

Article

Study of the Effect of Tetrabutylammonium Halide Aqueous Solutions on the Gas Storage of Methane and Carbon Dioxide

Parisa Naeiji ^{1,2,*}, Tom K. Woo ¹, Ryo Ohmura ³ and Saman Alavi ^{1,*} ¹ Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, ON K1A 0R6, Canada; tom.woo@uottawa.ca² School of Chemical and Bioprocess Engineering, University College Dublin, D04 V1W8 Dublin, Ireland³ Department of Mechanical Engineering, Keio University, 3-14-1 Hiyoshi, Kohoku-Ku, Yokohama 223-8522, Japan; rohmura@mech.keio.ac.jp

* Correspondence: parisa.naeiji@ucd.ie (P.N.); salavish@uottawa.ca (S.A.)

Abstract: In this study, the effect of tetrabutylammonium halide aqueous solutions on the gas storage of CH₄ and CO₂ gases were studied with molecular dynamics (MD) simulations. The results show that the surface tension and the gas molecules adsorbed at the interface decreases and increases, respectively, in the presence of TBAX (X: Br, Cl, F) in the aqueous phase compared to pure water at similar gas pressures. Both of these factors may facilitate gas uptake into cages during semi-clathrate hydrate formation. CO₂ showed a stronger intermolecular interaction with the water molecules since it was preferentially adsorbed at the interface, leading to a higher surface density as compared to CH₄. Moreover, the relative increase in CH₄ adsorption on the surface was because of the hydrophobic interactions between the CH₄ molecules and the n-alkyl chains of the cation. The counter-ions of TBAXs can affect their surface activity. TBAX salts enhance the tetrahedral ordering of water molecules at the interface compared to the bulk, leading to a potential mechanism for forming semi-clathrate hydrates.

Keywords: interfacial tension; gas storage; tetrabutylammonium aqueous solutions; methane; carbon dioxide; gas hydrate



Citation: Naeiji, P.; Woo, T.K.; Ohmura, R.; Alavi, S. Study of the Effect of Tetrabutylammonium Halide Aqueous Solutions on the Gas Storage of Methane and Carbon Dioxide. *Energies* **2023**, *16*, 5001. <https://doi.org/10.3390/en16135001>

Academic Editor: Fabio Montagnaro

Received: 13 May 2023

Revised: 23 June 2023

Accepted: 26 June 2023

Published: 28 June 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Ionic clathrate hydrates, or semi-clathrates, which are formed by water molecules and quaternary ammonium salts, such as tetrabutylammonium bromide (TBAB), chloride (TBAC), and fluoride (TBAF), have attracted attention for their broad range of applications [1–5]. The formation conditions for the semi-clathrate hydrates of tetrabutylammonium halide with different gases, such as CH₄, CO₂, N₂, H₂, and so on, have been measured by some researchers. These semi-clathrate hydrates form under milder conditions compared to canonical gas hydrates, which greatly improves the stability conditions of gas storage. Chapoy et al. showed that TBAB hydrate is desirable for hydrogen storage applications. Binary H₂-TBAB semi-clathrate hydrates have greatly enhanced thermal and low-pressure stability when compared to canonical-structure-II H₂ hydrates. In addition, H₂-TBAB semi-clathrate hydrates have the added advantage that the hydrogen released upon decomposition is extremely pure [6]. Deschamps and Dalmazzone found that high concentrations of TBA salts can enlarge the CH₄/CO₂ hydrate stability zone [7]; however, these concentrations may be unfavorable for the separation of CO₂ from mixtures of gases [8]. It has been shown that the phase equilibrium temperature of gas captured from the semi-clathrate phase increased by a range of ~9–14 K compared to that of gas hydrate formed from a pure water system when the TBAB mass fraction was 0.4 [9]. Cryo-SEM images have shown that the specific surface area of the hydrate crystals significantly increased by adding TBAB, as compared to a pure water system [10]. The effect of the TBAB mass fraction in the solution on semi-clathrate promotion and stability was also studied by

Arjmandi et al. It was shown that hydrate stability increases with TBAB concentration [11]. Hassan et al. found that tetrabutylphosphonium bromide (TBPB) exerted a promoting effect on the equilibrium conditions of CH_4 + TBAB-formed hydrate [12].

TBAB has been shown to reduce the induction time of CH_4 hydrate formation over that of pure water by achieving faster nucleation. It has also been found that a TBAB- CH_4 hydrate system can form at lower pressures compared to those at which pure CH_4 hydrate can be formed [13]. Mohammadi and co-workers investigated the roles of TBAB, TBAC, and TBAF on the kinetics and phase equilibria of CH_4 , CO_2 , and N_2 hydrates [14–17]. They stated that the addition of low-weight fractions of TBAF increases the amount of CH_4 and CO_2 encaged in hydrate cavities and the storage capacity, and decreases the induction time of the hydrate formation process [14,15]. Moreover, the presence of TBAC can moderate CH_4 , CO_2 , and N_2 hydrate formation conditions remarkably, such that the pressure reduction is dependent on the TBAC concentration. By increasing the mass fraction of TBAC in the range of 0.05–0.22, its promotion effect shifts the p-T curves of double gas + TBAC semi-clathrate hydrate to milder stability regions [16]. Fan et al. compared the effect of TBAB, TBAC, and TBAF on CO_2/CH_4 mixed hydrates to the 2.93×10^{-3} mole fraction of TBA halide. The experimental results proved that the hydrate stability region in the presence of TBA salts was enlarged for the three additives in the order of TBAF > TBAC > TBAB, implying that TBAF is the best. At a temperature of 285 K, the phase equilibrium pressure of the CH_4 + CO_2 + TBA halide + water system were 37.4 bar, 27.6 bar, and 9.4 bar, respectively, compared to 73.0 bar for the CO_2 + CH_4 + water system [18]. Hashimoto et al. stated that the CO_2 capture properties of TBAF semi-clathrate hydrate may change with its formation conditions, such as aqueous composition and pressure, due to its complex structure [19].

