



Int. J. New. Chem., 2020, Vol. 7, Issue 3, 195-219.

International Journal of New Chemistry

Published online 2020 in <http://www.ijnc.ir/>.

Open Access



Print ISSN: 2645-7236

Online ISSN: 2383-188x

Original Research Article

Investigation the Kinetics of CO₂ Hydrate Formation in the Water System + CTAB + TBAF + ZnO

Seyed Esmaeil Mousavi¹ and Alireza Bozorgian¹ *

¹*Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

Received: 2019-09-24

Accepted: 2020-01-15

Published: 2020-03-28

ABSTRACT

In this study, the kinetics of gas hydrate formation in the presence of tetra-n-butyl ammonium fluoride (TBAF) and cetyl trimethyl ammonium bromide surface active ingredient (CTAB) with zinc nano oxide (ZnO) are investigated and the most important kinetic parameters of hydrate formation such as their induction time and storage capacity were measured. The kinetic experiments were carried out in a constant volume temperature method in a high pressure reactor. The storage capacity of carbon dioxide hydrate in water in the presence of ZnO and surfactants at different temperatures, pressures and concentrations of TBAF and CTAB additives was calculated and measured using time induction measurements. The results show that with increasing pressure and decreasing temperature, the storage capacity of CO₂ in hydrate increases. Finally, statistical analysis of the parameters affecting the induction time of hydrate formation showed that zinc oxide can reduce the induction time of hydrate formation compared to other additives.

Keywords: Butyl Ammonium Fluoride, Zinc Nano Oxide, Storage, Hydrate

*Corresponding Author: Tel.: 09169206615
E-mail: a.bozorgian@mhria.ac.ir

Introduction

In recent years, with the rise of greenhouse gases such as methane, carbon dioxide, water vapor and nitrogen oxide in the Earth's atmosphere, the global temperature has been increasing, causing unpleasant changes in the environment. Therefore, in 1997, under the Kyoto Convention, industrialized nations pledged to reduce their greenhouse gas emissions by 5% over the next ten years and to assist developing countries and provide financial support in increasing use of renewable energy such as solar and wind energy. Since most of the industrial flue gas composition is usually carbon dioxide and nitrogen and carbon dioxide is one of the most important greenhouse gases, its separation from the gas mixture is very important [1-5]. Natural gas mainly contains gaseous hydrocarbons, especially methane, but also contains acid gases such as hydrogen sulfide and carbon dioxide. Separation of these gases is one of the main problems of refineries, which is currently being carried out using adsorption and so on [6]. There are many ways to separate carbon dioxide from gas mixtures, the most important of which is gas absorption by the liquid, gas adsorption on the solid, and membrane utilization. These methods are expensive and finding cheaper ways is essential to separate these gases [7]. The hydration process is one of the newest methods used to separate these gases. Gas hydrates are crystalline compounds that are formed by trapping small gas molecules such as methane, ethane, carbon dioxide, hydrogen and ethylene in cavities formed by hydrogen bonding between water molecules [8].

A review of past material

Takayuki et al., examined the fuzzy equilibrium formation of clathrate-like hydrates in carbon Tetra-N-butyl ammonium bromide system with carbon dioxide and water (at 287.4 to 287.8 with TBAB weight percent, 0.05 to 0.45 and in the 0.3 Mpa, 0.6 Mpa and 1 Mpa pressure). Their results according to Fig. 10-2 show that equilibrium temperature of quaternary hydrates at all three pressures increases with increasing TBAB weight percent for WTBAB < 0.35 and decreases for WTBAB < 0.40 and the highest fuzzy equilibrium temperature is 0.35. WTBAB = WTBA = 0.40. It was also shown that the equilibrium temperature of clathrate-like hydrates formation in carbon Tetra-N-butyl ammonium bromide system with carbon dioxide and water under

atmospheric pressure is higher than the equilibrium temperature of Tetra-n-butyl ammonium bromide and it was concluded that the thermodynamic stability of this system is due to the introduction of CO₂ molecules into the hydrate cavities. Lee et al., investigated the equilibrium conditions of hydrate of carbon dioxide and hydrogen gas mixtures in the presence of tetra butyl ammonium bromide and water and they found that the addition of tetra-butyl ammonium bromide solution with a molar fraction of 0.14 to a gas mixture containing 39.2% carbon dioxide and 60.8% hydrogen causes the hydrate formation pressure at 278.75 K. Reach from 11/01 MPa to 3.15 MPa. This indicates a decrease of 71.38% in pressure. Also, with increasing TBAB from the molar fraction of 0.14 to 0.29, the hydrate formation pressure was reduced to 0.85 MPa, indicating a 92.3% decrease in pressure. They investigated the hydrate formation pressure in the mole fraction of 0.21, 0.50, 1, and 2.67.

Theory and Computation

Calculation of carbon dioxide gas mole consumed: To do the calculations, we have to rewrite the equation of state in terms of the Z-compressibility coefficient, using the Peng-Robinson equation of the equation (2-3) in Z [9-13]. In the above equations, v the molar volume, TC and PC are the temperature and pressure at the critical point, respectively, R the global constant of gases, and ω the centroid coefficient. By solving the equation in the vapor-liquid calculations, the highest value Z is obtained for the vapor phase and the lowest value for the liquid phase. Using the Z obtained at the initial (equilibrium) temperature and pressure, the number of primary and equilibrium moles is obtained:

$$x = \frac{\text{absorbed mole number}}{\text{solvent kg}} \quad \text{And } x = \frac{\text{Standard volume}}{\text{Solvent volume cm}^3}$$

To calculate the amount of dissolved carbon dioxide in the solvent using a volumetric method, the standard volume is calculated by the following equation:

The volume of carbon dioxide gas is calculated under standard conditions (i.e. atmospheric pressure and temperature 25 ° C).

P₀: Gas initial pressure (bar)

P_e: Gas equilibrium pressure (bar)

R: Global constant of gases (83.14 $\frac{\text{bar.cm}^3}{\text{mol.k}}$)

T: Temperature (bar)

Z_0 : Gas compressibility coefficient at initial pressure

Z_e : Gas compressibility coefficient at final pressure

V_0 : Gas initial volume (cm^3)

V_e : Gas final volume (cm^3)

Calculate storage capacity

In the equation of pressure, temperature and global constant of gases are considered in standard conditions. In this equation V_H is the volume of hydrate obtained (Here considered 100 cm^3).

Statistical analysis of the experimental experiments results

In this study, Design Expert Version 11 software was used to design the experiment. Response surface experiment design and Central Composite method were used for statistical analysis.

Table 1. Statistical analysis of the experimental experiments results

File Version	11.0.3.0		
Study Type	Response Surface	Subtype	Randomized
Design Type	Central Composite	Runs	25

In this method, five parameters affecting the process of carbon dioxide hydration in water are: pressure, temperature, TBAF, CTAB and zinc oxide nanoparticles and a response that is induced at induction time and once again for storage capacity. The pressure changing ranges is considered from 20 bar to 30 bar, temperatures ranging from 275 K to 279 K and additives ranging from 0 to 3 wt.

Statistical analysis of parameters affecting the induction time of hydrate formation

As mentioned above, the five parameters are the parameter a reactor pressure. Parameter B is reactor temperature, parameter C is TBAF concentration, parameter D is CTAB concentration, and parameter E is zinc oxide. The effect of the above parameters on R_1 factor induction time of

hydrate formation in the presence of nanoparticles and surfactants was studied and recorded in vitro. In this paper, the statistical analysis of the effect of regulatory parameters on induction time of hydrate formation is investigated. Values were determined in vitro.

