Thermodynamic and Kinetic Verification of Tetra-n-butyl Ammonium Nitrate (TBANO$_3$) as a Promoter for the Clathrate Process Applicable to Precombustion Carbon Dioxide Capture

*Ponnivalavan Babu[1], Minghuang Yao[1], Stuti Datta[1], Rajnish Kumar[2], Praveen Linga[1]**

[1]Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore 117 576

[2]Chemical Engineering and Process Development Division, CSIR- National Chemical Laboratory, Pune, India

10 pages

2 tables

7 figures

*corresponding author, Tel: (65) 6601-1487; e-mail: Praveen.linga@nus.edu.sg (P.Linga); Fax: (65) 6779-1936.

Table S1: Quantity of materials taken to prepare $TBANO_3$ solution.

$TBANO_3$ solution (mol %)	Weight of $TBANO_3$ (g)	Weight of Water (g)
0.5	4.21	49.50
1.0	8.05	45.00
1.5	11.25	43.50
2.0	14.20	41.00
3.0	19.10	36.80
3.7	22.20	34.20

Table S2: Hydrate Phase equilibrium conditions for fuel gas mixture in presence of $TBANO_3$

System (mol %)	Temperature (K)	Equilibrium Pressure (MPa)	Equilibrium gas phase composition (CO_2:H_2 mol%)	ΔH_d (kJ/mol) [R^2 or variance]
CO_2 (40%)/H_2 (60%)/$TBANO_3$ (0.5%)	277.1	2.06	34.54:65.46	181.27 [0.9711]
	278.0	3.22	32.33:67.67	
	278.8	4.11	33.27:66.73	
	279.7	5.11	33.43:66.57	
	280.3	5.71	33.52:66.48	
	280.9	6.53	34.97:65.03	
CO_2 (40%)/H_2 (60%)/$TBANO_3$ (1.0%)	277.5	1.97	33.16:66.84	192.06 [0.9920]
	278.5	2.35	34.19:65.81	
	279.4	2.86	33.50:66.50	
	280.1	3.63	32.62:67.38	
	280.7	4.32	33.19:66.81	
	281.4	5.23	34.87:65.13	
	281.8	5.80	33.55:66.45	
	282.4	6.86	33.91:66.09	
	283.0	7.32	33.53:66.47	
CO_2 (40%)/H_2 (60%)/$TBANO_3$ (2.0%)	279.9	1.86	33.89:66.11	206.03 [0.9671]
	280.4	2.77	33.93:66.07	
	281.1	3.64	34.08:65.92	
	281.9	4.57	33.64:66.36	
	282.7	5.64	34.88:65.12	
	283.3	6.45	34.38:65.62	
	283.8	7.49	34.06:65.94	
CO_2 (40%)/H_2 (60%)/$TBANO_3$ (3.0%)	280.44	2.02	33.64:66.36	237.7 [0.9770]
	281.13	2.88	34.46:65.54	
	281.59	3.80	35.03:64.97	
	282.28	4.70	35.41:64.59	
	282.87	5.67	35.28:64.72	
	283.24	6.40	34.25:65.75	
	283.80	7.27	34.55:65.45	
CO_2 (40%)/H_2 (60%)/$TBANO_3$ (3.7%)	281.31	2.01	32.53:67.47	366.5 [0.9847]
	282.05	3.59	33.60:66.40	
	282.54	4.55	32.64:67.36	
	283.15	6.35	33.19:66.81	
	283.49	7.21	33.39:66.61	

