

Supporting Information

Insight into the Role of Piperazine in the Thermodynamics and Nucleation Kinetic of Triethylenediamine - Methyl tertiary butyl ether System

Yufeng Quan^a, Yang Yang^a, Shijie Xu^a, Peipei Zhu^a, Shiyuan Liu^a, Lina Jia^a, Junbo Gong^{a, b, c}*

^aNational Engineering Research Center of Industry Crystallization Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China.

^b Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, People's Republic of China.

^c Key Laboratory of Modern Drug Delivery and High Efficiency, Tianjin University, Tianjin 300072, China.

*Corresponding author. E-mail address: junbo_gong@tju.edu.cn

Table S1. Correlated dissolution enthalpy values obtained from Van't Hoff equation

Table S2. Measured MSZWs data of TEDA in pure and impure systems at 308.15 K
(Each experiment was repeated five times)

Table S3. Measured MSZWs data of TEDA in pure and impure systems at 313.15 K
(Each experiment was repeated five times)

Table S4. Measured MSZWs data of TEDA in pure and impure systems at 318.15 K
(Each experiment was repeated five times)

Table S5. Nucleation kinetic parameters of eq. (13) under different amounts of piperazine at 308.15 K.

Table S6. Nucleation kinetic parameters of eq. (13) under different amounts of piperazine at 313.15 K.

Table S7. Nucleation kinetic parameters of eq. (13) under different amounts of piperazine at 318.15 K.

Figure S1. A tendency of supersaturation in different amount of piperazine under different cooling rates: ■ 3 K/h, ● 10 K/h, ▲ 30 K/h, ▼ 60 K/h at different saturation temperature: (a) 308.15 K, (b) 313.15 K, (c) 318.15 K

Figure S2. A tendency of nucleation Gibbs energy ΔG_{crit} in (a) pure TEDA-MTBE system, (b) TEDA-MTBE system with 1% piperazine, (c) TEDA-MTBE system with 3% piperazine under different cooling rates at different saturation temperature: ■ 308.15 K, ● 313.15 K, ▲ 318.15 K

Table S1. Correlated dissolution enthalpy values obtained from Van't Hoff equation

ω (piperazine)	$\Delta H_s/R_g$	R^2
0%	2407.8	0.9922
1%	2340.1	0.9800
3%	2455.5	0.9638

Table S2. Measured MSZWs data of TEDA in pure and impure systems at 308.15 K (Each experiment was repeated five times)

T_0 (K)	Cooling rate R (K/h)	ω (piperazine)		
		0%	1%	3%
308.15	3	5.55	4.95	4.05
		5.62	5.05	3.92
		5.55	5.10	4.37
		5.63	5.06	4.16
		5.51	5.08	4.27
	10	6.75	6.08	5.06
		6.87	6.14	5.38
		6.75	6.02	5.64
		6.64	6.20	5.18
		6.72	6.05	5.47
	30	8.59	7.96	7.20
		8.47	8.02	7.33
		8.68	8.08	7.42
		8.70	7.97	7.05
		8.78	7.91	7.25
	60	10.65	9.68	8.32
		10.52	9.62	8.62
		10.47	9.77	8.98
		10.48	9.37	8.52
		10.35	9.64	8.47

Table S3. Measured MSZWs data of TEDA in pure and impure systems at 313.15K (Each experiment was repeated five times)

T_0 (K)	Cooling rate R (K/h)	ω (piperazine)		
		0%	1%	3%
313.15	3	4.05	3.38	2.49
		4.02	3.35	2.49
		3.98	3.40	2.45
		3.98	3.21	2.58
		4.07	3.31	2.49
	10	5.22	4.51	3.28
		5.20	4.42	3.42
		5.32	4.55	3.35
		5.34	4.43	3.32
		5.22	4.60	3.33
	30	6.95	5.95	5.21
		6.85	5.90	5.30
		7.08	6.20	5.31
		6.94	6.25	5.25
		6.75	6.20	5.32
	60	9.15	8.11	7.4
		9.08	8.35	7.41
		8.75	8.20	7.25
		9.11	8.26	7.50
		8.95	8.36	7.35
	□			

Table S4. Measured MSZWs data of TEDA in pure and impure systems at 318.15 K (Each experiment was repeated five times)