Table 2. Results of Experimental Experiments to Determine Induction Time of Hydrate Formation

		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Response 1
Run	Build Type	A:Pressure	B:Temperature	C:TBAF	D:CTAB	E:ZnO	t ind
		bar	k	Wt%	Wt%	Wt%	SEC
1	NA	25	279	1.5	1.5	1.5	166
2	NA	30	275	0	3	1.5	169
3	NA	25	277	3	1.5	0	186
4	NA	30	279	3	0	3	160
5	NA	25	277	1.5	3	3	140
6	NA	30	275	3	0	0	206
7	NA	30	279	3	0	0	207
8	NA	20	277	1.5	1.5	3	139
9	NA	30	279	0	0	0	213
10	NA	25	277	0	1.5	3	162
11	NA	20	275	3	0	0	198
12	NA	20	275	3	3	1.5	167
13	NA	25	277	1.5	0	0	206
14	NA	30	279	0	3	3	145
15	NA	30	277	1.5	1.5	3	150
16	NA	20	279	0	0	3	152
17	NA	20	275	0	3	0	189
18	NA	20	275	0	0	0	205
19	NA	20	279	3	3	3	138
20	NA	20	279	0	3	3	151
21	NA	30	275	0	0	1.5	172
22	NA	25	275	1.5	1.5	1.5	174
23	NA	20	279	3	3	0	188
24	NA	25	277	1.5	1.5	1.5	175
25	NA	30	275	3	3	1.5	170

As can be seen, the software randomly designed 25 experiments and had to obtain the hydration

induction time for each and with the designed conditions and complete the table. That's what happened. What can be deduced from this table is that in the F-Value column the amount of zinc oxide is higher than the rest of the parameters over the hydrate induction time and then this is related to the CTAB which can affect the hydrate induction time. In the P-Value column, data less than 0.05 have a significant effect on responses. Here the selected model is validated and indicates the significance of the selected model. In addition, the effect of zinc oxide on the induction time of hydrate formation can be emphasized in this column.

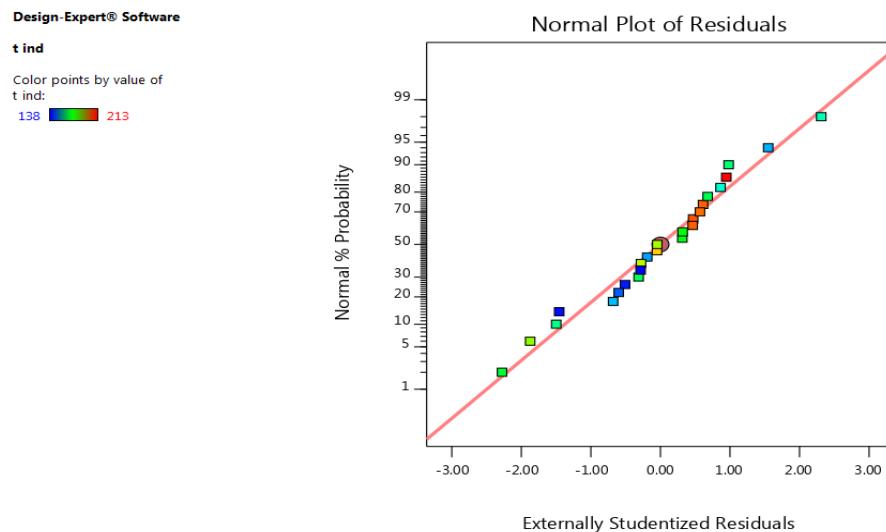
Table 3. Critical analysis table for linear model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	12698.40	5	2539.68	74.44	< 0.0001	significant
A-Pressure	89.46	1	89.46	2.62	0.1219	
B-Temperature	12.74	1	12.74	0.3734	0.5484	
C-TBAF	65.57	1	65.57	1.92	0.1817	
D-CTAB	516.11	1	516.11	15.13	0.0010	
E-ZnO	7729.72	1	7729.72	226.56	< 0.0001	
Residual	648.24	19	34.12			
Cor Total	13346.64	24				

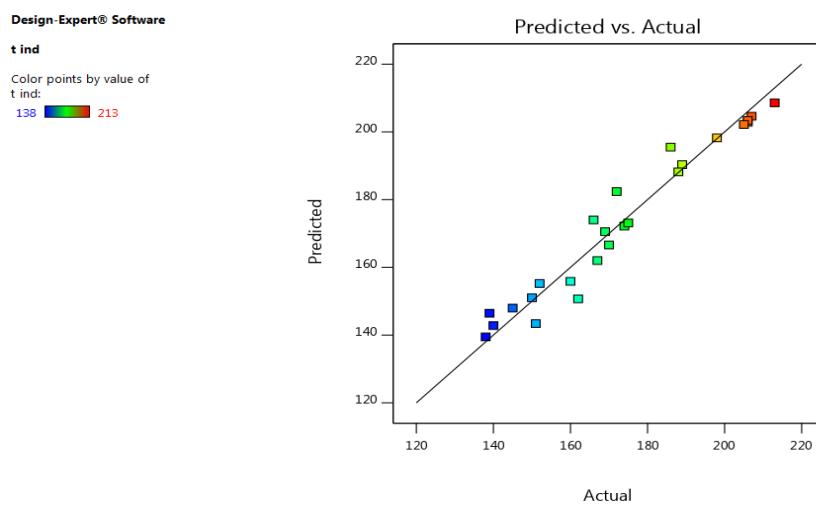
Table 4. Response statistics table

Std. Dev.	5.84	R ²	0.9514
Mean	173.12	Adjusted R²	0.9386
C.V. %	3.37	Predicted R²	0.9220
		Adeq Precision	24.1589

The coefficient of determination (R^2) indicates that the experimental data are consistent with the predicted data, and the closer this number is to one, the better the fit. This indicates that the experimental data are in good agreement with the numbers shown. To verify that the data obtained are of normal distribution

**Figure 1.** Normal data dispersion graph

The closer the points shown are to the 45-degree line and the more linear it is, so the data have a better normal distribution, which is shown in the Figure above, indicating the normal distribution of the data.

**Figure 2.** Graph of actual values versus predicted values

Investigation the effect of variables on hydrate formation induction time

In this section, the effect of each of the defined parameters on the hydrate formation induction time is discussed.

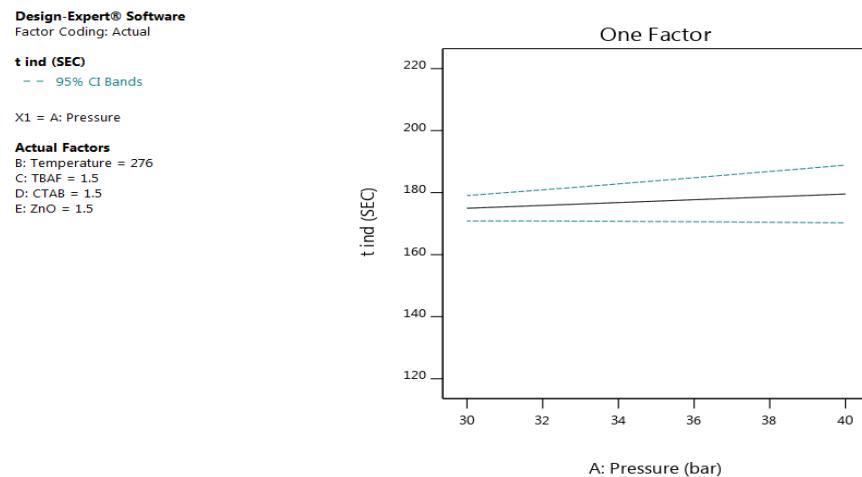


Figure 3. Effect of pressure on hydrate formation induction time

In this system, the pressure Figure shows little effect on the amount of induction time. However, with the increase in pressure, we see an increase in the induction time.