As it is known that gas hydrates and semi-clathrates tend to form at the solution/gas interface, the interfacial behaviors of TBAX aqueous solutions are important for the investigation of solid semi-clathrate phase formation. Koyanagi and Ohmura showed that the former CO_2 + TBAB semi-clathrate hydrate crystals settled downward and the latter grew to form a hydrate film covering the interface [20]. Microstructure pictures showed that the TBAB solution could make the surface of the CH_4 semi-clathrate more ordered and tighter. A PXRD revealed that an orthorhombic semi-clathrate structure was induced by the addition of gas in the presence of TBAB, due to the larger potential gas capacity in that solid phase, as compared to that of a tetragonal solid semi-clathrate structure [21]. Since the study of the molecular behavior and morphology of the hydrate via experimental instruments is not always possible, it is useful to apply molecular simulations for a comprehensive investigation of the interfacial phenomena of these phases. This study is an extension of our research on the interfacial properties of CH_4/CO_2 + TBAB (aq); the interfacial properties of TBAC and TBAF aqueous solutions in the presence of pure CH_4 and CO_2 and their mixtures were also investigated by using molecular dynamics (MD) simulations. The purpose of this work is to understand how TBA salts may affect gas storage through gas hydrate formation.

2. Materials and Methods

DL_POLY program version 2.20 [22] was used for performing the molecular dynamics (MD) simulations for the TBAX solutions at 273.15 and 298.15 K. To make an aqueous phase of TBAX, a $4 \times 4 \times 2$ -unit cell replica of TBAX semi-clathrate hydrate was melted at 500 K using an NVT ensemble. This phase has the same composition as the orthorhombic TBAB·38 H_2O semi-hydrate phase, containing 2432 water molecules and 64 TBAX molecules. The unit cell parameters for the TBAB·38 H_2O framework were: orthorhombic, space group Pmma, $a = 21.0329(15)$ Å, $b = 12.5972(9)$ Å, and $c = 12.0333(8)$ Å [23]. A simulation box of around $48 \times 50 \times 100$ Å³ was considered, with the aqueous solution in the center of the box and a vacuum on each side of the solution in the z direction to provide the free interfaces, as shown in Figure 1. Thereafter, the temperature of the system was reduced to 298 K for 2 ns, and finally it was equilibrated for 2 ns at the desired temperature. For

the simulations under higher pressures, gas molecules were added randomly into the empty space in the simulation cell and allowed to relax at a temperature of 400 K using *NVE* ensemble simulations, while the aqueous solution was frozen. Then, the system was equilibrated for 100 ps using an *NVT* ensemble at a given temperature. Finally, the system was simulated for 2 ns to collect the interfacial properties of the gas solution. The system pressure was measured according to the number of CH_4 and CO_2 molecules in the gas phase to simulate a constant volume.

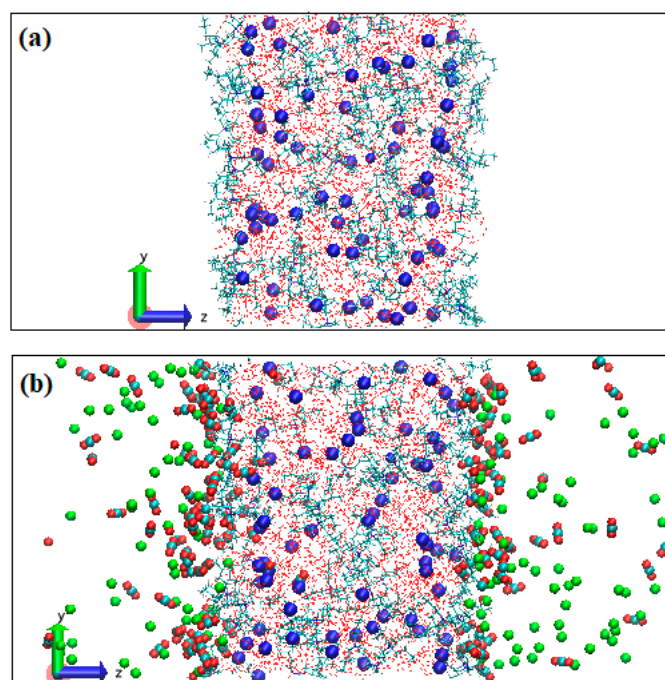


Figure 1. The initial configuration of the equilibrated TBAX aqueous solution at 273 K, viewed on the (100) surface, (a) in the absence of gases in contact with the surface, and (b) in the contact with a gas phase mixture of CO_2 and CH_4 gases. Water molecules are represented by red-dashed lines indicating hydrogen bonding. TBA^+ ions, anions, CH_4 , and CO_2 are, respectively, shown with line structures, violet, green, and Cyan-red spheres.

The water, CH_4 , and CO_2 molecules were simulated with the TIP4P/2005 model [24], TraPPE-UA model [25], and TraPPE rigid model [26], respectively. The TBAB, TBAC, and TBAF molecules were modeled with GAFF (General AMBER Force Field) [27] to determine the Lennard–Jones parameters. The electrostatic interactions were also calculated using the CHELPG method [28]. The CHELPG calculations were conducted with the Gaussian 09 suite of programs [29] at the B3LYP/6-311 ++ G(d,p) level of theory.

Table 1 gives the force field parameters used in this work. A cutoff radius of 23 Å was chosen for the van der Waals interactions, while long-range electrostatic interactions were handled using the Ewald method, with a relative error of 10^{-6} . Detailed information for the force field was given in our previous work [30]. The simulation was performed with periodic boundary conditions (PBCs) in all directions and a long cutoff radius of 23 Å gave the converged values of the interfacial tension for the simulated systems. The dimension of the system in the *z* direction was chosen to be large enough so that even with the long cutoff radius, the system and its images in the *z* direction would not interact. In this way, the interfacial behavior would not be affected by the PBCs.

Table 1. The force field parameters used in the simulation [24–27].

