advantages provide convenience for deep shale gas development, however, when the wellbore temperature exceeds 135°C, it is easy to cause the signal loss of rotary guidance tool. In this paper, based on the perspective of solid-liquid phase change and heat absorption to reduce the bottomhole temperature of drilling fluids, we prepared a y cucurbit[n]uril eutectic compound (CB[n]), which was structurally confirmed by infrared and nuclear magnetism, and evaluated the phase change temperature and latent heat value of CB[n], which was determined to have the potential to be used as a cooling agent for deep shale gas drilling fluids.

Keywords: melamine-ringed eutectic compounds; deep shale gas; high-temperature wells; cooling agents; phase change materials

1 Introduction

Phase change materials [1] rely on phase change heat absorption for heat storage, which has

received widespread attention in the fields of building energy saving, solar energy utilization, power peaking, and waste heat recovery, showing an attractive picture [2]. By adding phase change heat storage materials into drilling fluid, the heat generated from the formation can be stored at high temperatures, and released when the drilling fluid is circulated to lower temperatures, which realizes large-scale storage for the purpose of cooling the wellbore, thus promoting the development of deep and ultra-deep well drilling technology. This study utilizes the feature that the heat absorption of phase change materials can cool down or inhibit the warming of the surrounding fluid in which they are located, in order to solve the problem of signal failure of rotary guiding tools due to temperature increase, and specially carries out the research on the molecular design and thermal properties of its cooling agent.

From the perspective of the continuous phase of drilling fluid [3], organic alcohols, fatty acids, polymers, organic esters are all unsuitable for oil-based drilling fluid cooling materials due to their solubility, inorganic salts are mainly sulfates, nitrates, chloride salts and phosphates, etc., and from the perspective of the phase change temperature, the inorganic salts phase change temperature is only nitrate eutectic compounds with a low phase change temperature [4], but it is also in the range of 150-200 ° C, therefore, the The molecular design and preparation of a cooling material suitable for the phase change temperature and proper calorific value of drilling fluid is of practical significance.

2 Experimental section

2.1 Materials and experimental apparatus

The main raw materials, glycoluron, paraformaldehyde and hydrochloric acid (37%wt), were from Chengdu Cologne Chemical Reagent Company; the reaction device was a microwave reactor YK22-WBFY-205 from Beijing Oriental Chemical Glass Technology Co. Ltd, with adjustable power of 40-120W.

2.2 Synthetic route

The process route for the preparation of CB[n] eutectic compounds is shown in Fig. 1.
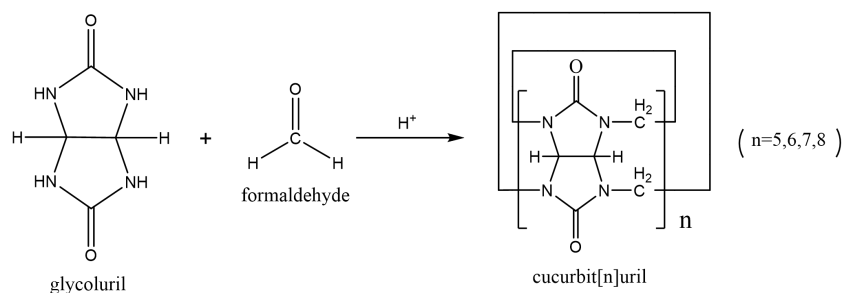
Fig. 1 Roadmap for the preparation of CB[n] eutectic compounds

Glyburide and paraformaldehyde were dissolved in a certain amount of 3M hydrochloric acid according to the ratio of feeding molar ratio of 2:1, and put into a microwave reactor after mixing uniformly, and the reaction was carried out under the power of 80 W, and the reaction time was controlled according to the amount of reactant added at 0.5 min -7 min. The reaction mixture was cooled down to room temperature and then vacuum extracted and filtered, and the white solid precipitate was recovered, and washed with purified water for 4-5 times, and dried to constant weight in a vacuum drying oven at 60 °C. After washing with pure water for 4-5 times, the mixture was dried to constant weight in a vacuum drying oven to obtain a mixture of CB[n] compounds. The mixture of CB[n] compounds was then transferred to a crucible and kept at 180°C for 12 h. Finally, the product was cooled to room temperature and milled to obtain the CB[n] eutectic compound.