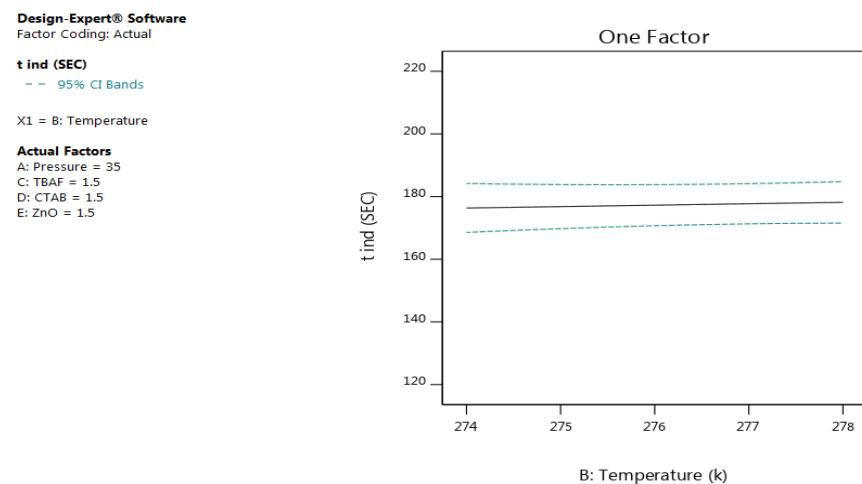
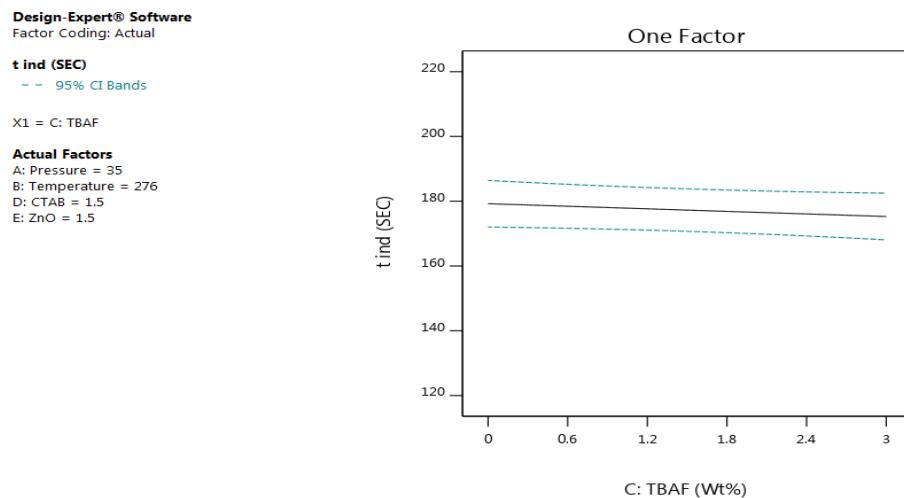
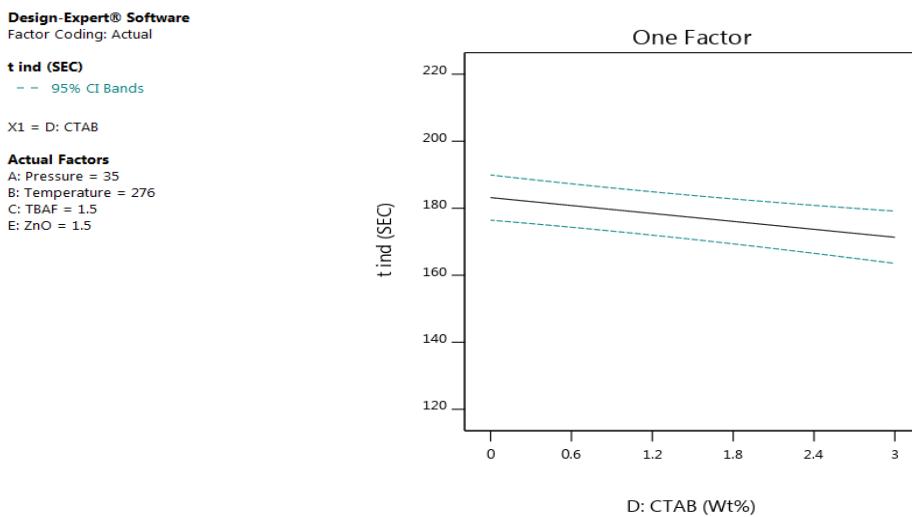


Figure 4. Effect of temperature on hydrate formation induction time

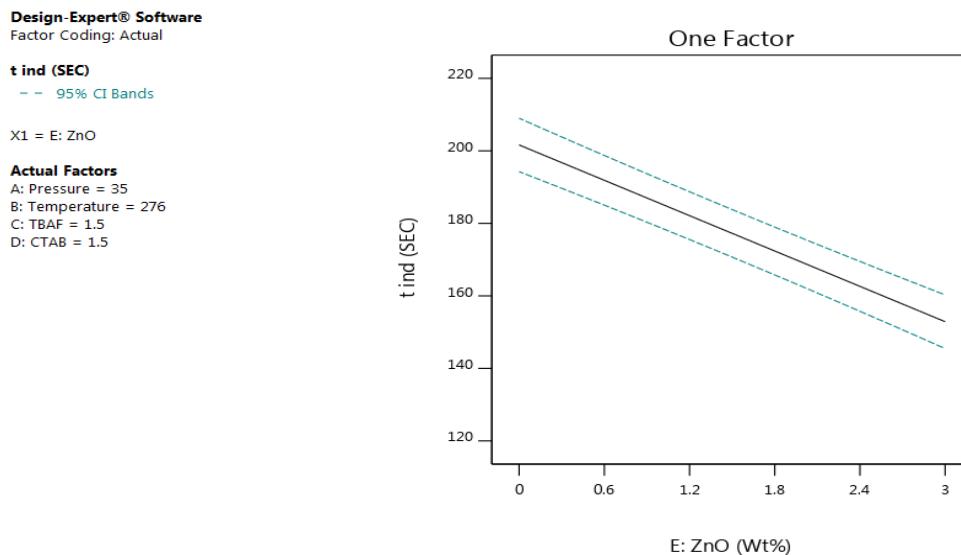
According to the temperature change Figure, there was no significant effect on that temperature range and the induction time changes are relatively constant. Adding TBAF to the system reduces the hydrate formation induction time.

**Figure 5.** Effect of TBAF on hydrate formation induction time

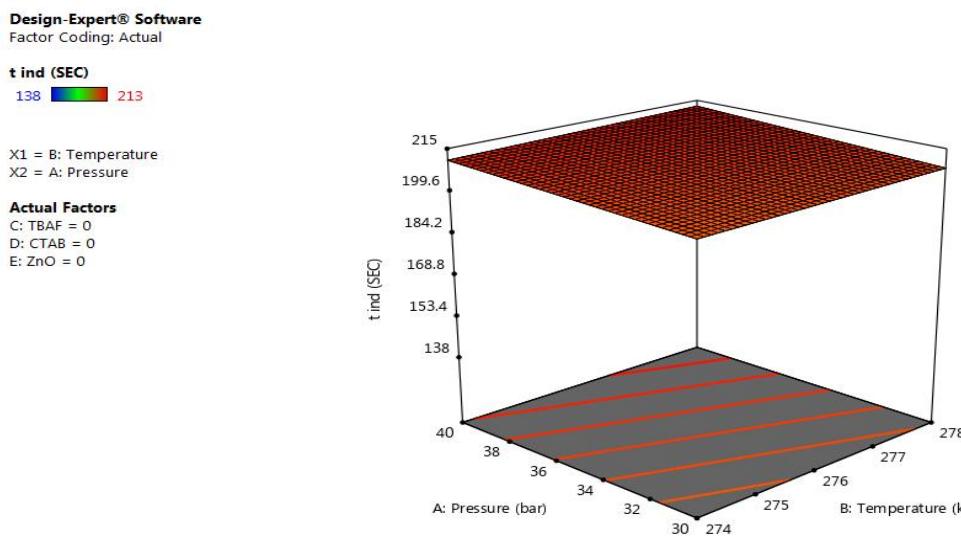
Addition of CTAB surfactant to the induction time reduction system resulted in a comparison of the two graphs showing that the effect of the CTAB surfactant in reducing the induction time was greater than that of TBAF.

**Figure 6.** Effect of CTAB on hydrate formation induction time

Although this has already been mentioned in the benchmark analysis table for the linear model, the comparison of the two graphs shows the effect of CTAB surfactant over TBAF on reducing induction time. Zinc oxide had the greatest effect on reducing induction time. According to the Figure, as the amount of zinc oxide increases, the hydrate formation induction time is reduced.

**Figure 7.** Effect of ZnO on hydrate formation induction time

What can be investigated is that at a constant temperature and pressure with each of the additives mentioned above, the induction time decreases.

