

Article

Promising Hydrate Formation Promoters Based on Sodium Sulfosuccinates of Polyols

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Abstract: The use of natural gas as an energy source is increasing significantly due to its low greenhouse gas emissions. However, the common methods of natural gas storage and transportation, such as liquefied or compressed natural gas, are limited in their applications because they require extreme conditions. Gas hydrate technology can be a promising alternative to conventional approaches, as artificially synthesized hydrates provide an economical, environmentally friendly, and safe medium to store energy. Nevertheless, the low rate of hydrate formation is a critical problem that hinders the industrial application of this technology. Therefore, chemical promoters are being developed to accelerate the kinetics of gas hydrate formation. In this paper, the effect of new sodium sulfosuccinate compounds, synthesized based on glycerol and pentaerythritol, on methane hydrate formation was studied. Experiments under dynamic conditions using high-pressure autoclaves demonstrated that the conversion of water-to-hydrate forms increased from $62 \pm 5\%$ in pure water to $86 \pm 4\%$ for the best promoter at concentration 500 ppm. In addition, the rate of hydrate formation increases 2–4 times for different concentrations. Moreover, none of the synthesized reagents formed foam, compared to sodium dodecyl sulfate, in which the foam rate was 3.7 ± 0.2 . The obtained reagents showed good promotional properties and did not form foam, which makes them promising promoters for gas hydrate technology.



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Keywords: methane hydrate; hydrate formation promoters; kinetic promoters; sulfosuccinates; natural gas storage and transportation

1. Introduction

Due to the rapid pace of global economic growth, energy consumption is expected to increase greatly in the next few years. As humanity strives to become more environmentally friendly and reduce its carbon footprint as much as possible, there is a tendency to reduce the use of coal and oil and increase new energy sources with fewer greenhouse gas emissions. Methane, which makes up to 98% of natural gas in different cases, contains a large amount of hydrogen relative to carbon, hence CO₂ emissions during its combustion is much lower than those for other hydrocarbon feedstocks [1]. Thus, it is considered a fairly clean source of energy.

The efficiency of natural gas storage and transportation is an important issue in resource use. Currently, there are several technologies for the storing and transporting of natural gas. Pipelines are the traditional way to transport hydrocarbons in large volumes, but this is sometimes restricted by geographical conditions [2]. Additionally, compressed natural gas (CNG) is more convenient and is used as a transport fuel, but requires high working pressure (up to 25 MPa), which poses a threat to human safety [3]. Additionally, the low capacity of CNG limits its application on a large scale [4]. Liquefied natural gas (LNG) has a higher capacity. Nevertheless, the very low temperatures required for LNG still result in high storage costs, frost damage from gas leaks, and the gas tends to boil out

during long-term storage [5]. For the technology of adsorbed natural gas (ANG), carbon materials and metal-organic frameworks are used as adsorbents. Although high-capacity values have been achieved by this technology, the presence of impurities, as well as the high cost of sorbents, prevents its use in industry [6].

Under suitable thermodynamic conditions, natural gas can exist in the form of solid gas hydrates [7]. Gas hydrates are crystalline compounds in which gas molecules (methane, ethane, hydrogen, carbon dioxide, and hydrogen sulfide) are trapped in hydrogen-bonded network of water molecules [8]. In this case, the system is stabilized through the van der Waals interactions between the gas molecule and the water cavity [9]. Gas hydrates are being studied in various applications, including water desalination [10], carbon dioxide capture and sequestration [11], gas separation [12], and cooling [13]. Gas hydrates present an alternative way to store and transport gas as they have a moderately large capacity, environmentally friendly nature, and do not require very high pressures and low temperatures [14].

The nucleation of hydrates is a probabilistic phenomenon, and it means that hydrate formation difficult to control. To improve the kinetics of the process, scientists mainly use mechanical (stirring and spraying [15,16]) and non-mechanical methods (chemical [17] and other additives [18,19]). Two types of chemical promoters are widely used: thermodynamic and kinetic. Thermodynamic promoters like tetrahydrofuran (THF) and tetrabutylammonium bromide (TBAB) shift phase equilibrium to more mild conditions, providing more driving force for hydrate growth [20]. However, the thermodynamic promoters often partly fill the hydrate cavities, therefore the gas storage capacity will become lower [21].