3 Results and Discussion

### 3.1. Structural confirmation of CB[n] compounds

CB[n] compounds were ground and pressed with potassium bromide, and the infrared absorption spectra of CB[n] were recorded with Fourier transform infrared spectrometer in the wave number range of 4000-500 cm-1, and the resulting infrared spectrum of CB[n] compounds is shown in Fig. 2.
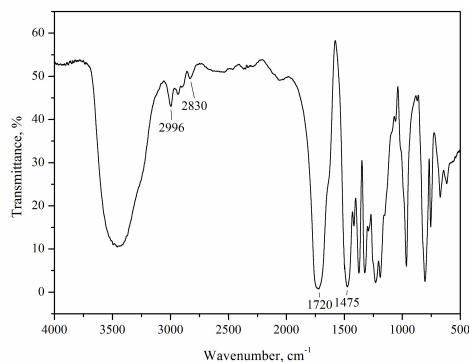
Fig. 2 Infrared spectra of CB[n]

From Fig. 2, it can be observed that 2996 cm-1, 2830 cm-1 and 1475 cm-1 are the symmetric telescopic vibration peaks, asymmetric telescopic vibration peaks and bending telescopic vibration peaks of the methylene bridge -CH2-, respectively, and 1720 cm-1 is the characteristic absorption peak of the carbonyl C=O in the glycoluronium structural unit, and these peaks indicate that the experimentally synthesized product is the target product CB[n] compounds.

The proton structure of CB[n] compounds was characterized by NMR means, and the resulting NMR spectra of CB[n] compounds are shown in Fig. 3.
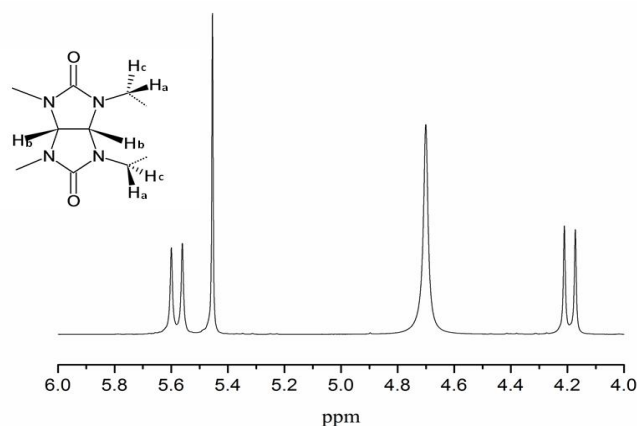
Fig. 3 1H NMR spectrum of CB [n]

The CB[n] compound is a centrosymmetric structure with three different protons, as can be observed in Fig. 3, two sets of mutually coupled duplex peaks and one set of single peaks, the absorption peak with chemical shift at δ4.70 ppm is the absorption peak of residual H in the deuterium reagent, which is disregarded. The two sets of mutually coupled duplex peaks are both H on the methylene bridge of the CB[n] compound port, with the protons chemically shifted at δ 5.601 ppm and δ 5.561 ppm being the protons Ha pointing inward to the ring from the methylene bridge, and the protons chemically shifted at δ 4.209 ppm and δ 4.168 ppm being the protons Hc pointing outward from the ring from the methylene bridge, whereas a single peak of tertiary carbon-based protons on the waist, Hb is located at δ 5.457 ppm.

3.2. Optimization of CB[n] preparation process

Using the results of one-way experiments, the main factors affecting the yield of CB[n] compounds were analyzed according to the experimental principle of response surface experimental design analysis method [5]. Response surface analysis experiments were designed for three levels of three factors: hydrochloric acid solution concentration, reaction time, and reactant feeding ratio (glycoluron: paraformaldehyde), and then the mathematical

regression model established based on the results of the response surface analysis experiments was used to optimize the preparation conditions of CB[n] compounds by using the model regression equations, and the results of the response surface analysis experiments are shown in Table 1.

