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Employing phosphorylated betaines as kinetic hydrate promoters for gas storage application

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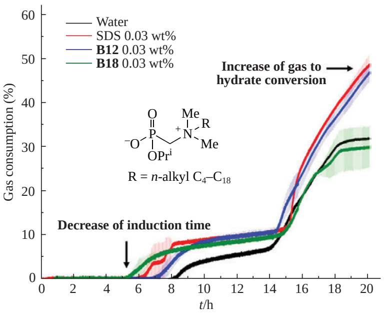
Pursuing an effective promoter of gas hydrate formation remains a relevant issue in the potential development of solidified natural gas technology. The promoting ability of isopropyl [(*N*-alkyl-*N*,*N*-dimethylammonio)methyl]-phosphonate betaines was assessed using rocking cells equipment. The results reveal that the varying alkyl length makes it possible to accelerate either the nucleation or the growth of model natural gas hydrate.

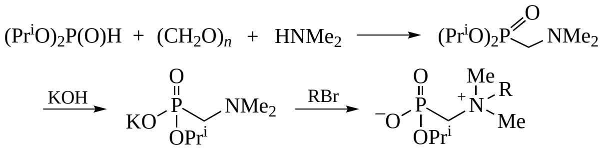


Keywords: gas hydrates, kinetic hydrate promoters, betaines, quaternary ammonium compounds, phosphonates, rocking cells, gas storage, solidified natural gas.

Gas hydrates, which are clathrate compounds, represent promising alternative for storing and transporting natural gas in solid form. This approach is particularly interesting for Russia as a northern country since the natural cold would facilitate hydrate formation and storage. The advantages of the hydrate-based method in comparison with liquefied and compressed natural gas technologies are moderate temperature and pressure conditions as well as safety for people and the environment.[1] Furthermore, gas hydrates have a rather high capacity (up to 170 gas volumes per hydrate volume) and exhibit the self-preservation effect, allowing for gas storage in solid form at atmospheric pressure and temperature below the ice melting point.[2] Gas hydrates have also been considered for gas mixture separation, water desalination, cold storage, and other applications.[3] The primary factor limiting the implementation of hydrate technologies is the low efficiency of gas conversion to the hydrate state. It has been found that promotional agents can increase both the rate of hydrate formation and the process completeness. To date, two types of reagents are distinguished for accelerating the hydrate formation, *viz*. those exerting thermodynamic or kinetic action.[4,5] The former type of reagent shifts the gas (aqueous solution)–hydrate equilibrium curve to lower pressure and higher temperature, thereby increasing the driving force of the hydrate formation process, all other conditions being equal.[6] However, the range of such reagents is extremely limited. Besides, hydrate framework stabilization occurs by incorporating an auxiliary molecule into its cavities, which lowers its gas capacity.[7] In the case of kinetic reagents, various factors related to the interactions of the promoter molecules with both water molecules in solution and the hydrate surface cause the hydrate formation enhancement (for example, the solution–gas and hydrate–hydrate-forming medium interfacial tension play an important role).[8,9] Such substances can be various compounds that exhibit surface activity. The variation in their structure and types is almost unlimited. Numerous kinetic promoters of gas hydrate formation have been reported previously.[10–14] Moreover, new insights into the well-known promoters' action mechanisms are constantly being discovered.[15] However, the structure–property relationship for chemical compounds affecting the hydrate formation process has not yet been completely unraveled.

This work describes zwitterionic phosphorylated betaines as possible intramolecular phosphorylated analogs of quaternary ammonium salts. Zwitterionic compounds are widely used as hair shampoo components,[16] in antifouling applications,[17] in biological and medical fields,[18,19] as surfactants in oil recovery,[20,21] and corrosion inhibitors.[22,23] Amino acids, many of which are zwitter ionic compounds, are being intensively studied for their effect on hydrate formation.[24,25] However, the data on betaine effect on hydrate formation are limited.[26–28] The introduction of higher alkyl substituents to the nitrogen atom would cause the appearance of surface-active properties in such compounds, and it may make them kinetic hydrate promoters.[29] The activity of betaines to increase a methane–propane hydrate formation rate was evaluated in comparison with the known promoter of hydrocarbon gas hydrate growth such as sodium dodecyl sulfate (SDS).

The synthesis of phosphorylated betaines is based on the preparation of α-dialkylamino phosphonates by the Kabachnik–Fields reaction in a three-component system followed by alkaline hydrolysis to give the corresponding potassium salts (Scheme 1).