Molecule	Atom	$\sigma/\text{\AA}$	$\epsilon/\text{kcal mol}^{-1}$	q/e
H ₂ O	O	3.159	0.1852	0.0000
	H	0.0000	0.0000	0.5564
	M	0.0000	0.0000	−1.1128
CO ₂	C	2.800	0.0536	0.7000
	O	3.050	0.1569	−0.3500
CH ₄ (UA)	C	3.730	0.2941	0.0000
	C	3.340	0.1090	−1.3360 ^a
TBA ⁺	H	H(CH ₃): 1.960 H(CH ₂): 2.649	0.0160	1.7760 ^a
	N	3.250	0.1700	0.5600
Br [−]		3.97	0.2055	−1.0000
Cl [−]		3.65	0.1984	−1.0000
F [−]		3.12	0.0610	−1.0000

^a Sum of charges of all C or H atoms.

The interfacial tension, γ , for the two simulation sets of solution/vacuum and solution/gas was calculated by the following equation [31]:

$$\gamma = \frac{L_z}{2} \left(P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right) \quad (1)$$

where P_{xx} , P_{yy} , and P_{zz} are the diagonal components of the pressure tensor and L_z is the length of the simulation box along the z direction.

3. Results

This study is an extension of our previous research on the interfacial properties of TBAB (aq), with and without the presence of CH₄ and CO₂ [30]. In this study, to determine the effect of the anion size and charge density of the tetrabutylammonium halides on the interfacial properties of gas/water systems, aqueous solutions of TBAC and TBAF were simulated, and their results were compared to those of the TBAB systems in our previous work [30]. The z -density profiles for the water molecules and ions in the pure TBAC (aq) and TBAF (aq) at 273.15 K, as well as that for a pure water phase at the same temperature, are shown in Figure 2. The z density for the water across the slab in the TBAX solution is non-uniform, with a higher density near the solution–vacuum interface, as opposed to the interface of the pure water. In addition, the TBA⁺ (atoms N and C) and anions are inhomogeneously distributed in the aqueous phase along the z direction, such that the TBA⁺ ions have the highest density at the interface, and the anions are close to the maximum density of the water molecules at the interface and the bulk of the solution.

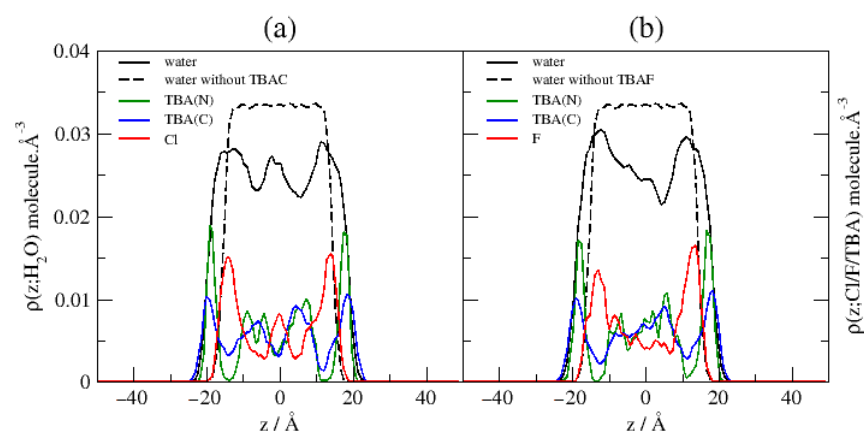
**Figure 2.** The z -density profiles for water, Cl/F, and TBA⁺ (atoms C and N) in the (a) TBAC- and (b) TBAF-water systems at 273.15 K. The z -density profiles for pure water are shown with dashed lines.

Figure 3 shows the z -density profiles of water, CH_4 , CO_2 , Cl^- , and TBA^+ in the water-TBAC/gas system at 298.15 K and at two different pressures. As shown, the z -density profiles of the water molecules are not so sensitive to the pressure and anion type, while the TBA^+ cations' z density at the interface with non-polar CH_4 gas is slightly increased when compared to that of the solution exposed to CO_2 . It is obvious that, at approximately the same gas pressure, the gas molecules' density at the interface in the TBAC solutions is higher than that in the pure water system; it also increases with an increasing gas pressure at the solution interface. Moreover, the surface density of the CO_2 is enhanced to a greater absolute degree compared to that of CH_4 at a similar pressure, because the CO_2 molecules show stronger intermolecular interactions with the water molecules at the interface.

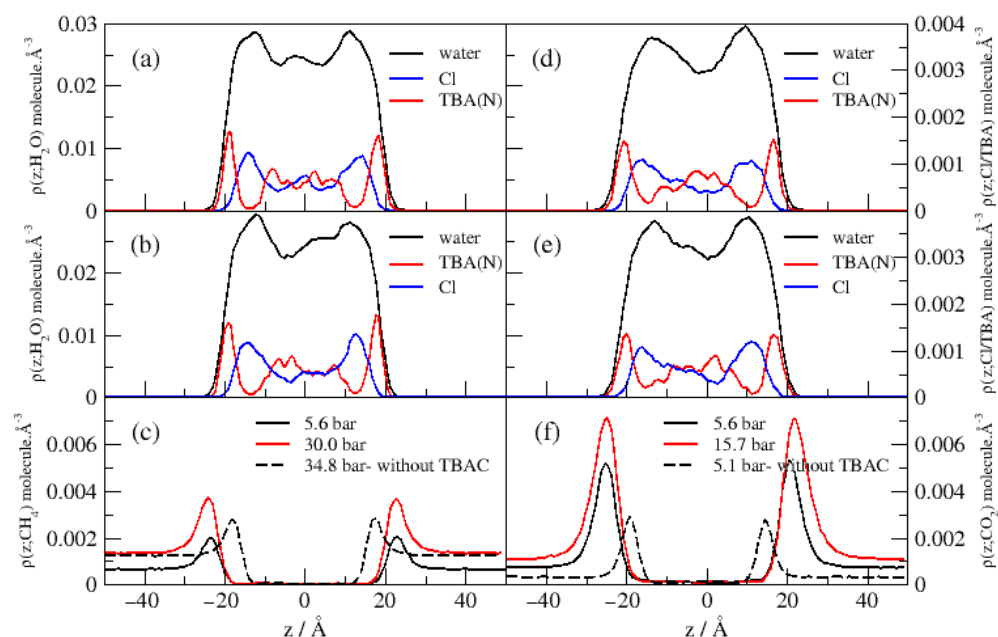


Figure 3. The z -density profiles of the water-TBAC/ CH_4 system for water, Cl^- , and TBA^+ (atom N) at (a) 5.6 bar, (b) 30.0 bar, and for (c) CH_4 . The z -density profiles of the water-TBAC/ CO_2 system for water, Cl^- , and TBA^+ (atom N) at (d) 5.6 bar, (e) 15.7 bar, and for (f) CO_2 at two gas-phase hydrostatic pressures under 298.15 K. The z -density profiles for the gases at the same pressure in a pure water system are also given in (b,d).