**Figure 8.** Effect of system additives on pressure and temperature on induction time

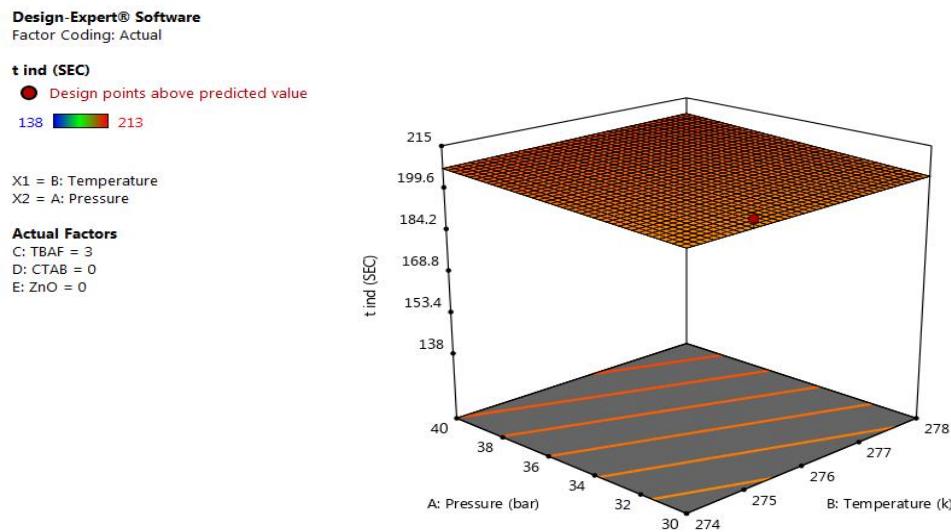


Figure 9. Effect of system additives on pressure and temperature on induction time

According to the Figure, the amount of induction time was decreased by adding TBAF at constant pressure and temperature.

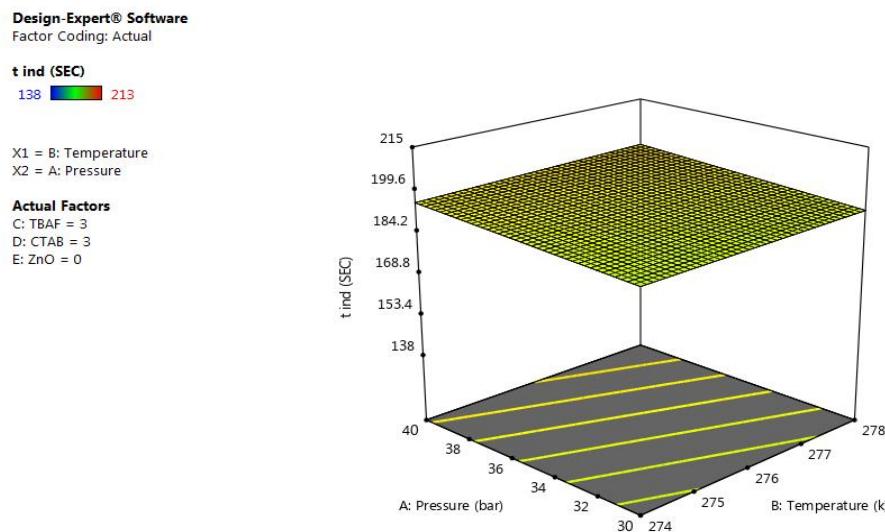
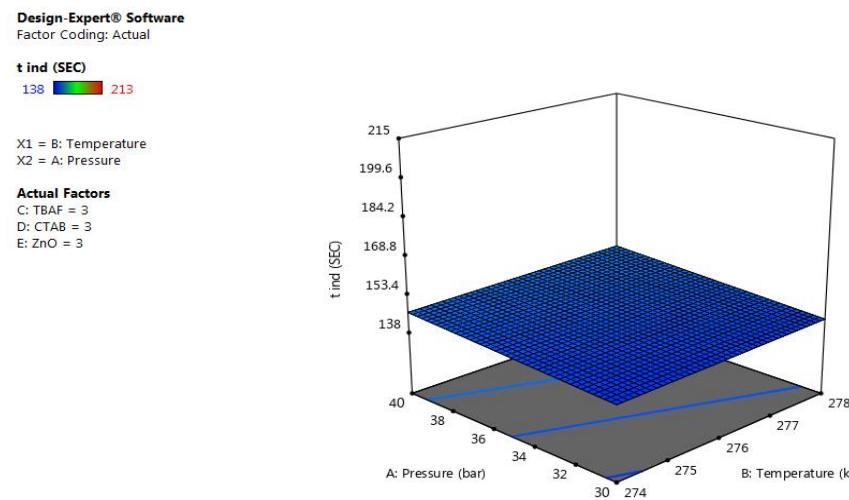


Figure 10. Effect of system additives on pressure and temperature on induction time

The presence of CTAB and its addition to the system at a pressure and temperature indicates a decrease in the amount of induction time. This decreasing trend is further enhanced by the addition of zinc oxide and the lowest amount of induction time is related to a system containing the highest amount of additive that can be optimized.

**Figure 11.** Effect of system additives on pressure and temperature on induction time

Optimization conditions

The results of induction time optimization using the software are shown below. It should be noted that table shows the optimal laboratory conditions for the least amount of hydrate formation induction time.

Table 5. Optimal laboratory conditions for the least amount of induction time

Number	Pressure	Temperature	TBAF	CTAB	ZnO	t ind	Std Err(t ind)	Desirability	Selected
1	30.000	275.050	3.000	2.993	3.000	142.292	3.634	0.943	
2	30.000	275.019	3.000	2.989	2.998	142.319	3.644	0.942	
3	30.000	275.413	3.000	2.999	3.000	142.434	3.502	0.941	
4	30.000	274.964	2.921	3.000	2.987	142.545	3.627	0.939	
5	30.045	275.643	3.000	2.997	3.000	142.564	3.431	0.939	
6	30.000	274.800	2.557	3.000	3.000	142.735	3.552	0.937	
7	30.000	274.545	2.442	2.994	3.000	142.795	3.622	0.936	
8	30.032	274.673	2.693	2.925	3.000	142.812	3.644	0.936	
9	30.001	275.400	3.000	2.900	3.000	142.824	3.480	0.936	
10	30.000	275.888	2.801	3.000	3.000	142.905	3.258	0.935	
11	30.000	275.255	2.550	2.995	3.000	142.971	3.364	0.934	
12	30.610	274.919	2.628	3.000	3.000	142.975	3.609	0.934	
13	30.000	275.027	2.536	2.967	3.000	142.993	3.440	0.933	
14	30.041	276.653	3.000	3.000	3.000	143.008	3.183	0.933	

15	30.552	274.678	2.468	3.000	3.000	143.051	3.644	0.933	
16	30.000	276.821	2.999	3.000	3.000	143.066	3.151	0.932	
17	30.000	276.857	2.999	3.000	3.000	143.082	3.146	0.932	
18	30.433	274.563	2.361	3.000	3.000	143.083	3.644	0.932	
19	30.027	276.618	3.000	3.000	2.994	143.089	3.184	0.932	
20	30.067	276.955	3.000	3.000	3.000	143.161	3.143	0.931	
21	30.000	275.083	2.500	3.000	2.984	143.200	3.405	0.931	
22	30.000	274.596	2.657	2.893	2.984	143.202	3.644	0.931	
23	31.554	275.659	3.000	2.999	3.000	143.258	3.644	0.930	
24	31.036	274.967	2.621	2.996	2.996	143.274	3.644	0.930	
25	30.273	277.156	3.000	2.999	3.000	143.345	3.154	0.929	
26	30.000	274.480	1.983	2.998	3.000	143.350	3.522	0.929	
27	30.000	275.198	2.221	3.000	3.000	143.356	3.275	0.929	
28	30.003	274.563	2.662	2.766	2.999	143.435	3.644	0.928	
29	31.136	276.498	3.000	3.000	3.000	143.441	3.377	0.927	
30	30.000	274.861	2.016	3.000	3.000	143.473	3.358	0.927	
31	30.171	275.291	3.000	2.716	3.000	143.573	3.500	0.926	
32	30.087	276.151	2.374	3.000	3.000	143.626	3.027	0.925	
33	30.581	274.353	1.917	3.000	3.000	143.641	3.644	0.925	
34	31.966	276.173	3.000	3.000	3.000	143.675	3.579	0.924	
35	30.007	274.645	2.786	2.748	2.980	143.687	3.644	0.924	
36	30.000	274.652	2.734	2.983	2.927	143.690	3.641	0.924	
37	30.000	276.960	2.542	3.000	3.000	143.730	2.926	0.924	
38	31.570	276.593	3.000	2.987	3.000	143.734	3.427	0.924	
39	30.227	274.155	1.649	3.000	2.998	143.777	3.644	0.923	
40	30.008	275.068	1.837	3.000	3.000	143.806	3.232	0.923	
41	31.071	277.543	3.000	3.000	3.000	143.883	3.263	0.922	
42	30.000	275.505	1.899	3.000	3.000	143.918	3.076	0.921	
43	30.030	274.036	1.328	2.995	3.000	144.038	3.644	0.919	
44	30.007	277.890	2.677	3.000	2.993	144.086	2.951	0.919	
45	30.443	274.952	3.000	2.568	3.000	144.131	3.643	0.918	
46	30.111	277.448	2.432	3.000	3.000	144.146	2.868	0.918	
47	31.204	274.481	1.765	3.000	3.000	144.185	3.644	0.918	
48	30.012	277.977	2.509	3.000	3.000	144.238	2.894	0.917	
49	30.007	274.441	1.276	3.000	3.000	144.260	3.440	0.917	
50	30.000	274.145	1.152	3.000	3.000	144.287	3.578	0.916	