Table 1 Experimental results of response surface analysis

Run	Concentration of hydrochloric acid solution (M)	response time (min)	Mass ratio of reaction materials	Product yield (%)
1	3.50	2.50	2.00	70.2
2	3.00	2.50	2.50	64.7
3	3.00	2.50	1.50	58.4
4	4.00	2.50	1.50	57.3
5	3.50	2.50	2.00	70.2
6	3.50	2.50	2.00	70.2
7	3.50	2.50	2.00	70.2
8	3.00	3.00	2.00	61.6
9	4.00	2.00	2.00	63.9
10	4.00	3.00	2.00	59.8
11	3.50	3.00	2.50	58.1
12	3.50	2.00	1.50	56.5
13	3.00	2.00	2.00	64.3
14	3.50	2.00	2.50	70.2
15	3.50	3.00	1.50	53.5
16	4.00	2.50	2.50	63.8
17	3.50	2.50	2.00	70.2

According to the experimental results of response surface analysis in Table 1, the analysis was performed and mathematical model regression equation was established in Design Expert software:

$$Y = -351.0375 + 90.6 \times c + 110.375 \times t + 125.625 \times r - 1.4 \times c \times t + 0.2 \times c \times r$$
$$- 9.1 \times t \times r - 12.65 \times c^2 - 18.55 \times t^2 - 23.95$$
$$\times r^2 \qquad\qquad (1)$$

Y —— Product yield (%);

c —— Concentration of hydrochloric acid solution (M);

t —— response time (min);

$$r \text{——Mass ratio of reaction materials}$$

For each influence factor c, t and r in the regression equation (1), the first partial derivation is obtained, and the right end of the equation is zero. The derivations are as follows:

$$90.6 - 1.4 \times t + 0.2 \times r - 25.3 \times c = 0 \#(2)$$

$$110.375 - 1.4 \times c + 9.1 \times r - 31.7 \times t = 0 \#(3)$$

$$125.625 + 0.2 \times c - 9.1 \times t - 47.9 \times r = 0 \#(4)$$

Equations (2), (3) and (4) are combined to solve the equations, and the optimal values of each influencing factor are obtained: c=3.47, t=2.30, r=2.20. By substituting the values of the influencing factors into the regression equation (1), the product yield Y=71.87% was obtained.

Finally, variance analysis was performed on the mathematical model, and the analysis results were listed in Table 2.

Table 2 Analysis of variance of the model

Source	Sum of squares	df	mean square	F value	P value
Model	518.42	9	57.6	32.52	< 0.0001
A-hydrochloric acid solution concentration	2.2	1	2.2	1.25	0.3013
B- Reaction time	59.95	1	59.95	33.85	0.0007
C-reactant feed ratio	120.9	1	120.9	68.26	< 0.0001
AB	0.49	1	0.49	0.28	0.6151
AC	1.00×10^{-2}	1	1.00×10^{-2}	5.65×10^{-3}	0.9422
BC	20.7	1	20.7	11.69	0.0112
A^2	42.11	1	42.11	23.78	0.0018
B^2	90.55	1	90.55	51.13	0.0002
C^2	150.95	1	150.95	85.23	< 0.0001
Residual error	12.4	7	1.77	-	-
Missing fit	12.4	3	4.13	-	-
Error term	0	4	0	-	-
Sum total	530.82	16	-	-	-

According to the law of model significance test, when the model P value is less than 0.01, the model is considered to be highly significant; when the model P value is less than 0.05, the model is considered to be statistically significant. Table 2 shows that the model P value established in this regression experiment is less than 0.0001, which indicates that the regression model is highly significant and statistically significant. Therefore, the regression equation established according to the regression model can simulate the real results of the experiment. In addition, according to the data in the table, we can see that P(B), P(C), P(BC),

$P(A^2)$, $P(B^2)$, and $P(C^2)$ all have significant effects on the reaction.