As given in Tables 2 and 3, the results are generally similar to those for TBAB, with some notable differences. From Table 2, the interfacial tension of the TBAC and TBAF solutions are less by ~3–15% compared to that of pure water, which is approximately the same decrease as observed in the TBAB aqueous solution at the same concentration. For a gas/liquid system, the presence of TBAC or TBAF in the solution also causes a decrease of 10–40% in the surface tension, and an increase of 2–145% in the adsorbed gas molecules at the interface (adsorption percent), compared to those for gas/water systems at similar pressures. A general comparison of the results for the two gas/aqueous solutions shows that the adsorption percent of CH_4 molecules was more sensitive to the addition of tetrabutylammonium halides, with an increase of up to 145%, as compared to the pure water system. The interfacial tension of the systems, including CO_2 , was also highly affected by these ions. As previously shown, the z -density profiles of the ions of TBAX are not appreciably affected by changing the gas pressure applied to the system. It seems that monolayer coverage of the surface was achieved by the TBAX ions and so the excess gas molecules could not be absorbed at the surface at higher pressures. This is similar to the findings of previous work performed by Massoudi and King, which showed that surface-active TBAB achieves complete monolayer coverage, leaving the surface exposed to the gas unchanged at concentrations in excess of this [32].

Table 2. The calculated interfacial tension ($\text{mN}\cdot\text{m}^{-1}$) at 273.15 and 298.15 K at different gas hydrostatic pressures. The total number of gas molecules in the simulation, $N_{\text{gas}}(\text{tot})$, required to generate the stated gas pressure is given for each simulation, along with the number of adsorbed gas molecules at the TBAX (aq)/gas interface, $\langle N_{\text{gas}}(\text{ad}) \rangle$.

System	273.15 K				298.15 K			
	P_{zz}/bar	$N_{\text{gas}}(\text{tot})$	$\langle N_{\text{gas}}(\text{ad}) \rangle$	γ	P_{zz}/bar	$N_{\text{gas}}(\text{tot})$	$\langle N_{\text{gas}}(\text{ad}) \rangle$	γ
Pure H_2O		0	0	70.1		0	0	68.4
TBAB (aq)		0	0	67.6		0	0	57.5
TBAC (aq)		0	0	67.9		0	0	57.6
TBAF (aq)		0	0	65.0		0	0	60.6
Pure $\text{H}_2\text{O}/\text{CH}_4$	17.9	133	47.1	67.5	34.8	106	19.3	62.4
TBAB (aq)/ CH_4	1.7	133	63.1	65.3	5.4	133	53.4	54.8
	22.6	266	114.8	62.5	30.4	266	101.4	47.8
TBAC (aq)/ CH_4	1.7	133	62.9	60.4	5.6	133	54.9	56.9
	22.7	266	116.7	59.8	30.0	266	103.2	49.0
TBAF (aq)/ CH_4	1.6	130	61.6	64.3	4.8	130	55.6	54.6
	21.9	266	118.6	60.7	29.2	266	118.6	51.1
Pure $\text{H}_2\text{O}/\text{CO}_2$	5.6	133	101.1	63.5	5.1	50	27.3	61.4
TBAB (aq)/ CO_2	1.5	350	267.2	51.2	4.9	266	176.2	43.9
	4.7	450	338.2	41.7	15.2	400	257.4	42.4
TBAC (aq)/ CO_2	1.3	350	261.1	47.6	5.6	266	174.3	42.3
	4.5	450	331.0	38.7	15.7	400	254.3	39.5
TBAF (aq)/ CO_2	1.6	345	259.9	45.2	5.8	266	174.8	42.1
	4.9	445	330.6	47.8	16.3	400	255.0	42.5

Table 3. The calculated interfacial tension ($\text{mN}\cdot\text{m}^{-1}$) and the simulated average number of adsorbed gas molecules, $\langle N_{\text{X}}(\text{ad}) \rangle$, in the water-TBAX/($\text{CO}_2 + \text{CH}_4$) system, with $x_{\text{CO}_2} \approx 0.35$. The total number of carbon dioxide (C) and methane (M) molecules in the simulation are also given.

T/K	Solution	P_{zz}/Bar	$\text{CH}_4:\text{CO}_2$ in the Gas Phase mol%	$\text{CH}_4:\text{CO}_2$ at the Surface mol%	CH_4		CO_2		γ
					$N_{\text{M}}(\text{tot})$	$\langle N_{\text{M}}(\text{ad}) \rangle$	$N_{\text{C}}(\text{tot})$	$\langle N_{\text{C}}(\text{ad}) \rangle$	
273.15	Pure H_2O	24.9	70.7:29.3	33.2:66.8	133	48.6	133	98.0	61.3
	TBAB (aq)	10.8	66.7:33.3	37.4:62.6	133	56.8	133	94.9	52.5
		37.4	66.6:33.4	35.9:64.1	266	102.9	266	184.1	44.6
	TBAC (aq)	10.9	66.5:33.4	38.8:61.2	133	61.6	133	97.1	50.5
		37.7	66.1:33.9	35.8:64.2	266	101.3	266	181.4	46.2
	TBAF (aq)	10.2	67.1:32.9	39.0:61.0	133	63.2	133	98.7	54.1
		37.2	64.8:35.2	37.1:62.9	266	105.5	266	178.7	47.4
	TBAB (aq)	18.4	62.4:37.6	37.2:62.8	133	48.6	133	82.1	47.8
		56.2	61.1:38.8	36.2:63.8	266	86.1	266	151.7	36.8
	TBAC (aq)	17.9	62.3:37.7	38.6:61.4	133	53.4	133	84.8	46.2
298.15		54.7	61.1:38.9	36.3:63.7	266	86.5	266	151.5	39.6
	TBAF (aq)	18.4	62.8:37.2	38.2:61.8	133	52.9	133	85.7	43.7
		55.0	61.2:38.8	36.7:63.3	266	89.2	266	153.7	43.1