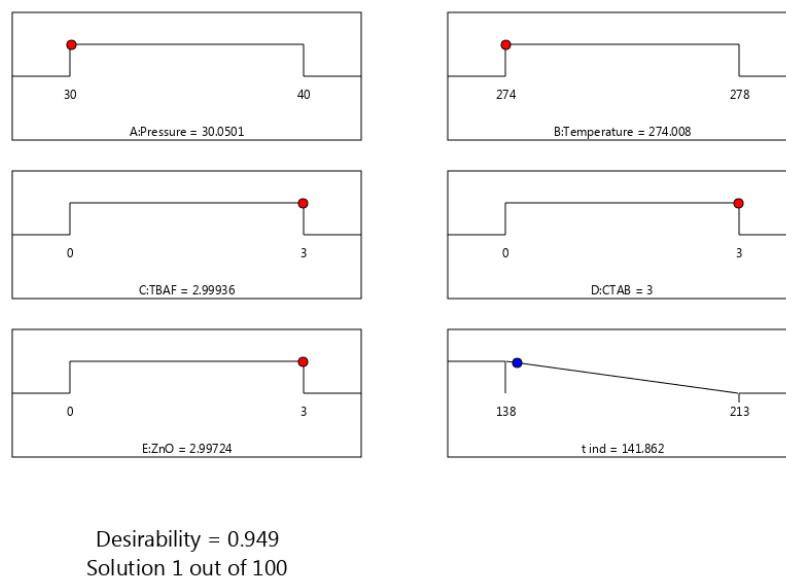
51	30.000	276.490	1.839	3.000	3.000	144.442	2.787	0.914	
52	30.000	274.001	1.066	2.960	3.000	144.493	3.639	0.913	
53	30.000	274.420	1.047	3.000	3.000	144.549	3.443	0.913	
54	32.706	275.782	2.635	2.977	2.988	144.603	3.644	0.912	
55	30.000	276.505	1.680	3.000	3.000	144.659	2.756	0.911	
56	30.000	276.099	1.409	3.000	3.000	144.832	2.819	0.909	
57	30.000	274.085	0.714	2.998	2.996	144.913	3.618	0.908	
58	32.550	278.000	2.835	3.000	3.000	144.986	3.471	0.907	
59	30.000	274.020	0.772	2.994	2.984	145.008	3.640	0.907	
60	30.000	276.295	2.974	2.451	2.999	145.048	3.098	0.906	
61	30.000	276.254	2.994	2.413	3.000	145.131	3.114	0.905	
62	30.509	274.208	0.549	3.000	3.000	145.342	3.644	0.902	
63	30.008	275.222	0.722	3.000	3.000	145.342	3.121	0.902	
64	33.349	277.932	2.956	2.932	2.998	145.455	3.644	0.901	
65	30.000	274.593	0.306	3.000	3.000	145.602	3.442	0.899	
66	32.611	275.090	2.191	2.749	2.995	145.619	3.644	0.898	
67	30.000	276.669	1.024	2.969	3.000	145.719	2.686	0.897	
68	30.001	275.378	0.432	3.000	3.000	145.791	3.110	0.896	
69	30.000	274.000	0.704	2.730	3.000	145.874	3.597	0.895	
70	30.000	276.388	0.610	2.997	3.000	146.024	2.801	0.893	
71	32.332	274.768	0.957	2.978	2.996	146.054	3.644	0.893	
72	30.976	274.575	0.070	3.000	3.000	146.352	3.639	0.889	
73	30.000	277.527	0.627	3.000	3.000	146.505	2.710	0.887	
74	30.126	276.292	0.024	3.000	2.999	146.806	3.002	0.883	
75	30.020	277.536	0.260	3.000	3.000	147.001	2.815	0.880	
76	31.840	274.330	1.560	2.367	3.000	147.174	3.644	0.878	
77	30.231	277.919	3.000	2.067	3.000	147.349	2.897	0.875	
78	31.895	275.315	2.991	1.943	3.000	147.437	3.644	0.874	
79	30.000	274.000	0.049	2.440	2.996	147.946	3.644	0.867	
80	30.000	278.000	2.954	1.889	3.000	148.041	2.830	0.866	
81	34.308	277.552	0.968	3.000	3.000	148.045	3.549	0.866	
82	30.000	274.717	2.818	1.423	3.000	148.579	3.644	0.859	
83	30.000	275.597	0.007	2.428	3.000	148.704	2.972	0.857	
84	30.004	274.842	2.898	1.323	3.000	148.928	3.644	0.854	
85	30.000	278.000	3.000	2.583	2.769	149.002	2.874	0.853	
86	30.000	275.064	2.977	1.079	3.000	149.882	3.644	0.842	

87	30.001	277.951	3.000	1.237	3.000	150.533	2.910	0.833	
88	33.419	275.669	2.694	1.475	2.999	150.558	3.644	0.833	
89	30.115	275.191	2.951	0.890	3.000	150.774	3.644	0.830	
90	35.020	275.671	1.289	2.051	2.988	151.033	3.644	0.826	
91	35.576	278.000	2.309	1.953	3.000	151.197	3.644	0.824	
92	30.000	277.793	0.000	1.943	3.000	151.621	2.560	0.818	
93	35.928	277.520	0.788	2.152	3.000	152.360	3.644	0.809	
94	30.000	278.000	2.999	0.825	2.978	152.533	3.004	0.806	
95	33.875	277.977	3.000	0.997	3.000	153.271	3.538	0.796	
96	30.535	278.000	0.000	1.437	3.000	153.958	2.627	0.787	
97	35.916	277.375	0.290	1.747	3.000	154.540	3.644	0.779	
98	30.000	274.315	0.162	0.679	3.000	154.823	3.643	0.776	
99	30.000	274.178	0.000	3.000	2.421	155.219	3.522	0.770	
100	31.217	278.000	0.000	1.173	2.998	155.339	2.754	0.769	

According to the table above to achieve the minimum amount of induction time in hydrate with laboratory conditions is stated in row 1, which was previously achieved in the interpretation of graphs and this was predictable. The slope Figure below can also be examined. The slope will be as follows for the least amount of induction time.