Kinetic promoters shorten the nucleation time and intensify hydrate growth without obviously affecting the equilibrium conditions. Kinetic promoters include surfactants (anionic, cationic, and nonionic) [22], nanomaterials [23], amino acids [24], and EDTA amides [25,26]. The promotion activity of anionic surfactants, such as sodium dodecyl sulfate (SDS), is more significant than that of nonionic and cationic surfactants. Surfactants with sulfonate and sulfate groups in their chemical structure show the best promotion efficiency [27]. However, the formation of large amounts of foam in surfactant systems at the stage of gas recovery obstacles the use of hydrate-based technology [28].

In the present study, four new reagents—sodium sulfosuccinates of glycerol and pentaerythritol were synthesized. Their activities as kinetic promoters on the formation of gas hydrates was studied at different concentrations in comparison with water and sodium dodecyl sulfate.

2. Materials and Methods

Pentaerythritol and glycerol were provided by Sigma-Aldrich, St. Louis, MI, USA. Maleic anhydride (99%) and sodium bisulfite (99%) were obtained from Acros Organics BVBA, Belgium. Additionally, SDS (99%) was purchased from Panreac, Spain. For methane hydrates formation experiments, gaseous methane with a purity of 99.95% was used. All chemicals were used and received without any further purification.

As shown in Figure 1, sulfonated alcohols **2a–d**, were synthesized through a simple two-step reaction process, followed by esterification of alcohols with maleic anhydride, sulfonation of maleate with sodium bisulfite. Firstly, 0.05 mmol of corresponding polyols (glycerol or pentaerythritol) and 30 mL of DMFA were weighted in a 100 mL round bottom flask and stirred at 60 °C until complete dissolution of the alcohols. Maleic anhydride (0.15 mmol for **1a**, 0.2 mmol for **1c**, and 0.1 mmol for **1b**, **1d**) was then added and the temperature was raised to 75 °C. After 12 h, the intermediate compounds **1a–d** were obtained after solvent removal with a rotatory evaporator and used without further purification. In the second step, compounds **1a–d** reacted with sodium bisulfite (equimolar to maleic anhydride in the first step) in an aqueous isopropanol solution ($V_{\text{I-Propanol}}:V_{\text{water}} = 1:2$) at 100 °C for 24 h. Upon the completion of the reaction, the solvent was evaporated under reduced pressure in a rotary evaporator. As minor impurities, mono-sulfonated alcohols and other products were formed, which were separated by washing with ethyl acetate

3 × 30 mL and then dried under vacuum in a rotary evaporator to obtain pale yellow solids **2a–d**. The target products **2a–d** were obtained including diastereomers and regioisomers. Structures of compounds were ascertained by NMR and FT-IR spectroscopy, which are presented in the Supplementary Materials (Figures S1–S12). In addition to the fragment signals of the corresponding polyols, signals of the sulfosuccinate group appeared in the ^1H , ^{13}C NMR and IR spectra of compounds **2a–d**.