The effect of hydrostatic pressures and temperature on the interfacial tension of the TBAX (aq)/gas systems are shown in Figure 4. The interfacial tensions decrease as the temperature increases and the pressure decreases, as expected. At approximately the same pressure, the interfacial tensions of TBAX (aq)/ CO_2 are significantly lower than those of TBAX (aq)/ CH_4 , due to the higher surface adsorption of CO_2 gas. In addition, it can be seen that there is no significant difference between the three aqueous solutions in interfacial tension; however, it could be that TBAC (aq) mainly affects both gas/aqueous solution systems more than the other two aqueous solutions.

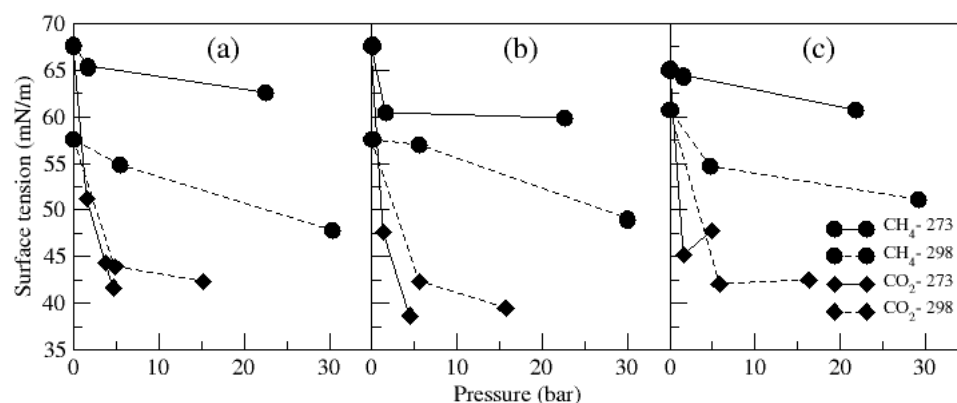


Figure 4. The calculated interfacial tension of (a) water-TBAB/pure gas, (b) water-TBAC/pure gas, and (c) water-TBAF/pure gas systems at different gas phase pressures (P_{zz}) from this work at 273.15 K and 298.15 K.

The results for the surface tension and the number of adsorbed molecules at the surface of the gas mixture/TBAX aqueous systems are given in Table 3. The effects of TBAC and TBAF on CO₂ + CH₄ gas mixtures/aqueous solutions are similar to those of TBAB. With the same starting number of molecules in the gas phase, it was observed that TBAC and TBAF significantly decreased the gas pressure, by as much as 56% and 59%, respectively, compared to the pure water system. Additionally, the surface tension at the gas-solution interface decreased compared to that of the gas–water interface (~12–17%). They also increased the gas adsorption of CH₄ (~26–30%), with no significant change in the adsorption of CO₂ molecules.

To better understand the effect of tetrabutylammonium salts on the water surface, the F_3 profiles for the aqueous phase in pure water, and the TBAX (X: Br, Cl, F) solutions along the z direction at 273.15 and 298.15 K, were calculated and are shown in Figure 5. The F_3 local-order parameter can be used as a measure of the tetrahedral arrangement of the water molecules of the different layers parallel to the z direction of the simulation box, in which case the mean value of the $F_3(z)$ parameter is reported for each layer separately. The F_3 value becomes zero when the water molecules are perfectly tetrahedrally coordinated, such as in ice and in clathrate hydrate phases [31,33]. F_3 can be defined as [33]:

$$F_{3i} = \left\langle \left[\cos\theta_{jik} \cos\theta_{jik} + \cos^2 109.47 \right]^2 \right\rangle_{jk} = \begin{cases} 0.1 \text{ liquid water} \\ 0.0 \text{ solid water (ice, hydrate)} \end{cases} \quad (2)$$

where atom i is in the center of a spherical shell of 0.35 nm, including atoms j and k . θ_{jik} indicates the angle between the three oxygen atoms of the water molecules that are close together.

Figure 5 shows that the water molecules in the central regions of the slabs have F_3 values between 0.08 and 0.09, which are characteristic of liquid water. The F_3 parameter decreases in all three solutions at the Gibbs dividing surface and moves further into the gas region, implying that water molecules have more ordered tetrahedral arrangements in the interface region than in the bulk, as also previously observed by Reed and Westacott [34]. The decrease in the F_3 value at the surface compared to the bulk suggests that the water at the TBAB (aq) interface is structured to facilitate the formation of clathrates with gas molecules that may be present. If there are no gas molecules present, the surface is also in a suitable configuration to form TBAX semi-clathrate hydrates with empty D cages or ice [34]. The presence of TBAX at the interface in the solution leads to a sharper decrease in the F_3 parameter for the water of the interfacial region compared to that of pure water. Tamaki (1967) states that the strong internal cohesion of the water structure causes a strong association between the cations and anions of tetrabutylammonium halides near

the interface to minimize the disturbance to the water phase structure [35]. This may then enhance the rate of semi-clathrate hydrate formation.