Table 6. The Results of Experimental Experiments to Determine Storage Capacity

		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Response 1
Run	Build Type	A:Pressure	B:Temperature	C:TBAF	D:CTAB	E:ZnO	SC
		bar	k	Wt%	Wt%	Wt%	
1	NA	30	275	0	0	1.5	90.0029
2	NA	30	279	0	0	0	82.6424
3	NA	30	279	3	0	0	90.0441
4	NA	30	275	0	3	1.5	118.817
5	NA	30	275	0	3	0	99.7843
6	NA	25	277	0	1.5	3	78.2529
7	NA	20	275	3	0	0	30.883
8	NA	30	279	0	3	3	123.566
9	NA	30	275	3	3	1.5	120.204
10	NA	20	277	1.5	1.5	3	46.3346
11	NA	25	277	1.5	0	0	55.0128
12	NA	30	279	3	0	3	105.668
13	NA	25	279	1.5	1.5	1.5	75.0942
14	NA	20	279	3	3	0	56.537
15	NA	25	277	1.5	3	3	96.2981
16	NA	20	275	3	3	1.5	58.7105
17	NA	30	275	3	0	0	93.2004
18	NA	25	277	1.5	1.5	1.5	75.4897
19	NA	25	275	1.5	1.5	1.5	75.9909
20	NA	20	279	0	3	3	52.6568
21	NA	30	277	1.5	1.5	3	111.997
22	NA	20	279	0	0	3	35.8149
23	NA	20	279	3	3	3	63.2603
24	NA	25	277	3	1.5	0	74.4667
25	NA	20	275	0	0	0	15.6236

**Figure 8.** The sloping surface Figure in the optimizing mood

In the Figure above the sloping surfaces, the points indicated in the range of variables are shown to indicate the optimum point, which is the minimum of induction time in hydrates formation.

Statistical analysis of parameters affecting carbon dioxide storage capacity in hydrate

As previously mentioned, Design Expert software version 11 was used to design the experiment. Response surface test method and Central Composite method were used for statistical analysis.

For each experiment conducted at different temperatures and pressures and different concentrations of nanoparticles and surface materials, the values were determined in vitro.

In this design the proposed model is a linear model. What can be concluded is that the amount of CTAB and pressure are higher than the rest of the parameters on the storage capacity, and the influence of temperature on the storage capacity can be ignored.

Table 7. Critical analysis table for linear model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	19721.40	5	3944.28	379.86	< 0.0001	significant
A-Pressure	17428.78	1	17428.78	1678.50	< 0.0001	
B-Temperature	0.6220	1	0.6220	0.0599	0.8093	

C-TBAF	395.74	1	395.74	38.11	< 0.0001	
D-CTAB	2162.66	1	2162.66	208.28	< 0.0001	
E-ZnO	649.69	1	649.69	62.57	< 0.0001	
Residual	197.29	19	10.38			
Cor Total	19918.69	24				

The table of determination coefficient (R^2) shows the concordance of the experimental data with the predicted data, the closer this number is to a better one, the better. According to the numbers shown, the experimental data are in excellent agreement.

Table 8. Response statistics table

Std. Dev.	3.22	R²	0.9901
Mean	77.05	Adjusted R²	0.9875
C.V. %	4.18	Predicted R²	0.9801
		Adeq Precision	66.0881

Investigating the effect of variables on storage capacity

In this section, we examine the effect of parameters stated on carbon dioxide gas storage capacity.

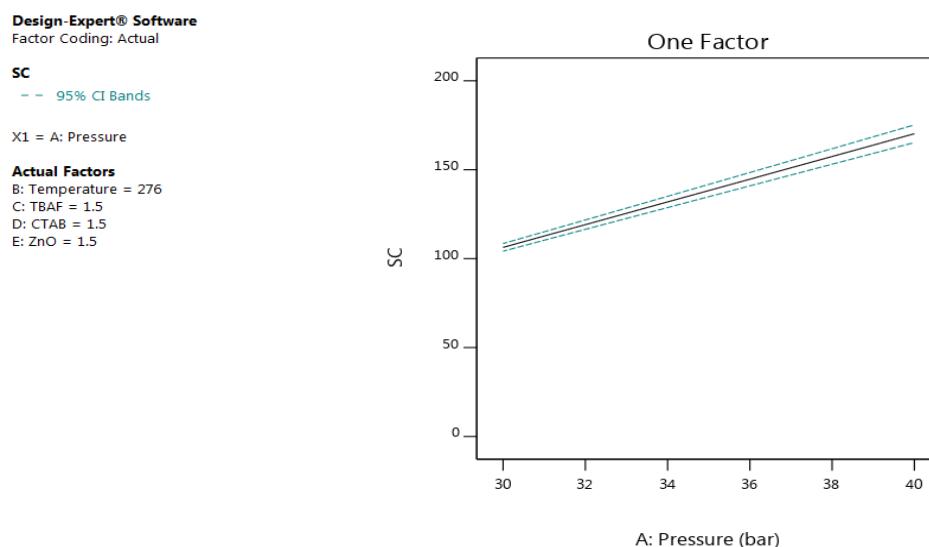


Figure 9. Effect of pressure on storage capacity

In this system, the amount of storage capacity has increased dramatically with increasing pressure.

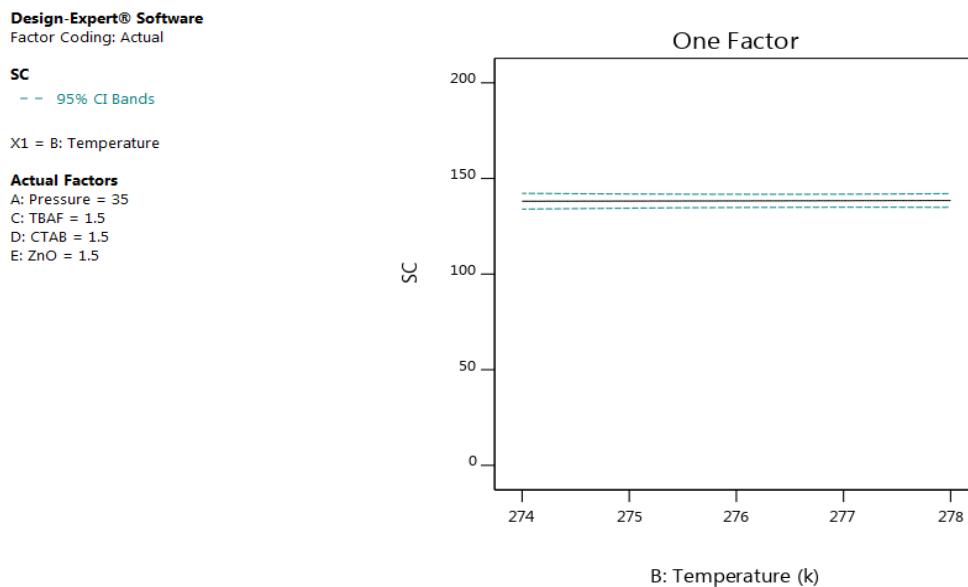


Figure 10. Effect of temperature on storage capacity

According to the temperature change Figure, it has little effect on the temperature range and the storage capacity changes have been relatively constant.

Adding the amount of TBAF to the system increases the relative amount of storage capacity.

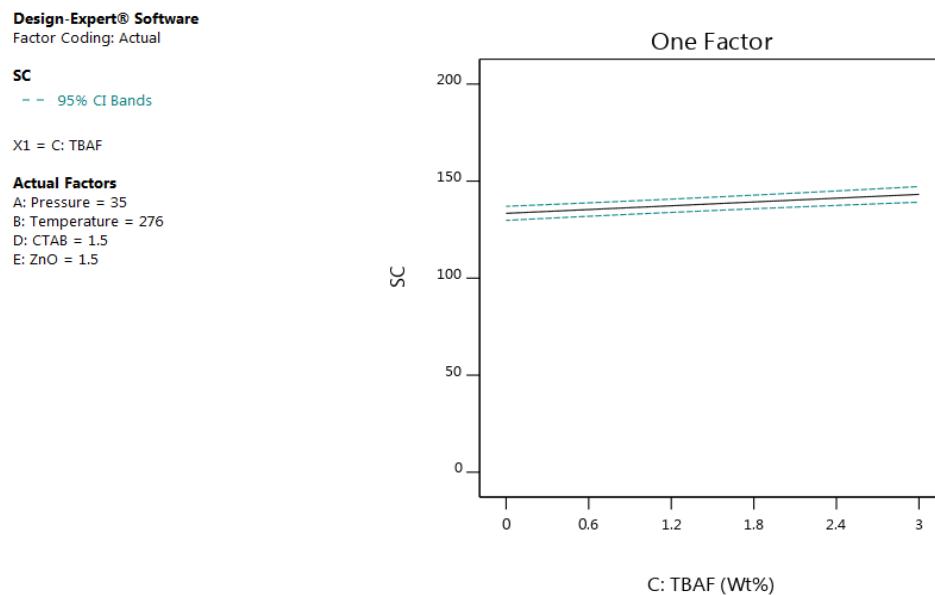


Figure 11. Effect of TBAF on storage capacity

Addition of CTAB surfactant to the system resulted in increasing storage capacity, which was steeper compared to TBAF. And this is an effective story of this article.