T_0 (K)	Cooling rate R (K/h)	ω (piperazine)		
		0%	1%	3%
318.15	3	3.02	2.42	1.92
		2.99	2.5	1.84
		2.95	2.57	2.01
		2.91	2.55	2.02
		2.87	2.50	1.90
	10	4.07	3.50	2.86
		4.13	3.51	2.72
		4.11	3.49	2.66
		4.01	3.31	2.77
		3.98	3.3	2.92
	30	5.94	5.37	4.92
		5.88	5.42	4.64
		5.85	5.32	4.87
		5.85	5.51	4.68
		5.73	5.34	4.85
	60	8.11	7.55	6.32
		8.09	7.52	6.38
		8.06	7.57	6.66
		7.67	7.63	6.55
		7.61	7.55	6.44
	□			

Table S5. Nucleation kinetic parameters of eq. (13) under different amounts of piperazine at 308.15 K.

piperazine (wt%)	Slope	Intercept	$10^{-3}f/A$	γ (mJ/m ²)	R^2
0%	-2.41	-34.73	0.814	1.59	0.9969
1%	-2.99	-43.20	0.832	1.45	0.9959
3%	-4.65	-68.75	1.080	1.29	0.9794

Table S6. Nucleation kinetic parameters of eq. (13) under different amounts of piperazine at 313.15 K.

piperazine (wt%)	Slope	Intercept	$10^{-3}f/A$	γ (mJ/m ²)	R^2
0%	-10.56	-161.47	1.370	1.23	0.9725
1%	-15.26	-235.22	1.590	1.05	0.9781
3%	-26.21	-407.88	1.890	0.87	0.9599

Table S7. Nucleation kinetic parameters of eq. (13) under different amounts of piperazine at 318.15 K.

piperazine (wt%)	Slope	Intercept	$10^{-3}f/A$	γ (mJ/m ²)	R^2
0%	-5.17	-77.06	1.99	0.97	0.9836
1%	-7.86	-118.74	2.15	0.84	0.9771
3%	-14.86	-228.07	2.33	0.73	0.9832

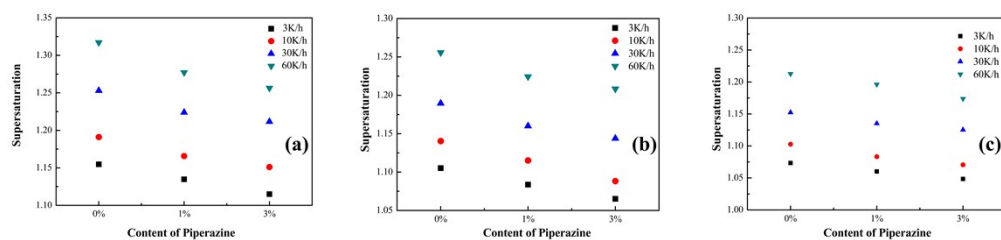


Figure S1. A tendency of supersaturation in different amount of piperazine under different cooling rates: ■ 3 K/h, ● 10 K/h, ▲ 30 K/h, ▼ 60 K/h at different saturation temperature: (a) 308.15 K, (b) 313.15 K, (c) 318.15 K

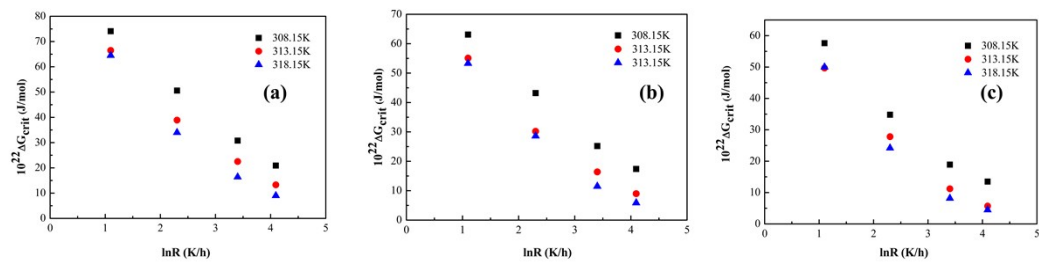


Figure S2. A tendency of nucleation Gibbs energy ΔG_{crit} in (a) pure TEDA-MTBE system, (b) TEDA-MTBE system with 1% piperazine, (c) TEDA-MTBE system with 3% piperazine under different cooling rates at different saturation temperature: ■ 308.15 K, ● 313.15 K, ▲ 318.15 K