B4–B18

B4	R = n-C_4H_9	**B12**	R = n-$C_{12}H_{25}$
B6	R = n-C_6H_{13}	**B14**	R = n-$C_{14}H_{29}$
B8	R = n-C_8H_{17}	**B16**	R = n-$C_{16}H_{33}$
B10	R = n-$C_{10}H_{21}$	**B18**	R = n-$C_{18}H_{37}$

Scheme 1

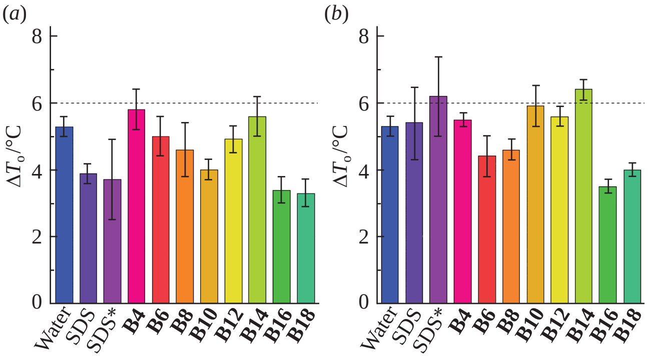


Figure 1 Subcooling values for the samples tested at concentrations of (*a*) 0.03 and (*b*) 0.3 mass%.

In the final step, the reaction between the obtained potassium salts and alkyl bromides occurred at amino group to afford the target ammonium phosphonate betaines. The synthesis of compounds **B8**–**B18** was described elsewhere,[30,31] while lower homologs **B4** and **B6** are new (for details, see Online Supplementary Materials).

The influence of obtained betaines on hydrate formation was studied at 0.03 and 0.3 mass%. The cooling of the system at a constant stirring rate (by rolling a steel ball while the cell is tilted from the horizontal position) allows the hydrate onset subcooling values (Table 1 and Figure 1) and gas absorption into the hydrate (Table 1, Figures 2 and 3) to be determined with good reproducibility. The latter parameter was calculated as follows:

$$\text{Gas consumption} = \frac{P_{\text{wh}} - P_{\text{h}}}{P_{\text{wh}}} \times 100,$$

where P_h, P_wh are the actual pressure with hydrate formed and the hypothetical pressure in the absence of hydrate formation (without hydrate) in the cell at the same temperature, respectively.

The experimental data obtained showed that **B16** and **B18** samples at the studied concentrations significantly reduced hydrate onset subcooling compared with water (almost 2 °C, see Table 1), which suggests the kinetic promotion of hydrate nucleation by these compounds under dynamic conditions. A weaker effect was observed for **B6** and **B8** (less than 1 °C) at 0.3 mass% and **B10** (over 1 °C) at 0.03 mass%. The other betaines either do not affect the hydrate nucleation or have a weak inverse effect (inhibition). The reference SDS also acts as a nucleation promoter at 0.03 mass%. At the same time, judging by the standard deviation, a wider distribution was obtained in the case of 0.03 mass% SDS*, including the subcooling value for **B16** and **B18** samples (no statistically significant difference between them). At a concentration of 0.3 mass%, SDS either did not affect the nucleation of methane–propane hydrate or slightly inhibited this process under experimental conditions. Previously, similar effects of SDS on the nucleation of hydrocarbon gas hydrates depending on the concentration and thermobaric conditions were observed.[32]

Table 1 Results of RC5 rocking cell tests (hydrate onset subcooling ΔT_o and gas consumption).

Sample	Concentration (mass%)	ΔT_o/°C	Gas consumption (%)
Water	–	5.3 ± 0.3	29 ± 4
SDS[a]	0.03	3.9 ± 0.3	13 ± 6
	0.3	5.4 ± 1.1	26 ± 14
SDS*[a]	0.03	3.7 ± 1.2	49 ± 3
	0.3	6.2 ± 1.2	47 ± 6
B4	0.03	5.8 ± 0.6	18 ± 7
	0.3	5.5 ± 0.2	44 ± 2
B6	0.03	5.0 ± 0.6	29 ± 6
	0.3	4.4 ± 0.6	37 ± 4
B8	0.03	4.6 ± 0.8	28 ± 12
	0.3	4.6 ± 0.3	44.9 ± 0.4
B10	0.03	4.0 ± 0.3	42 ± 3
	0.3	5.9 ± 0.6	48 ± 2
B12	0.03	4.9 ± 0.4	47 ± 2
	0.3	5.6 ± 0.3	49.5 ± 0.5
B14	0.03	5.6 ± 0.6	46 ± 2
	0.3	6.4 ± 0.3	48.3 ± 0.2
B16	0.03	3.4 ± 0.4	34 ± 2
	0.3	3.5 ± 0.2	35 ± 6
B18	0.03	3.3 ± 0.4	30 ± 5
	0.3	4.0 ± 0.2	33 ± 6

[a] Sodium dodecyl sulfates SDS and SDS* differ in test parameters (see experimental technique).