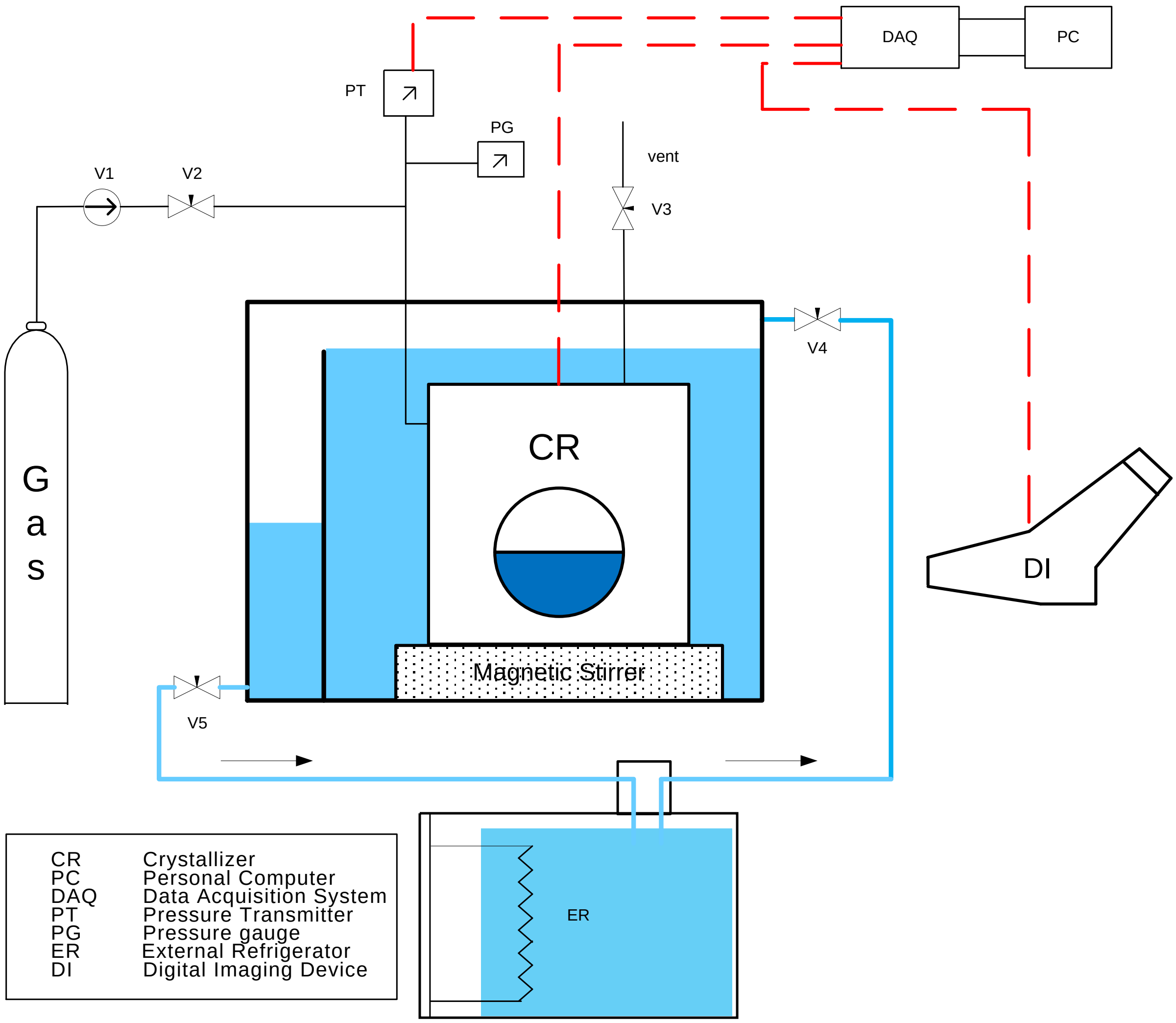

Figure S1. Schematic of the experimental setup employed for the kinetic measurements.