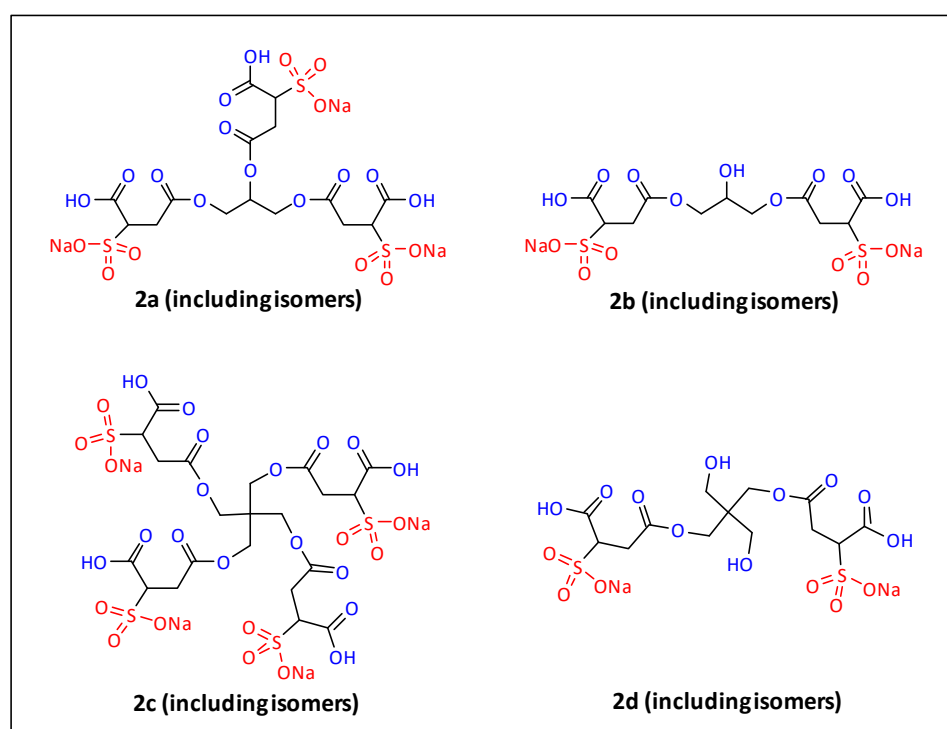
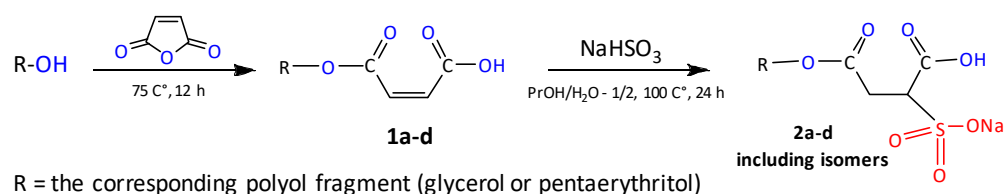


Figure 1. Synthesis procedure of sulfonated alcohols.

^1H , ^{13}C NMR spectra were recorded using Avance 400 (Bruker, Ettlingen, Germany) at operating frequency of 400 and 101.56 MHz, respectively. Chemical shifts were measured relative to the residual protons of the solvent (D_2O). The following abbreviations are used to describe coupling: d = duplet, t = triplet, br. t = broad triplet, q = quartet, br. q = broad quartet, m = multiplet, br. m = broad multiplet.

The Spectrum Two FT-IR spectrometer (Perkin-Elmer, Waltham, MA, USA) with single reflection diamond UATR accessory was used to record infrared spectra in the range from 2000 to 450 cm^{-1} .

Isothermal experiments with stirring were carried out to evaluate the promoting activity of the synthesized reagents with respect to methane hydrates using high-pressure autoclaves with an internal volume of 284 cm^3 . The setup diagram is shown in Figure 2. At the beginning of the experiment, 50 mL of pure water or a promoter solution were poured into the autoclave cell so that the stirring element provided good circulation of the solution (400 rpm), into which the thermocouple was also placed. Residual air was removed from the free volume of the autoclave cell by purging with methane, and the required pressure (such that it was 9 MPa at $+1\text{ }^\circ\text{C}$) was set using a gas booster at $+20\text{ }^\circ\text{C}$. Next, the stirrer was turned on and the temperature program was started: cooling from $+20\text{ }^\circ\text{C}$ to $+1\text{ }^\circ\text{C}$ in

1 h under isochoric conditions, followed by an isotherm at +1 °C for 8 h. A sharp drop in pressure and an increase in temperature indicate the formation of gas hydrates. For each sample, at least three measurements were taken to improve the accuracy of the results.