In order to investigate the interaction of three main factors, reaction time, hydrochloric acid solution concentration and reactant feed ratio, on the yield of CB[n] compound, the corresponding simulation surface was established with each of the two factors as coordinates.
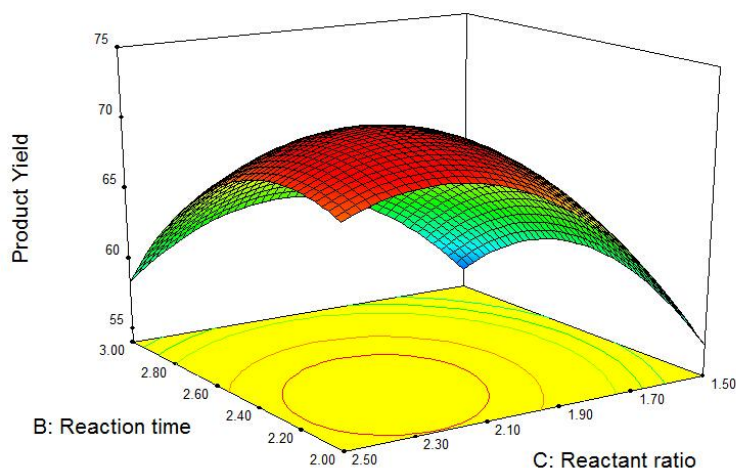
Fig. 3 shows the interaction between reaction time and concentration of hydrochloric acid solution on product yield. FIG. 4 shows the interaction between reaction time and the ratio of reactants to the product yield. Figure 5 shows the interaction between hydrochloric acid solution concentration and reactant feed ratio of product yield.
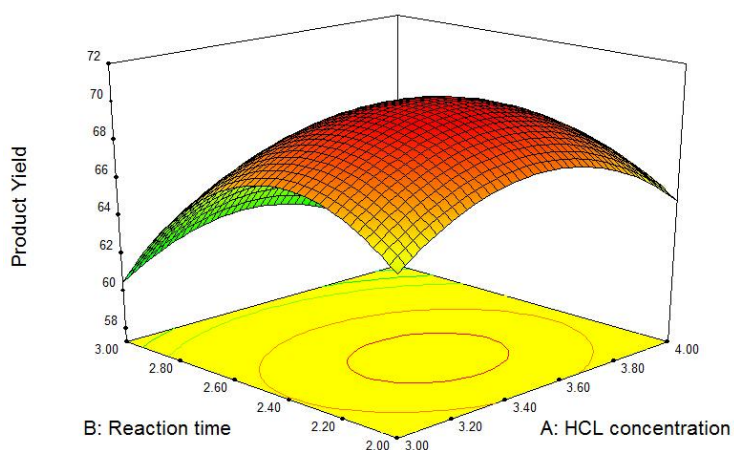
Fig. 3 Interaction between reaction time and concentration of hydrochloric acid solution

It can be observed from the surface in Figure 3 that with the increase of reaction time or concentration of hydrochloric acid solution, the product yield presents a trend of first increasing and then decreasing, and the surface of reaction time on product yield is steeper than that of concentration of hydrochloric acid solution, indicating that the effect of reaction time on product yield is more significant than that of concentration of hydrochloric acid solution.
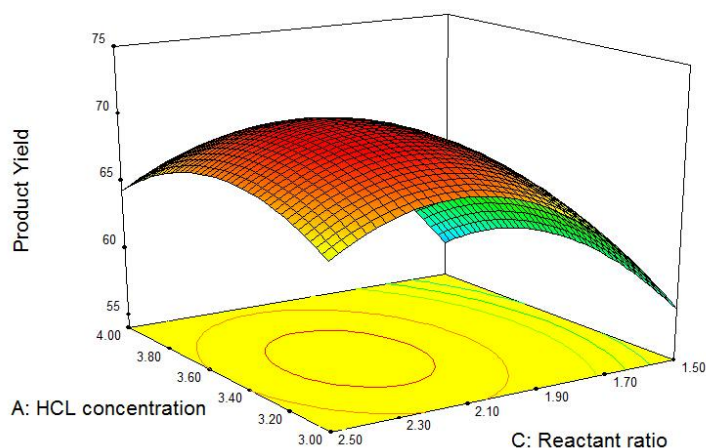
In addition, it can be observed from the contour diagram of the interaction between reaction time and concentration of hydrochloric acid solution that the contour line along the reaction time axis is denser than that along the concentration axis of hydrochloric acid solution, which also proves that the effect of reaction time on product yield is more significant than that of concentration of hydrochloric acid solution. In addition, it can be observed that the contour line presents an elliptical shape. This indicates that the interaction between reaction time and concentration of hydrochloric acid solution is strong and significant.

Fig. 4 Interaction between reaction time and reactant feed ratio

It can be observed from the surface in Figure 4 that the product yield increases first and then decreases with the increase of reaction time or reactant feeding ratio. However, the slope of the surface of product yield caused by reaction time is not much different from that of the surface of product yield caused by the concentration of hydrochloric acid solution, which is very steep, indicating that both reaction time and reactant feeding ratio have significant effects on product yield.

Then, by observing the contour diagram of the interaction between reaction time and reactant feeding ratio, it can be found that the contour line along the reactant feeding ratio is denser than that along the reaction time axis, indicating that the effect of the reactant feeding ratio on the product yield is more significant than that of the reaction time. In addition, it can be observed that the contour line presents an elliptical shape. This indicates that the interaction between reaction time and reactant feeding is stronger than that between the two factors, and the effect is significant.