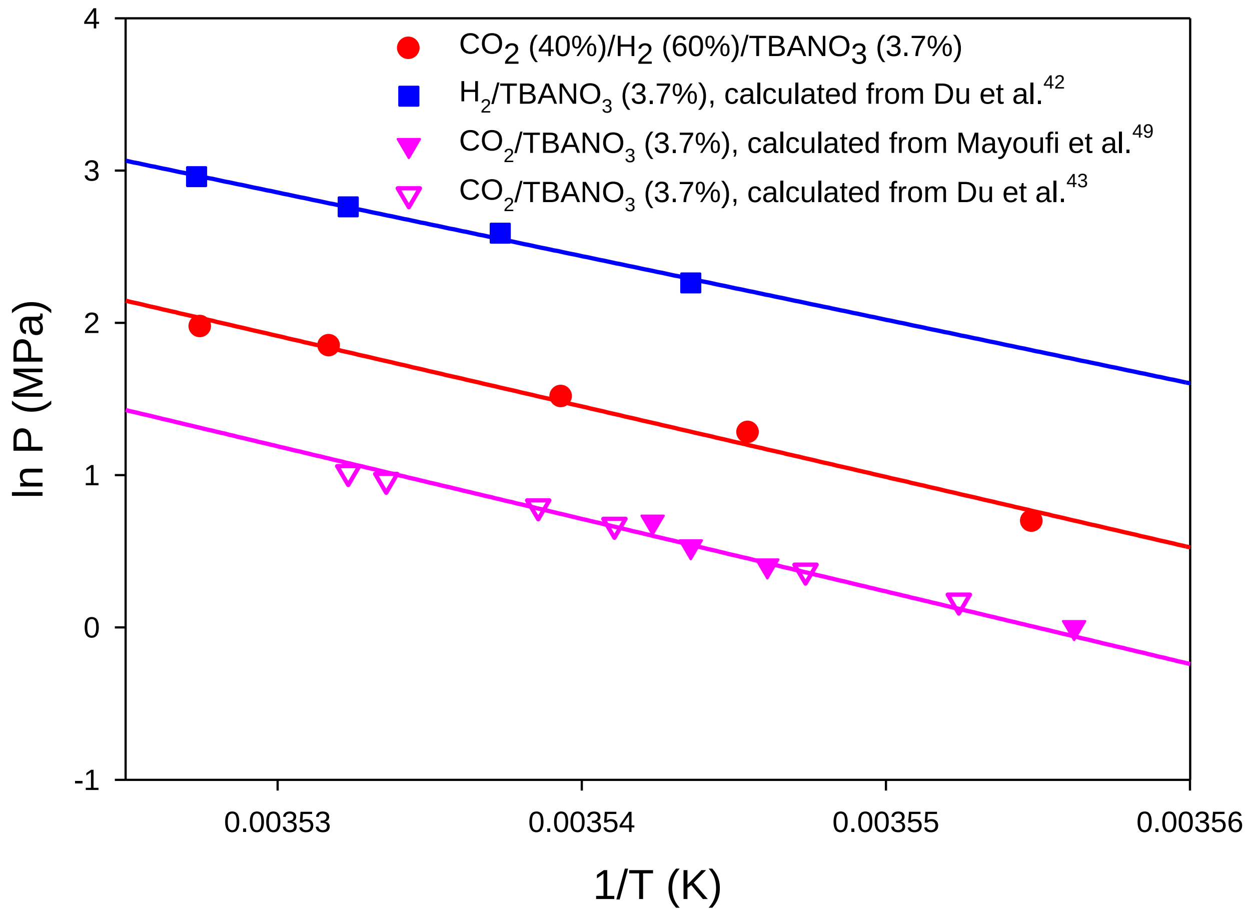

Figure S2. Clausius – Clapeyron plot for CO_2, H_2 and fuel gas mixture in presence of 3.7 mol% $TBANO_3$ solution.