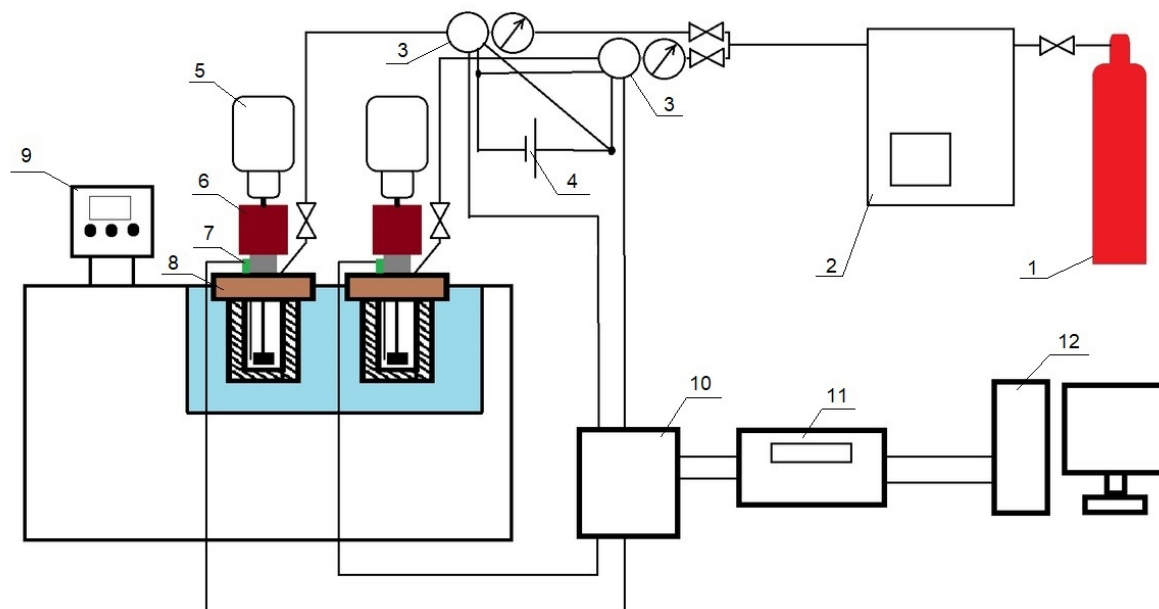


Figure 2. Scheme of the experimental setup for studying hydrate formation under dynamic conditions (KFU): 1—cylinder with methane; 2—gas booster; 3—pressure sensor; 4—direct current source; 5—overhead stirrer; 6—magnetic clutch; 7—thermocouple; 8—autoclave; 9—thermostat; 10—switch; 11—data collection system (Thercon); 12—computer.

The foaming properties of the obtained compounds were compared with one of the most studied promoters of hydrate formation, sodium dodecyl sulfate. Reagent solutions at a concentration of 500 ppm (100 mL) were made using distilled water to find the foaming rate and half-life. The foam formation was studied using a laboratory blender LB20ES (6000 rpm, 1 min). The foam quality was determined as the ratio of the volume of the formed foam to the volume of the initial solution of the promoter in a dimensional cylinder with a volume of 1000 mL. The foam half-life time was determined as the time from the end of foam formation until the promoter solution reached a volume of 50 mL (50% of the initial volume of the promoter solution) as a result of liquid drainage and foam destruction. All experiments were conducted at room temperature.

3. Results

3.1. Evaluation of Hydrate Promoting Effect

The results of the hydrate formation study in high-pressure autoclaves are presented in Figure 3 and Table 1. The graphs of gas consumption versus time were plotted for all tested samples at three concentrations (Figure 3a–d) in comparison with pure water and SDS. In the graphs, the areas with the highest slope correspond to the most intense hydrate formation, while the exit to the plateau reports the completion of the hydrate formation process. Maximum gas consumption and conversion of gas to hydrate were calculated from the pressure change in the cell based on the ratio between the guest molecules and water molecules $1\text{CH}_4:6\text{H}_2\text{O}$ [29] (Table 1). Rate constants of methane hydrate growth during 1/2 of the reaction time ($K_{1/2}$) and during 2/3 of the reaction time ($K_{2/3}$) were calculated in accordance with the equation proposed by Englezos et al. [30,31] (Table 1).