The reactor material seems to have some effect (on both nucleation and gas hydrate growth from SDS solutions). For example, it was shown that obtaining reliable data on hydrate growth from SDS solutions in these steel cells requires a unique testing program (compare the gas consumption curves in Figure 2). Obviously, in the case of larger sample volume (15 *vs.* 10 ml) and more intense rocking (±45° deviation from the horizontal axis at 10 min^{-1} *vs.* ±20° deviation at 5 min^{-1}), foam/solution/hydrate ingress into the capillary connecting the cell free volume to the pressure sensor causes its blocking and incorrect displaying of the pressure reading. This assumption is supported by the fact that the hydrate growth from various promoter solutions is virtually independent of stirring (it is required only for the nucleation) and the rapid hydrate formation in the foam.[33,34] Since the attention is rarely paid to this error (for example, capillaries plugging in the same RC5 rig seems to be likely observed[35]), the influence of the mixing regime in the rocking cells setup, cell material, and P, T conditions on the reliability of gas consumption data will be discussed in more detail in our following paper. At the same time, experimental P, T-curves of hydrate formation in the methane–propane–aqueous solution system (see Rocking cells data in Online Supplementary Materials) show that the relative gas consumption is a reliable criterion for comparing the promoters efficiency assessment by rocking cells. Indeed, the volume of the test solution/tilt angle/rocking frequency were 10 ml/±20°/5 min^{-1} for SDS* (RC5), 15 ml/±45°/10 min^{-1} for betaine **B12** (RC5), and 10 ml/±45°/10 min^{-1} for 0.25 wt% Syntanol ALM-7 (RSC6) with

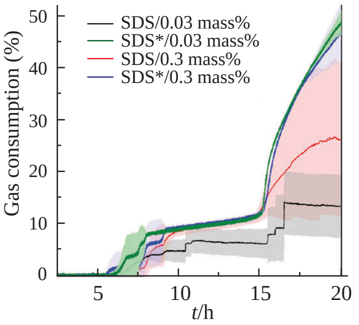


Figure 2 Comparison of gas absorption during hydrate formation from SDS solutions as a function of test parameters (solution volume/rocking angle/rocking frequency): 15 ml/±45°/10 min^{-1} (SDS) and 10 ml/±20°/5 min^{-1} (SDS*).

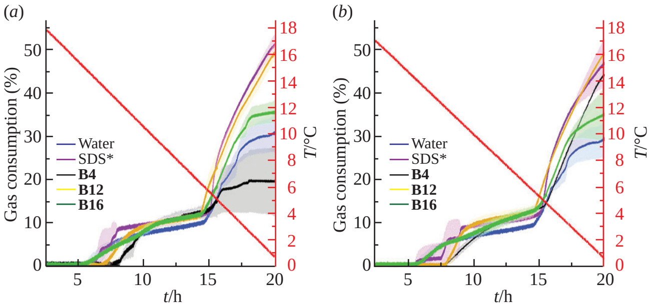


Figure 3 Gas consumption curves for some betaines solutions at (*a*) 0.03 mass% and (*b*) 0.3 mass%; the red line corresponds to the temperature in the cells.

a cell volume equalling 30 and 22 ml for RC5 and RCS6, respectively (data on Sintanol ALM-7 were obtained by the authors earlier[36]). The initial pressure and temperature, the temperature program, and the hydrate-forming gas were the same in all cases. Thus, in rocking cells rigs, the hydrate formation in the presence of growth promoters occurs regardless of gas to liquid volume ratio and the rocking mode; apparently, only thermobaric conditions (the driving force of the process) have an effect. Thus, the data obtained for betaines were compared with SDS*.

Figure 3 and Table 1 show the gas consumption during hydrate formation in the studied solutions. This parameter reached values similar to those of SDS for samples **B12** and **B14** at both investigated concentrations as well as for sample **B10** at 0.3 mass%. In general, an increase in gas consumption rate (by slope after 15 h; see Figure 3) was observed in the series **B4**–**B8**–**B10** (**B6** does not fall on this dependence) up to almost constant value for **B10**, **B12** and **B14** followed by a sharp decrease of this parameter for **B16** and **B18** betaines. The conversion for the latter samples is close to the values for pure water. Taking into account values of subcooling and kinetics of gas absorption, betaine **B12** can be considered optimal. It does not influence hydrate nucleation (within the standard deviation) and ensures rapid gas-to-hydrate binding.

In summary, the length of the alkyl substituent in *N*-alkyl-*N*-[(isopropoxy)(oxido)phosphorylmethyl]-*N*,*N*-dimethylammonium betaines affects both nucleation and growth of methane–propane hydrate. At the same time, the introduction of C_{16} and C_{18} alkyls leads to a significant decrease in hydrate onset subcooling (by about 2 °C) at a low conversion rate (promotion of nucleation), while samples with C_{10}, C_{12} and C_{14} alkyls show gas-to-hydrate absorption dynamics similar to SDS with slight nucleation inhibition for C_{14} substituent (promotion of hydrate growth). Such compounds may be of interest for further design of hydrate formation promoters for developing hydrate-based solidified natural gas technology.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.008.

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