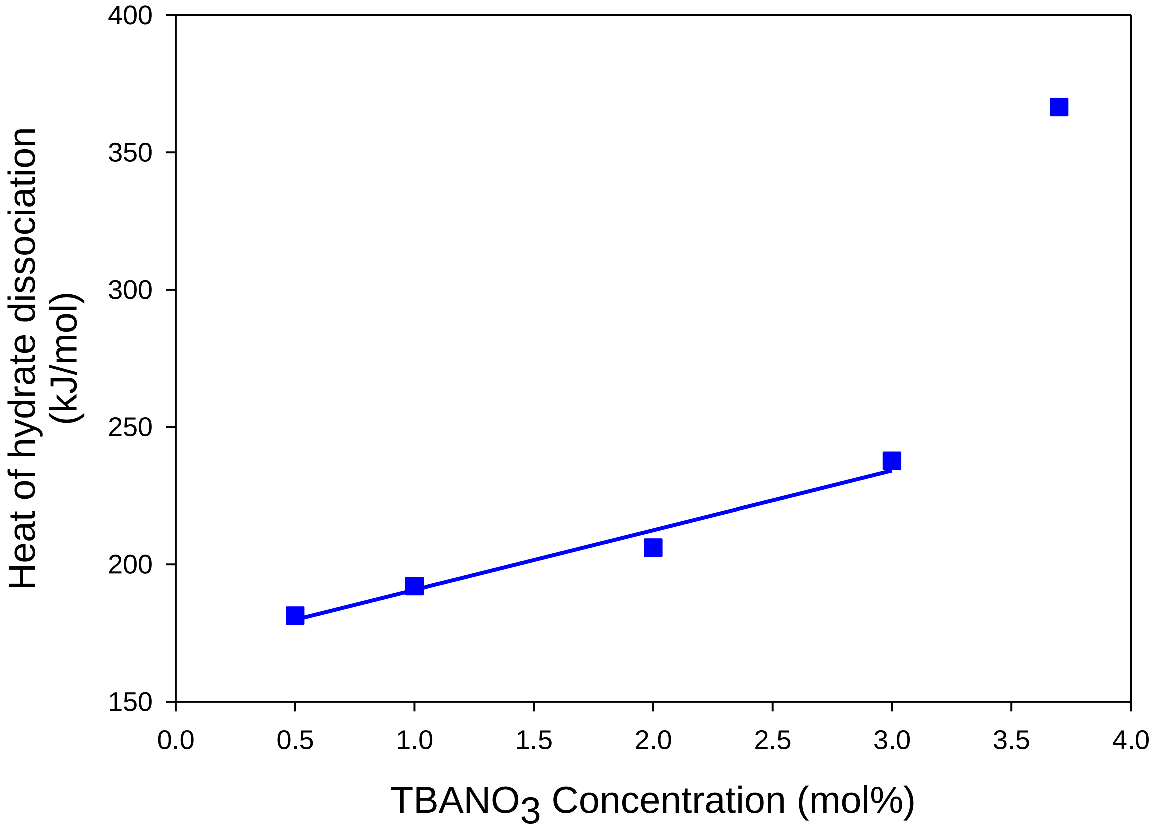

Figure S3. Effect of $TBANO_3$ concentration on the heat of hydrate dissociation.