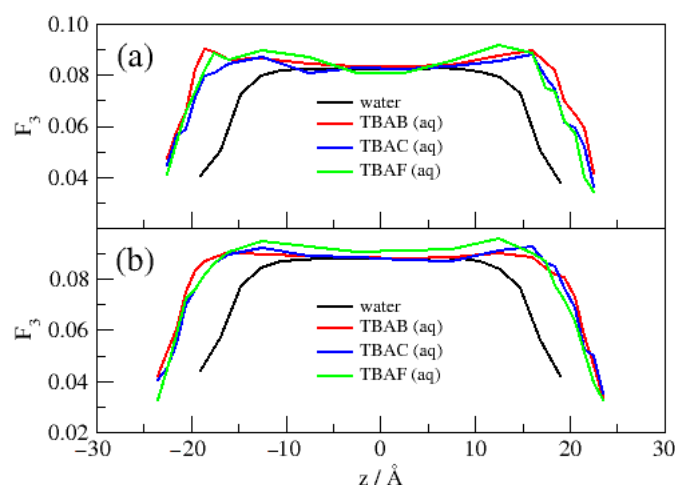


Figure 5. The F_3 profile for pure water and TBAX (aq) (X: Br, Cl, F) solutions along the z direction at (a) 273.15 and (b) 298.15 K.

Figure 6 shows the halide–water radial distribution functions (RDF) in the TBAX aqueous solutions. Distinct peaks at around 2.4–3.2 Å are observed for the X–water RDFs, with the relative heights implying that the F^- ions had the strongest interactions with the water molecules in the solution and at the interface. It was previously found that the lifetimes of chloride and bromide ion–water hydrogen bonds are shorter than those of fluoride ion–water hydrogen bonds, but longer than those of water–water hydrogen bonds. In addition, the hydration shell of fluoride is much more rigid than that of other ions, implying it may be more stable [36].

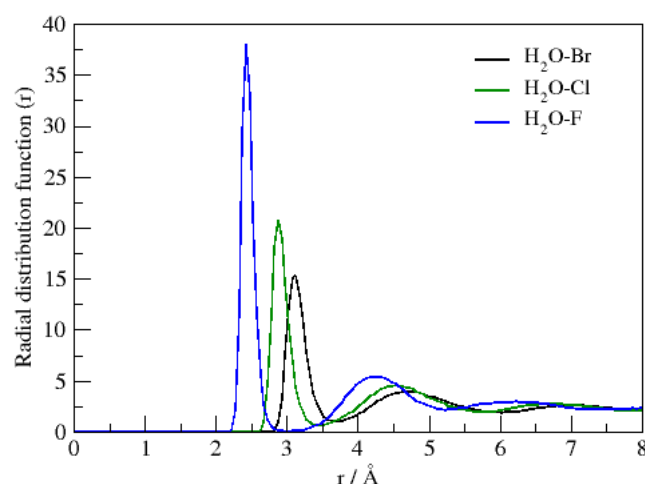


Figure 6. Radial distribution functions of Br^- , Cl^- , and F^- with water oxygen in the TBAX (aq) (X: Br, Cl, F) system at 273.15 K.

These results point to TBAF causing greater changes in the tetrahedral ordering of water molecules at the solution bulk and interface, implying different thermodynamics and kinetics of TBAF semi-clathrate hydrate formation.

Figure 7 represents a general comparison of the three TBAX (X: Br, Cl, F) solutions for the adsorption percent of gas molecules and surface tension at the gas/liquid interface. In the presence of the gas mixture, TBAF often increased gas adsorption and TBAB had the lowest adsorption value. The effect of the anion type of TBAX on the surface tension is not clear; nevertheless, it was found that TBAF often causes a greater decrease in surface tension

at low pressures, while further surface tension decreases were observed in the presence of TBAB and TBAC for both pure and mixed gas systems at high pressures. However, while the anions are primarily positioned inside the surface of the TBAX aqueous solution and interact less strongly with the gases at the solution surface, they can still affect the interfacial properties of TBAX aqueous solutions, and consequently gas capturing into the hydrate cavities.

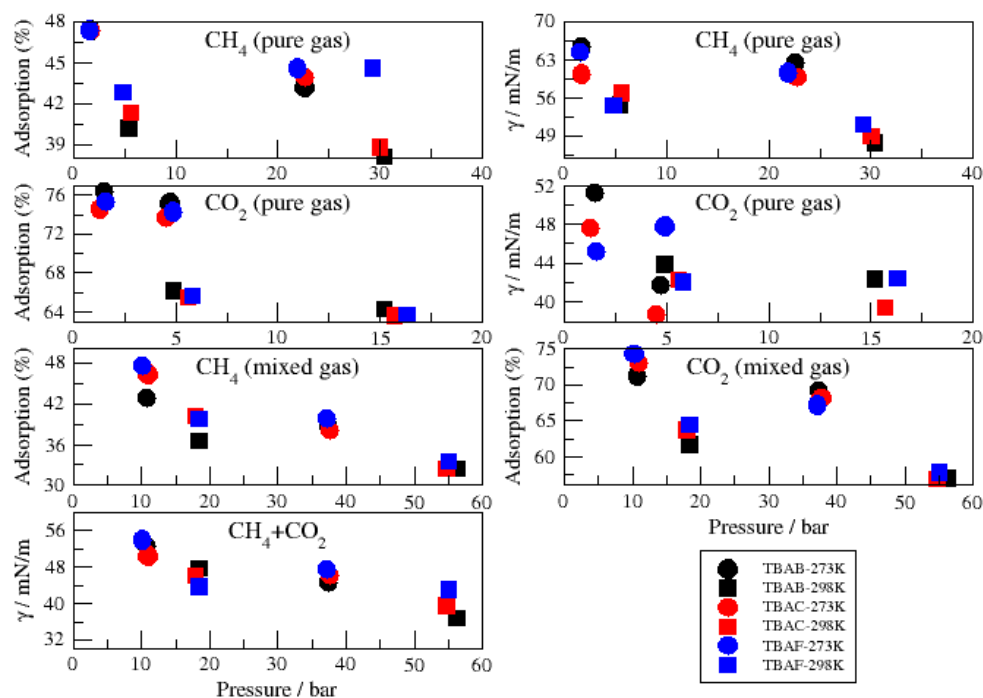


Figure 7. The adsorption of gas molecules and surface tension of TBAX (X: Br, Cl, F) solutions/gas systems.