Fig. 5 Influence of hydrochloric acid solution concentration on product yield by reactant feed ratio

It can be observed from the surface in Fig. 5 that the product yield increases first and then decreases with the increase of the concentration of hydrochloric acid solution or the reactant feeding ratio. The surface of the product yield of the reactant feeding ratio is steeper than that of the concentration of hydrochloric acid solution, indicating that the effect of the reactant feeding ratio on the product yield is more significant than that of the concentration of hydrochloric acid solution. In addition, it can be observed from the contour diagram of the interaction between the concentration of hydrochloric acid solution and the reactant feed ratio that the contour line along the reactant feed ratio is denser than that along the axis of the concentration of hydrochloric acid solution, which also proves that the effect of the reactant feed ratio on the product yield is more significant than that of the concentration of hydrochloric acid solution. In addition, it can be observed that the contour line presents an elliptical shape. This indicates that the interaction of hydrochloric acid solution concentration and reactant feeding is stronger than that of the two factors, and the influence is significant.

3.3. Thermal properties of CB[n] eutectic compounds

The key to use as heat-absorbing phase change materials in high temperature Wells is appropriate phase change temperature and sufficient heat. In this paper, a thermogravimetric analyzer [6] was used to measure the change of heat and weight of the sample combined with the change of temperature and time.

First, CB[n] eutectic compound samples were dried in a vacuum oven at 40°C for 12 h. After that, nitrogen was used as a protective atmosphere, the temperature range was set at 40°C-350°C, and the heating rate was 10°C/min. STA449C-QMS403C thermal analyzer was used for testing. FIG. 6 shows the thermal analysis curve of CB[n] eutectic compounds.
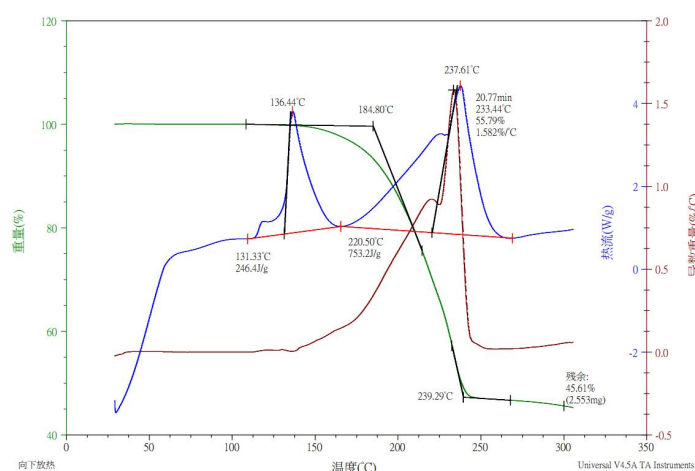
Fig. 6 Thermal analysis spectra of CB[n]@MT

It can be seen from Fig. 6 that the heat flow curve of CB[n] sample is divided into two stages. The temperature range of 131.33°C-163.4°C is the first endothermic stage, which is mainly due to the absorption of heat by CB[n] sample, the solid skeleton molecules obtain enough energy, and the motion properties are released, resulting in the apparent morphogenetic transformation from solid and semi-solid to liquid state. It can be seen from Figure 6 that the heat absorption of the first phase transformation is about 246.4J/g, and the weight loss starts at 136.44°C, about 1.5%. After that, at 220.50°C, rapid weight loss began, and an obvious heat absorption peak appeared, with the heat absorption value as high as 753.2J/g. The temperature range was from 220.50°C to 260.7°C, and the weight loss in this temperature range reached 65.4%, indicating that the chemical bond of carbon and nitrogen was broken at this stage, and the CB[n] eutectic compounds decomposed. In the process of decomposition and conversion into the gas phase, resulting in weightlessness.

The above experimental results show that CB[n] eutectic compounds have moderate temperature and high heat of phase transition, and may be the best materials for downhole cooling of oil-based mud.

4. Conclusion

The CB[n] eutectic compounds were successfully prepared by FT-IR and 1H NMR. Using the response surface method, we observed the presence of factor synergies and the existence of optimal preparation process conditions. Thermal behavior analysis shows that CB[n] has a suitable phase transformation temperature and a high latent heat of phase transition, which can be used as a deep shale gas drilling fluid to cool the bottom hole and effectively inhibit the rise of wellbore temperature. In addition, it is intended to further study, for example, the effect of CB[n] on drilling fluid properties and the application of CB[n] in the drilling process of high-temperature Wells to improve drilling efficiency.

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