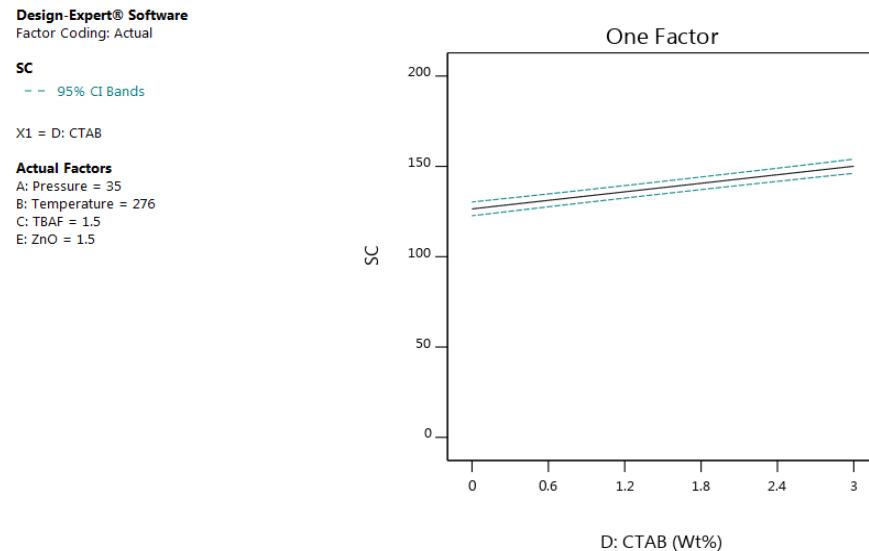


Figure 12. Effect of CTAB on storage capacity

According to the Figure, as the amount of zinc oxide increases, the storage capacity increases.

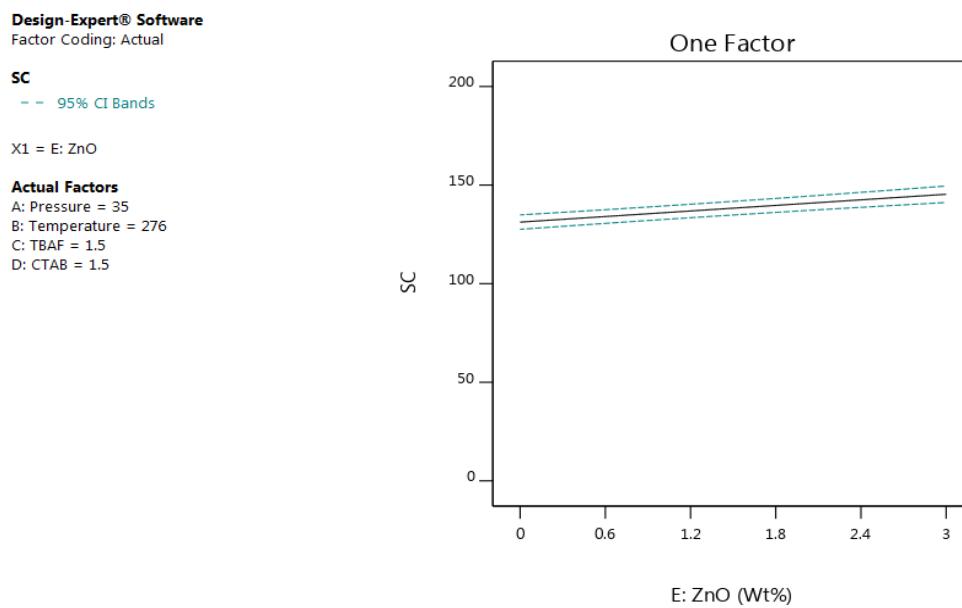


Figure 13. Effect of ZnO on storage capacity

Optimization conditions

The results of storage capacity optimization by using the software are shown below. It should be

noted that the table of optimal laboratory conditions for maximum storage capacity is stated.

Table 9. Optimal laboratory conditions for maximum storage capacity

Number	Pressure	Temperature	TBAF	CTAB	ZnO	SC	Desirability	
1	35.728	276.118	1.510	0.390	2.344	138.221	1.000	
2	30.508	275.203	2.927	2.963	1.653	126.392	1.000	
3	32.822	274.466	0.106	2.934	0.266	125.156	1.000	
4	35.868	274.608	0.818	0.892	0.079	130.004	1.000	Selected
5	32.040	274.589	0.271	2.952	1.265	125.557	1.000	
6	34.654	274.042	2.602	0.098	0.653	124.451	1.000	
7	36.172	274.521	0.029	2.716	2.329	154.310	1.000	
8	38.605	275.271	1.806	1.051	1.572	159.043	1.000	
9	34.855	276.726	1.138	0.320	2.547	131.895	1.000	
10	34.384	274.306	0.589	1.504	2.329	135.147	1.000	
11	36.692	277.567	1.328	1.911	2.077	154.643	1.000	
12	38.114	274.856	1.336	2.607	0.542	161.742	1.000	
13	39.624	274.844	0.361	1.118	1.885	162.817	1.000	
14	34.351	275.893	2.165	0.930	1.021	129.559	1.000	
15	34.342	274.048	2.255	1.588	1.083	135.082	1.000	
16	34.513	277.075	0.281	1.973	0.420	129.953	1.000	
17	33.219	277.427	2.523	2.435	2.619	143.007	1.000	
18	35.732	276.293	1.089	0.843	0.046	129.643	1.000	
19	37.836	275.298	1.128	2.500	2.558	167.980	1.000	
20	31.629	275.830	2.911	2.237	1.864	128.849	1.000	
21	37.417	274.460	1.802	1.971	1.499	158.259	1.000	
22	38.891	276.970	0.772	1.236	0.915	156.039	1.000	
23	32.623	277.156	1.401	2.257	2.519	133.646	1.000	
24	36.183	277.282	2.851	0.436	0.653	138.019	1.000	
25	37.182	274.199	0.922	0.797	2.582	149.724	1.000	
26	37.972	277.282	2.122	2.902	0.004	163.423	1.000	
27	38.617	274.139	1.546	2.158	0.364	161.197	1.000	
28	32.906	275.752	0.892	1.625	1.695	124.800	1.000	
29	32.240	274.310	2.484	1.970	2.052	129.988	1.000	
30	38.932	274.225	2.560	1.560	1.159	165.553	1.000	
31	35.045	274.787	2.338	0.689	0.367	129.471	1.000	
32	35.020	277.090	2.993	1.147	0.596	136.361	1.000	