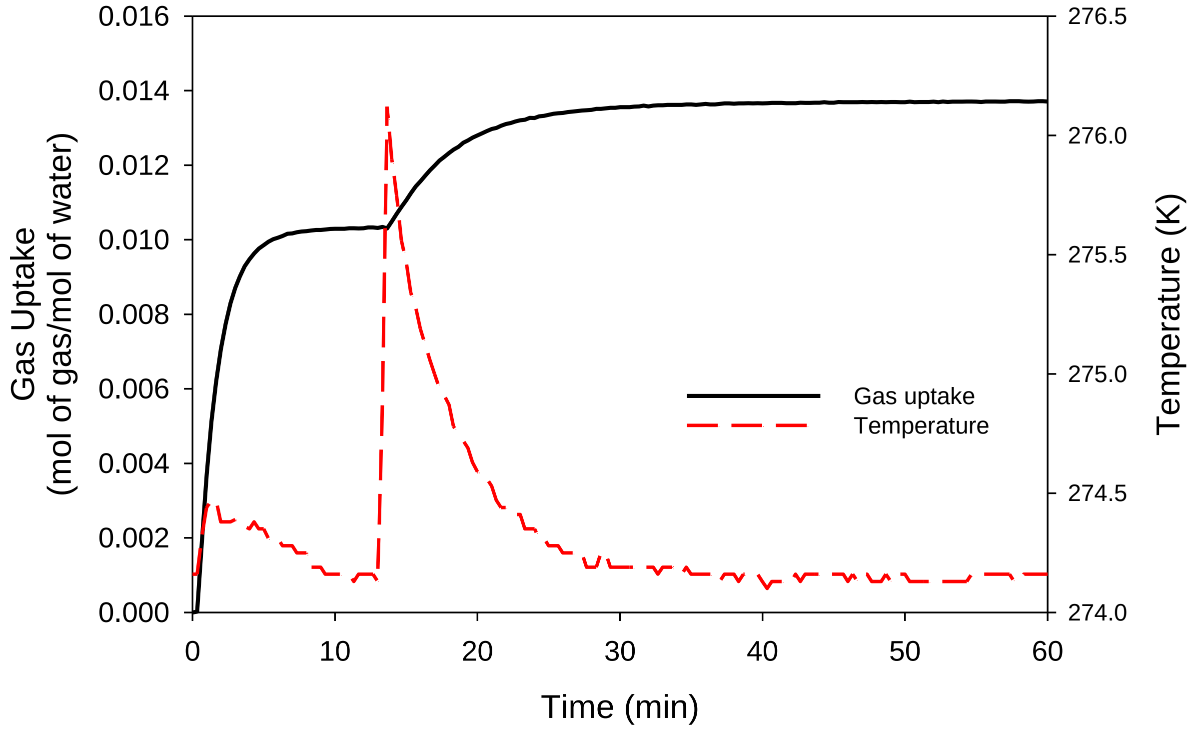

Figure S4.Typical gas uptake measurement curve along with temperature profile at 6.0 MPa, 274.2 K and 0.5 mol% $TBANO_3$ solution (Experiment 1).