4. Discussion

The interfacial behavior of aqueous solutions of TBAB, TBAC, and TBAF with and without CH_4 and CO_2 gases was investigated using molecular dynamics (MD) simulations. Since the TBAX aqueous phase causes a decrease in surface tension and an increase in gas adsorption at the interface compared to pure water at similar gas pressures, it may help facilitate gas uptake into cages during the semi-clathrate hydrate formation process. The presence of TBAX at the interface leads to an increased rate of the tetrahedral ordering of water molecules in the interfacial region. The F^- , Cl^- , and Br^- halide ions have different hydrogen bonding strengths and lifetimes with water, which can also affect the tetrahedral ordering of the water molecules in the bulk. The radial distribution function of the TBAX aqueous systems for X-water show that the F^- ions had the strongest interactions with water molecules.

The TBA^+ and anions were heterogeneously distributed in the solution with respect to the z direction, so that the TBA^+ ions had the highest density at the interface, and the anions were located near the peak densities of the water molecules. The hydrophobic interactions between the n -alkyl chains of the cation and CH_4 led to a relative increase in CH_4 adsorption on the surface. In the presence of mixed gas, TBAF often increased gas adsorption and TBAB mostly had the lowest value. As a result, TBAF causes a further change in the tetrahedral arrangement of the water molecules at the solution bulk and interface, implying probably a greater impact on semi-clathrate hydrate formation.

In addition, there is an interesting insight that the ionic polarity index [37] could be considered in future work to quantify the polarity of the different anions and investigate the anion effect on gas capture. However, two points must be considered. First, in an aqueous solution, the polarity of the anions may manifest differently than in pure ionic

liquids, for which this polarity index was defined. Second, as seen in Figures 2 and 3, the anions are actually positioned inside the surface of the TBAX aqueous solution, and interact less strongly with the gases at the solution's surface.

Author Contributions: Conceptualization, R.O. and S.A.; Methodology, P.N., R.O. and S.A.; Software, R.O.; Validation, P.N.; Formal analysis, P.N., R.O. and S.A.; Investigation, P.N. and S.A.; Resources, T.K.W.; Data curation, S.A.; Writing—original draft, P.N.; Writing—review & editing, T.K.W., R.O. and S.A.; Visualization, P.N. and S.A.; Supervision, T.K.W. and S.A.; Project administration, S.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare there are no conflict of interest.

References

- Ogoshi, H.; Takao, S. Air-conditioning system using clathrate hydrate slurry. *JFE Tech. Rep.* **2004**, *3*, 1–5.
- Sakamoto, J.; Hashimoto, S.; Tsuda, T.; Sugahara, T.; Inoue, Y.; Ohgaki, K. Thermodynamic and raman spectroscopic studies on hydrogen+tetra-n-butyl ammonium fluoride semi-clathrate hydrates. *Chem. Eng. Sci.* **2008**, *63*, 5789–5794. [\[CrossRef\]](#)
- Mahmoudi, B.; Naeiji, P.; Varaminian, F. Study of tetra-n-butylammonium bromide and tetrahydrofuran hydrate formation kinetics as a cold storage material for air conditioning system. *J. Mol. Liq.* **2016**, *214*, 96–100. [\[CrossRef\]](#)
- Xu, J.; Chen, Q.; Du, J. Promotion of methane storage in tetra-n-butylammonium sulfate semi-clathrate hydrate by inducing pure methane hydrate. *Chem. Eng. Sci.* **2021**, *417*, 127988. [\[CrossRef\]](#)
- Irannezhad, H.; Javanmardi, J.; Rasoolzadeh, A.; Mehrabi, K.; Mohammadi, A.H. Semi-clathrate hydrate phase stability conditions for methane + tetrabutylammonium bromide (TBAB)/tetrabutylammonium acetate (TBAA) + water system: Experimental measurements and thermodynamic modeling. *Oil Gas Sci. Technol.* **2021**, *76*, 75. [\[CrossRef\]](#)
- Chapoy, A.; Anderson, R.; Tohidi, B. Low-pressure molecular hydrogen storage in semi-clathrate hydrates of quaternary ammonium compounds. *J. Am. Chem. Soc.* **2007**, *129*, 746–747. [\[CrossRef\]](#)
- Deschamps, J.; Dalmazzone, D. Dissociation enthalpies and phase equilibrium for TBAB semi-clathrate hydrates of N₂, CO₂, N₂ + CO₂ and CH₄ + CO₂. *J. Therm. Anal. Calorim.* **2009**, *98*, 113–118. [\[CrossRef\]](#)
- Li, X.S.; Xia, Z.M.; Chen, Z.Y.; Yan, K.F.; Li, G.; Wu, H.J. Gas hydrate formation process for capture of carbon dioxide from fuel gas mixture. *Ind. Eng. Chem. Res.* **2010**, *49*, 11614–11619. [\[CrossRef\]](#)
- Zang, X.; Wang, J.; Zhou, X.; Wan, L.; Liang, D. Phase equilibria of the synthesized ternary CH₄/CO₂/N₂ mixed-gas hydrates in tetrabutylammonium bromide aqueous solutions at different concentrations. *J. Chem. Eng. Data* **2021**, *66*, 1290–1295. [\[CrossRef\]](#)
- Zang, X.; Wang, J.; He, Y.; Zhou, X.; Liang, D. Formation kinetics and microscopic characteristics of synthesized ternary gas mixture hydrates in TBAB aqueous solutions. *Energy* **2022**, *245*, 123327. [\[CrossRef\]](#)
- Arjmandi, M.; Chapoy, A.; Tohidi, B. Equilibrium data of hydrogen, methane, nitrogen, carbon dioxide, and natural gas in semi-clathrate hydrates of tetrabutyl ammonium bromide. *J. Chem. Eng. Data* **2007**, *52*, 2153–2158. [\[CrossRef\]](#)
- Hassan, H.; Zebardast, S.; Gandomkar, M. A new highly stable methane hydrate from the synergic mixture of common promoters: Experimental and modeling surveys. *J. Nat. Gas. Sci. Eng.* **2021**, *93*, 104056. [\[CrossRef\]](#)
- Mech, D.; Gupta, P.; Sangwai, J.S. Kinetics of methane hydrate formation in an aqueous solution of thermodynamic promoters (THF and TBAB) with and without kinetic promoter (SDS). *J. Nat. Gas. Sci. Eng.* **2016**, *35*, 1519–1534. [\[CrossRef\]](#)
- Mohammadi, A. The roles TBAF and SDS on the kinetics of methane hydrate formation as a cold storage material. *J. Mol. Liq.* **2020**, *309*, 113175. [\[CrossRef\]](#)
- Mohammadi, A.; Pakzad, M.; Mohammadi, A.H.; Jahangiri, A. Kinetics of (TBAF + CO₂) semi-clathrate hydrate formation in the presence and absence of SDS. *Pet. Sci.* **2018**, *15*, 375–384. [\[CrossRef\]](#)
- Mohammadi, A.; Manteghian, M.; Mohammadi, A.H. Phase equilibria of semiclathrate hydrates for methane + tetra n butylammonium chloride (TBAC), carbon dioxide + TBAC, and nitrogen + TBAC aqueous solution systems. *Fluid Phase Equilibria* **2014**, *381*, 102–107. [\[CrossRef\]](#)
- Mohammadi, A.; Manteghian, M.; Mohammadi, A.H. Dissociation data of semiclathrate hydrates for the systems of tetra-n butylammonium fluoride (TBAF) + methane + water, TBAF + carbon dioxide + water, and TBAF + nitrogen + water. *J. Chem. Eng. Data* **2013**, *58*, 3545–3550. [\[CrossRef\]](#)
- Fan, S.; Li, Q.; Nie, J.; Lang, X.; Wen, Y.; Wang, Y. Semiclathrate hydrate phase equilibrium for CO₂/CH₄ gas mixtures in the presence of tetrabutylammonium halide (bromide, chloride, or fluoride). *J. Chem. Eng. Data* **2013**, *58*, 3137–3141. [\[CrossRef\]](#)
- Hashimoto, H.; Ozeki, H.; Yamamoto, Y.; Muromachi, S. CO₂ capture from flue gas based on tetra-n-butylammonium fluoride hydrates at near ambient temperature. *ACS Omega* **2020**, *5*, 7115–7123. [\[CrossRef\]](#) [\[PubMed\]](#)
- Koyanagi, S.; Ohmura, R. Crystal growth of ionic semiclathrate hydrate formed in CO₂ gas + tetrabutylammonium bromide aqueous solution system. *Cryst. Growth Des.* **2013**, *13*, 2087–2093. [\[CrossRef\]](#)