33	33.946	275.066	1.357	1.782	1.592	133.647	1.000	
34	35.091	276.666	0.458	0.105	1.773	125.850	1.000	
35	36.778	275.739	1.104	0.625	2.903	148.050	1.000	
36	36.684	275.657	1.130	1.053	2.696	149.922	1.000	
37	34.715	275.666	2.188	0.266	1.611	129.485	1.000	
38	36.355	274.575	0.931	0.950	2.921	147.317	1.000	
39	34.762	277.889	1.092	1.153	0.778	129.497	1.000	
40	34.735	277.343	2.509	1.270	0.511	133.547	1.000	
41	38.473	275.103	2.377	2.446	0.425	165.628	1.000	
42	37.367	274.088	1.040	1.604	2.546	157.464	1.000	
43	34.393	274.490	2.624	0.992	0.267	128.118	1.000	
44	38.858	277.160	0.530	1.298	2.906	164.920	1.000	
45	33.623	274.832	1.408	0.464	2.366	124.998	1.000	
46	38.862	274.387	0.840	1.045	2.393	161.273	1.000	
47	34.335	275.509	0.405	0.906	1.333	124.961	1.000	
48	32.376	274.196	0.554	2.852	1.272	127.821	1.000	
49	34.807	275.393	0.498	1.209	0.392	126.225	1.000	
50	31.590	275.231	1.688	2.125	2.709	127.640	1.000	
51	34.218	274.384	0.994	2.795	2.215	145.040	1.000	
52	36.228	274.070	1.452	0.116	1.108	133.045	1.000	
53	34.396	277.348	0.565	1.314	1.341	129.314	1.000	
54	34.809	275.648	1.181	1.728	1.564	138.089	1.000	
55	35.482	275.455	1.042	2.651	2.804	155.018	1.000	
56	35.797	276.705	2.384	0.897	1.261	140.463	1.000	
57	35.329	277.796	0.693	0.132	1.290	126.180	1.000	
58	34.018	276.217	1.493	1.128	1.882	130.887	1.000	
59	39.256	276.783	1.567	1.843	1.305	167.558	1.000	
60	37.248	276.237	1.661	1.828	0.014	148.787	1.000	
61	37.588	276.686	1.877	0.419	2.522	152.425	1.000	
62	34.077	277.029	0.446	2.358	0.894	132.958	1.000	
63	34.087	277.853	0.229	1.373	0.896	124.665	1.000	
64	36.343	277.760	1.138	2.032	0.475	145.223	1.000	
65	31.985	274.640	1.610	2.041	1.951	125.622	1.000	
66	34.509	277.621	0.269	2.253	0.196	131.091	1.000	
67	39.605	275.768	1.889	1.430	2.545	173.321	1.000	
68	38.247	274.584	2.022	1.283	2.073	161.580	1.000	

69	34.222	277.173	0.888	0.462	2.776	129.282	1.000	
70	32.726	275.413	1.994	2.258	1.360	130.617	1.000	
71	33.888	276.489	2.707	1.615	1.417	135.675	1.000	
72	34.291	274.431	1.012	0.579	2.189	128.002	1.000	
73	34.077	274.407	2.921	1.051	0.199	127.207	1.000	
74	38.318	274.152	0.914	1.046	2.640	159.178	1.000	
75	39.398	276.398	0.133	0.389	2.034	155.739	1.000	
76	36.643	275.053	0.551	2.486	2.042	155.905	1.000	
77	31.420	277.368	1.174	2.120	2.813	125.548	1.000	
78	38.706	276.937	2.209	2.391	0.567	166.990	1.000	
79	34.743	276.940	0.147	2.001	0.349	130.864	1.000	
80	35.226	274.736	0.270	0.856	2.938	137.297	1.000	
81	33.500	274.903	0.099	2.231	0.417	124.692	1.000	
82	33.832	275.952	1.753	1.750	0.924	130.910	1.000	
83	33.130	274.965	2.939	2.476	1.461	138.423	1.000	
84	39.830	277.820	1.050	1.616	0.056	161.981	1.000	
85	37.584	275.311	2.439	0.803	2.621	157.576	1.000	
86	39.584	277.882	2.971	0.778	2.613	172.112	1.000	
87	38.656	276.542	0.785	1.412	1.243	157.468	1.000	
88	33.475	275.590	2.900	1.020	1.164	127.707	1.000	
89	34.252	274.805	1.143	0.892	2.156	130.530	1.000	
90	37.045	275.707	0.840	0.929	0.373	139.372	1.000	
91	32.573	275.766	1.937	2.844	1.666	135.538	1.000	
92	31.997	277.019	1.574	2.728	0.466	124.249	1.000	
93	37.841	274.123	0.547	1.776	0.580	150.990	1.000	
94	32.280	274.721	2.665	1.878	2.906	134.168	1.000	
95	33.142	276.013	0.573	2.717	1.607	133.480	1.000	
96	39.854	275.178	2.052	2.378	2.405	182.182	1.000	
97	39.005	276.076	1.611	2.174	0.018	162.581	1.000	
98	34.731	275.742	0.033	2.315	2.086	140.934	1.000	
99	36.697	274.541	0.128	1.295	1.089	140.963	1.000	
100	36.613	274.756	1.669	0.960	1.418	144.382	1.000	

According to the table above to achieve maximum storage capacity with laboratory conditions is expressed in row 4.

Conclusion

In this study, the effects of TBAF and CTAB surfactant and zinc oxide on the induction time of hydrate formation and carbon dioxide storage capacity were investigated. For this purpose, Design Expert software was used to design the experiment. Finally, statistical analysis of the parameters affecting the induction time of hydrate formation showed that zinc oxide can decrease the induction time of hydrate formation compared to other additives. In addition, by investigating the effect of variables on carbon dioxide storage capacity can be concluded that increasing the amount of CTAB surfactant and pressure have had the most effect on the increase of carbon dioxide storage capacity.

References

- [1] A. Bozorgian, Z. Arab Aboosadi, A. Mohammadi. B. Honarvar, A. Azimi, *Eurasian Chem. Commun.*, 2, 3 (2020).
- [2] M. Noormohammadi; M. Barmala, *Int. J. New. Chem.*, 6, 289 (2019).
- [3] S. Kumer, M. Ebrahimikia, M. Yari, *Int. J. New. Chem.*, 7, 74 (2020).
- [4] T. Bedassa; M. Desalegne, *Int. J. New. Chem.*, 7, 47 (2020).
- [5] M. Mota-Martinez, S. Samdani, A. Berrouk, C. Peters, *Ind. Eng. Chem.*, 53, 20032 (2014).
- [6] P.C. Okafor, C.B. Liu, Y.J. Zhu, Y.G. Zheng, *Ind Eng Chem Res.*, 50, 7273 (2011).
- [7] S.O. Yang, *Flu Phase Equilibr*, 175, 75 (2000).
- [8] J. Mashhadizadeh, A. Bozorgian, A. Azimi, *Eurasian Chem. Commun.*, 2, 4 (2019).
- [9] I. Ali, W.A. Wani, *Synth React Tnorg M Journal*, 43, 1162 (2013).
- [10] H. Roosta, *Scient Iranica C.*, 21, 753 (2014).
- [11] A. Bozorgian, Z. Arab Aboosadi, A. Mohammadi. B. Honarvar, A. Azimi, *Prog.*

Chem. Biochem. Res., 3, 31 (2020).

[12] Z. Sarikhani, M. Manoochehri, *Int. J. New. Chem.*, 7, 30 (2020).

[13] S. Someya, *Int J Heat Mass Transf.*, 48, 2503 (2005).

[14] S. Bergeron, *Fluid Phase Equilib.*, 276, 150 (2009).

[15] D. Iribarren, F. Petrakopoulou, J. Dufour, *Energy.*, 50, 477 (2013).

[16] M. Nabati, V. Bodaghi-Namileh, *Int. J. New. Chem.*, 6, 254 (2019).

[17] T. Bedassa; M. Desalegne, *Int. J. New. Chem.*, 7, 47 (2020).

[18] M. Noormohammadi; M. Barmala, *Int. J. New. Chem.*, 6, 289 (2019).

[19] A.H. Tarighaleslami, A. Bozorgian, B. Raei, *1st Territ Chem Ind Symp*, (2009).

[20] A. Mohasseb, *Int. J. New. Chem.*, 6, 215 (2019).

[21] S. Kumer, M. Ebrahimikia, M. Yari, *Int. J. New. Chem.*, 7, 74 (2020).

[22] A. Samimi, S. Zarinabadi, A. Bozorgian, *Prog. Chem. Biochem. Res.*, 2, 7 (2020).

[23] A. Bozorgian, M. Ghazinezhad, *J Biochem Tech.*, 2, 149 (2018).

[24] A. Samimi, S. Zarinabadi, A. Shahbazi Kootenaei, A. Azimi, M. Mirzaei, *Chem. Methodol.*, 4, 852 (2020).

How to Cite This Article

Esmaeil Mousavi and Alireza Bozorgian, “Investigation the kinetics of CO₂ hydrate formation in the water system + CTAB + TBAF + ZnO” International Journal of New Chemistry., 2020; 7(3), 195-219. DOI: 10.22034/ijnc.2020.121743.1096.