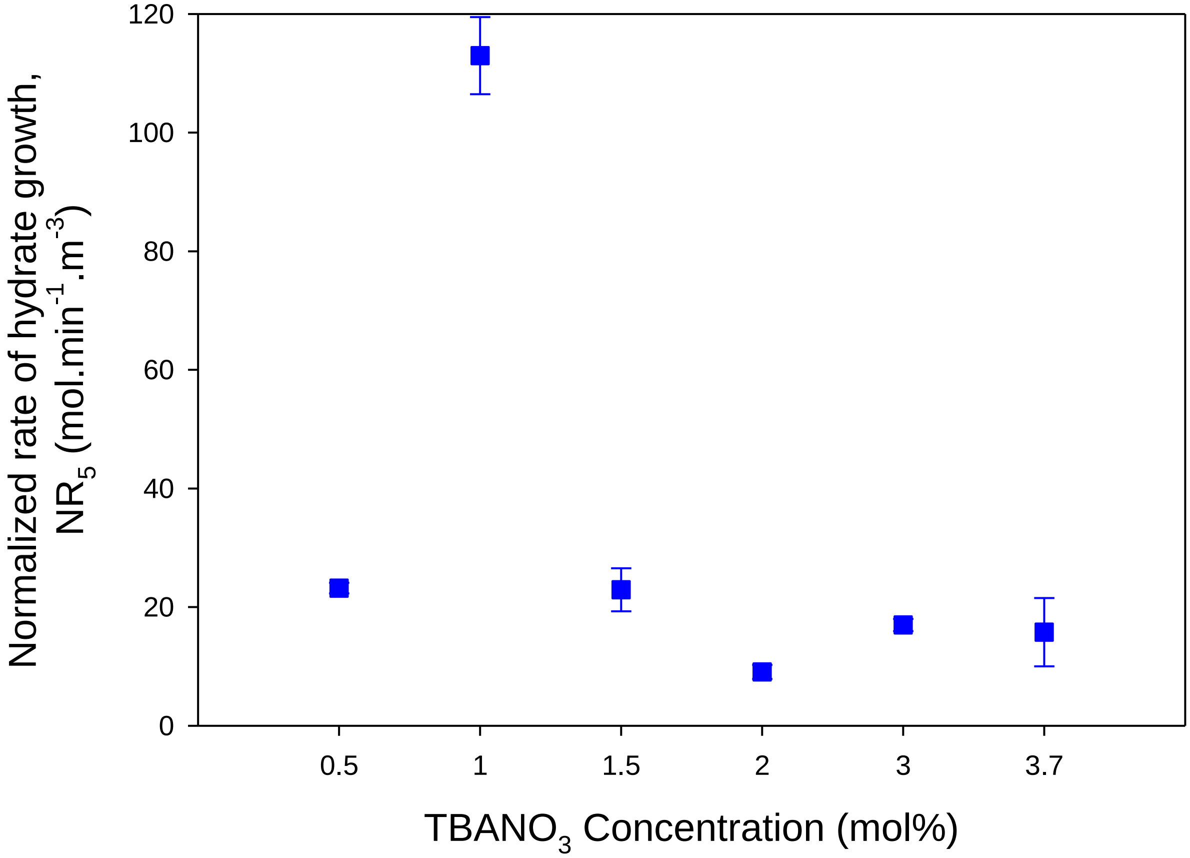

Figure S5. Effect of concentration of $TBANO_3$ on the normalized rate of hydrate formation for first 5 min after nucleation.