21. Shi, L.; Shen, X.; Ding, J.; Liang, D. Experimental study on the formation kinetics of methane hydrates in the presence of tetrabutylammonium bromide. *Energy Fuel* **2017**, *31*, 8540–8547. [\[CrossRef\]](#)
22. Smith, W.; Forester, T.R. DL_POLY_2.0: A general purpose parallel molecular dynamics simulation package. *J. Mol. Graph.* **1996**, *14*, 136–141. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Muromachi, S.; Udachin, K.A.; Alavi, S.; Ohmura, R.; Ripmeester, J.A. Selective occupancy of methane by cage symmetry in TBAB ionic clathrate hydrate. *Chem. Commun.* **2016**, *52*, 5621–5624. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Abascal, J.L.F.; Sanz, E.; García Fernández, R.; Vega, C. A potential model for the study of ices and amorphous water: TIP4P/Ice. *J. Chem. Phys.* **2005**, *122*, 234511. [\[CrossRef\]](#)
25. Martin, M.G.; Ilja Siepmann, J. Transferable potentials for phase equilibria. 1. United-atom description of n-alkanes. *J. Phys. Chem. B* **1998**, *102*, 2569–2577. [\[CrossRef\]](#)
26. Potoff, J.J.; Siepmann, J.I. Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide and nitrogen. *AIChE J.* **2001**, *47*, 1676–1682. [\[CrossRef\]](#)
27. Wang, J.; Wolf, R.M.; Caldwell, J.W.; Kollman, P.A.; Case, D.A. Development and testing of a general AMBER force field. *J. Comput. Chem.* **2004**, *25*, 1157–1174. [\[CrossRef\]](#)
28. Breneman, C.M.; Wiberg, K.B. Determining atom-centered monopoles from molecular electrostatic potentials. The need for high sampling density in formamide conformational analysis. *J. Comput. Chem.* **1990**, *11*, 361. [\[CrossRef\]](#)
29. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09, Revision D.01*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
30. Naeiji, P.; Woo, T.K.; Ohmura, R.; Alavi, S. Molecular dynamics simulations of interfacial structure, dynamics, and interfacial tension of tetrabutylammonium bromide aqueous solution in the presence of methane and carbon dioxide. *J. Chem. Phys.* **2022**, *157*, 154702. [\[CrossRef\]](#)
31. Alavi, S. *Molecular Simulations: Fundamentals and Practice*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2020.
32. Massoudi, R.; King, A.D., Jr. Effect of pressure on the surface tension of aqueous solutions. Adsorption of hydrocarbon gases, carbon dioxide, and nitrous oxide on aqueous solutions of sodium chloride and tetrabutylammonium bromide at 25.deg. *J. Phys. Chem.* **1975**, *79*, 1670–1675. [\[CrossRef\]](#)
33. Baez, L.A.; Clancy, P. Computer simulation of the crystal growth and dissociation of natural gas hydrates. *Ann. N.Y. Acad. Sci.* **1994**, *715*, 177–186. [\[CrossRef\]](#)
34. Reed, S.K.; Westacott, R.E. The interface between water and a hydrophobic gas. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4614. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Tamaki, K. The Surface Activity of Tetrabutylammonium Halides in the Aqueous Solutions. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 38–41. [\[CrossRef\]](#)
36. Chowdhuri, S.; Chandra, A. Dynamics of halide ion-water hydrogen bonds in aqueous solutions: Dependence on Ion Size and Temperature. *J. Phys. Chem. B* **2006**, *110*, 9674–9680. [\[CrossRef\]](#)
37. Liu, X.; O’Harra, K.E.; Bara, J.E.; Turner, C.H. Screening ionic liquids based on ionic volume and electrostatic potential analyses. *J. Phys. Chem. B* **2021**, *125*, 3653–3664. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.