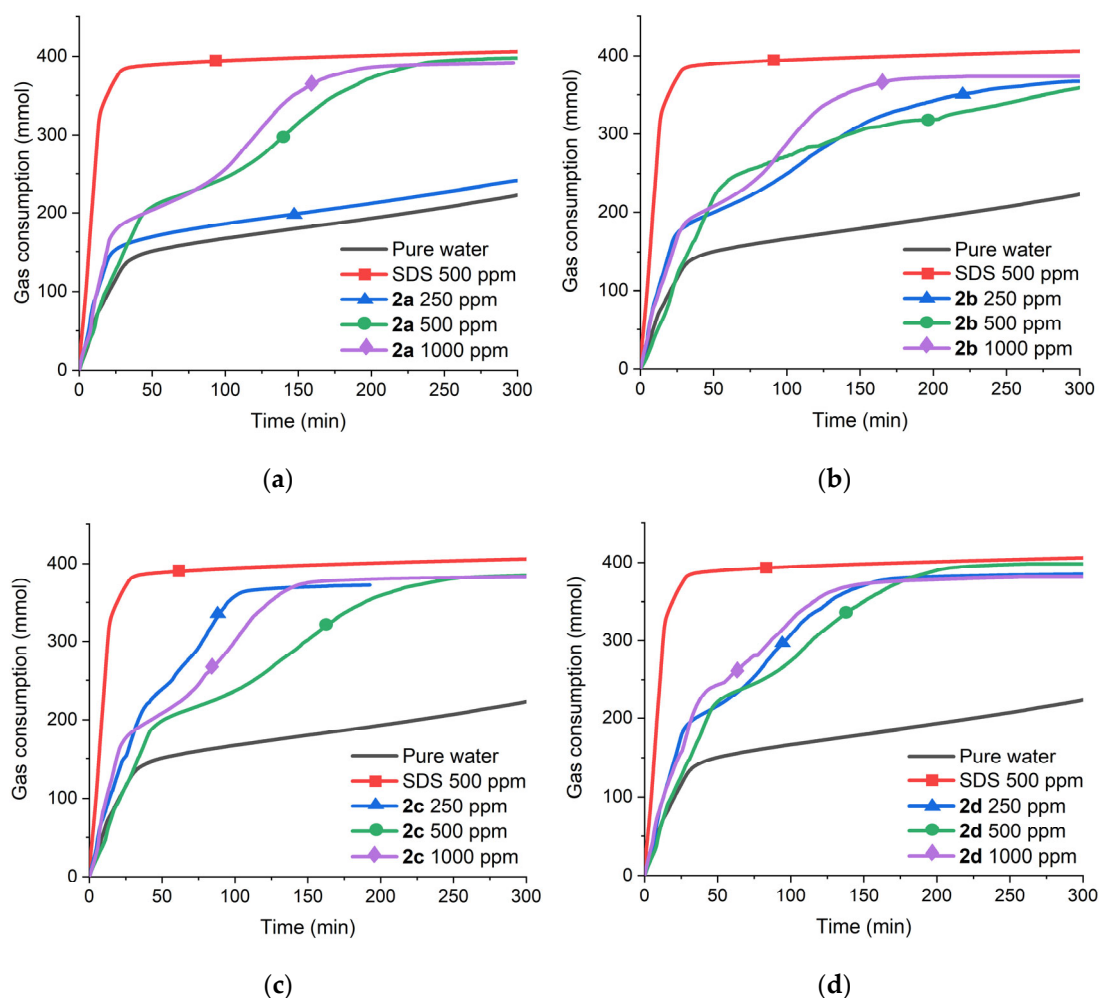


Figure 3. Gas consumption for samples: (a) 2a; (b) 2b; (c) 2c; and (d) 2d in comparison with pure water and SDS.

Table 1. Hydrate conversion, maximum mole consumption, and kinetic constants of methane hydrate formation for pure water and 2a–d solutions at different concentrations.

Sample	Concentration (ppm)	Methane Hydrate Conversion (%)	Maximum Gas Consumption (mmol)	Kinetic Constant at 1/2 of the Process Time (K1/2)	Kinetic Constant at 2/3 of the Process Time (K2/3)
Water	-	62 ± 5	285 ± 6	0.0024	0.0031
SDS	500	88 ± 6	406 ± 5	0.0493	0.0762
2a	250	52 ± 2	241 ± 4	0.0056	0.0068
	500	86 ± 4	398 ± 4	0.0048	0.0082
	1000	85 ± 5	392 ± 3	0.0032	0.0119
2b	250	79 ± 4	367 ± 4	0.0055	0.0079
	500	84 ± 1	389 ± 3	0.0039	0.0051
	1000	81 ± 3	373 ± 3	0.0071	0.0119
2c	250	81 ± 5	373 ± 3	0.0091	0.0151
	500	84 ± 3	387 ± 3	0.0048	0.0082
	1000	83 ± 3	384 ± 4	0.0068	0.0131
2d	250	83 ± 4	385 ± 3	0.0077	0.0128
	500	86 ± 4	398 ± 2	0.0057	0.0093
	1000	82 ± 4	381 ± 2	0.0103	0.0143