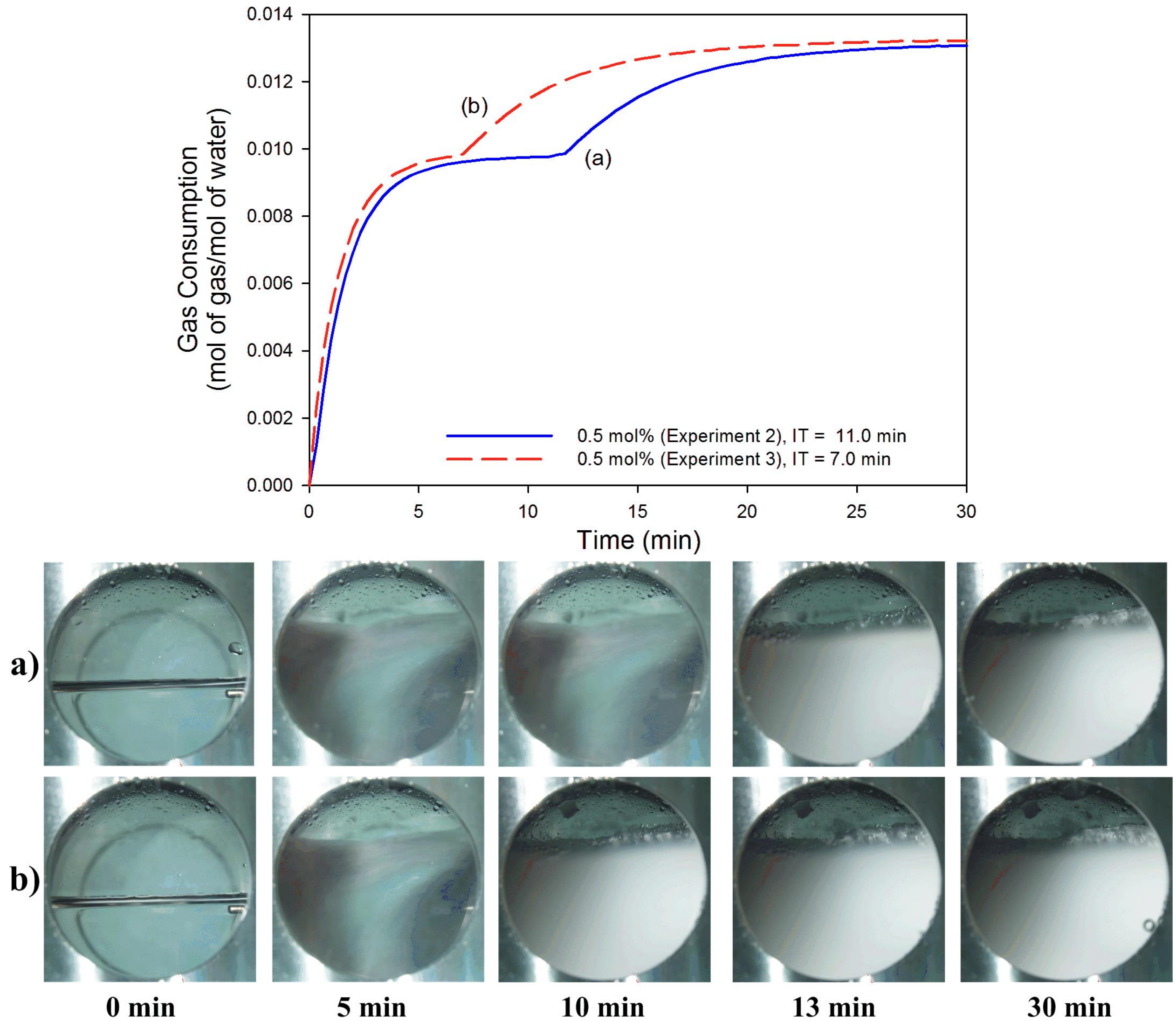

Figure S6. Comparison of gas uptake measurements and microscopic images at different times for experiments with 0.5 mol% $TBANO_3$ solution at 6.0 MPa and 274.2 Experiment 2 (a) Experiment 3 (b).

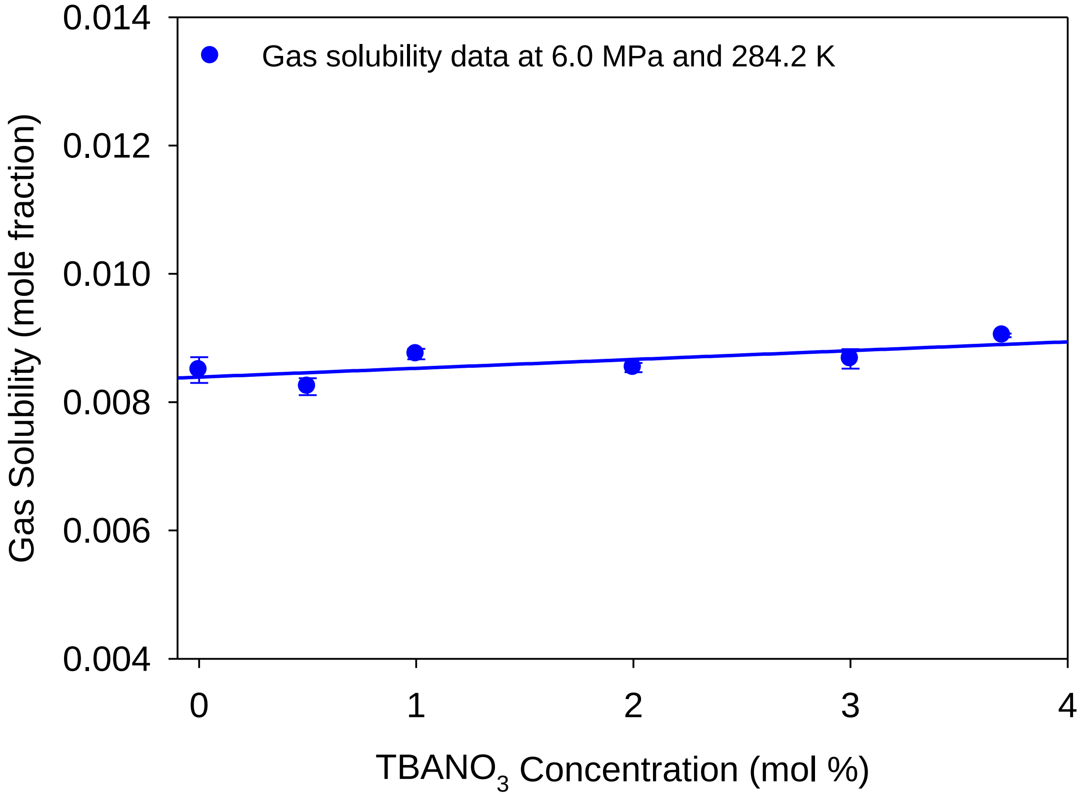

Figure S7. Effect of $TBANO_3$ concentration on the solubility of fuel gas mixture.