3.2. Foam Formation

Table 2 shows the results of studying the foaming of the synthesized samples at a concentration of 500 ppm. The appearance of the foam is shown in Figure 4.

Table 2. Foam formation of synthesized promoters and SDS.

Sample	Concentration (ppm)	Foam Rate	Half-Life (s)
2a	500	-	-
2b	500	-	-
2c	500	-	-
2d	500	-	-
SDS	500	3.7 ± 0.2	229 ± 6

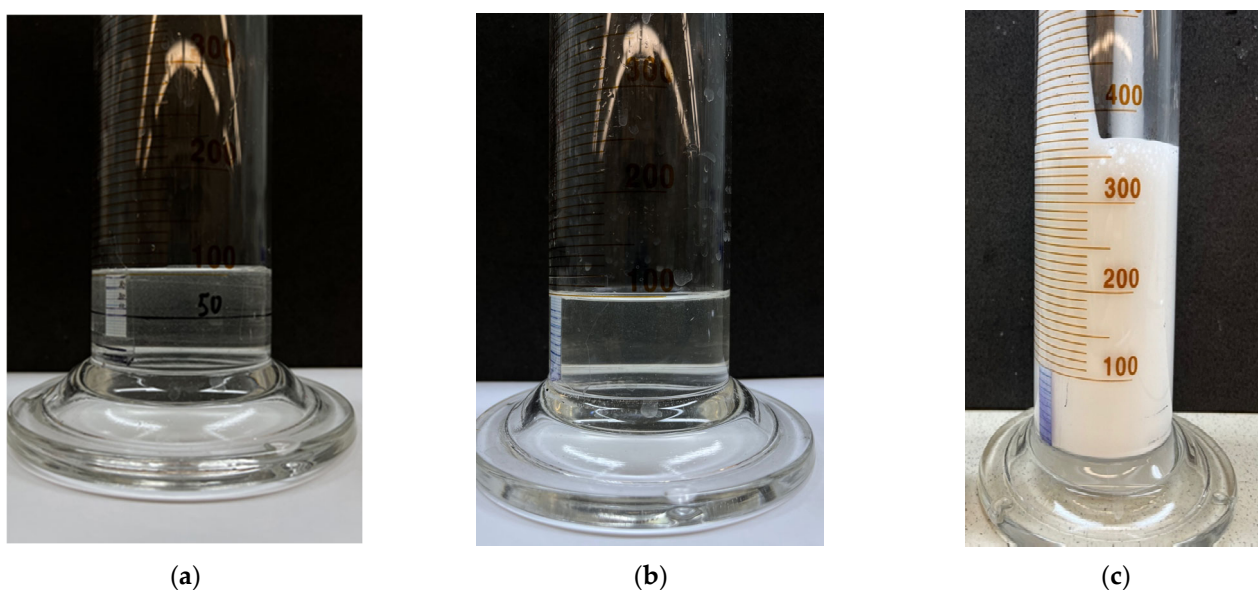


Figure 4. Foam appearance of synthesized compounds: (a) 2b; (b) 2d; and (c) SDS.

4. Discussion

4.1. Evaluation of Hydrate Promoting Effect

Figure 3 and Table 1 show that at concentrations above 250 ppm, all investigated samples exceeded water in the value of gas to hydrate conversion. When increasing the concentration of the reagent from 250 ppm to 500 ppm in general, the conversion rate increases, but upon further increasing the concentration up to 1000 ppm, there was no significant difference in performance; which indicated that 500 ppm could be chosen as the optimal concentration. The highest conversion values ($86 \pm 4\%$) showed samples based on glycerol and pentaerythritol with three and two sulfosuccinate groups, respectively, (2a and 2d). 2b at low concentrations showed a greater promotion effect than 2a, and with increasing concentration this effect was equalized. Samples 2a and 2d at a concentration of 500 ppm achieved conversions similar to SDS at the same concentration but lost out to the commercial promoter in the rate of reaching maximum gas absorption.

Based on the values of the kinetic constants of hydrate formation after 1/2 and 2/3 time after the start of the process, it can be seen that the rate of hydrate formation is generally higher in the presence of samples based on pentaerythritol. The value of the constant $K_{1/2}$ for the sample 2d reaches a maximum at a concentration of 1000 ppm and exceeds the same figure for water by four times (for other samples by two to three times). This means that among the presented reagents, sample 2d forms hydrate at the fastest rate.

4.2. Foam Formation

Foam formation studies have shown that all synthesized samples do not form foam at an optimum concentration of 500 ppm, unlike the well-known commercial reagent SDS (Table 2, Figure 4), which is explained by the lack of a long alkyl chain. The obtained promoters also did not form foam when decomposing methane hydrate formed from their solutions (Figure 5).

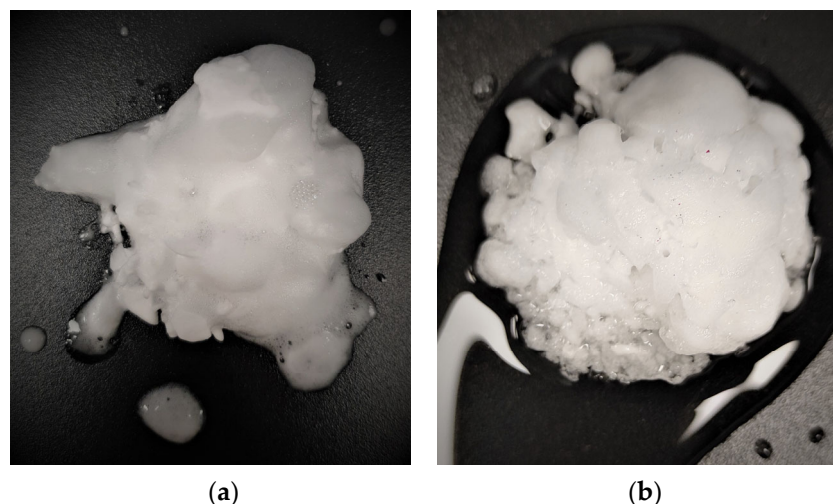


Figure 5. Exterior view of methane hydrate after regasification for samples: (a) SDS; and (b) 2d.

It should be noted that high foam-forming properties of promoters negatively affect the operational characteristics of the hydrate formed by them, as during regasification a persistent foam with a high rate, which can clog equipment and does not allow complete extraction of gas from hydrate, is formed. Thus, promising promoters can be considered as those that, in addition to effective hydrate formation, do not lead to foam formation during gas extraction from the hydrate.

5. Conclusions

Using a high-pressure reactor, the promoting effect of new synthesized reagents based on branched alcohols, glycerol and pentaerythritol, on the formation of methane hydrates was studied. All synthesized reagents significantly increased the conversion of gas to hydrate and the rate of hydrate formation relative to water, while 500 ppm was chosen as the optimal concentration. At this concentration, the foaming of the obtained samples was also studied. Branched alcohol sodium sulfosuccinates did not form stable foam, which is a significant advantage over the well-known reagent sodium dodecyl sulfate, since abundant foaming in the presence of a promoter complicates the extraction of gas from the hydrate during regasification and can lead to clogging of the operating equipment. However, the synthesized reagents still lose to SDS in the rate of hydrate formation. In general, alcohol sulfosuccinates are a promising class of hydrate formation promoters, which can help the development of hydrate technology for the storage and transportation of natural gas.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16010359/s1>, Tables S1–S4: FT-IR spectra data of compounds 2a–d; Figures S1–S8: ^1H NMR and ^{13}C NMR spectra of compounds 2a–d; Figures S9–S12: FT-IR spectra of compounds 2a–d.

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supervision, R.S.P. and M.A.V.; project administration, R.S.P. and M.A.V.; funding acquisition, M.A.V. All authors have read and agreed to the published version of the manuscript.

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