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Construction and Parametric Determination of a Thermodynamic Model for Heterogeneous Nucleation of Tetrahydrofuran Hydrate on Solid Surfaces Based on Classical Nucleation Theory

Lijun Jiao
Qingdao Technical college, China

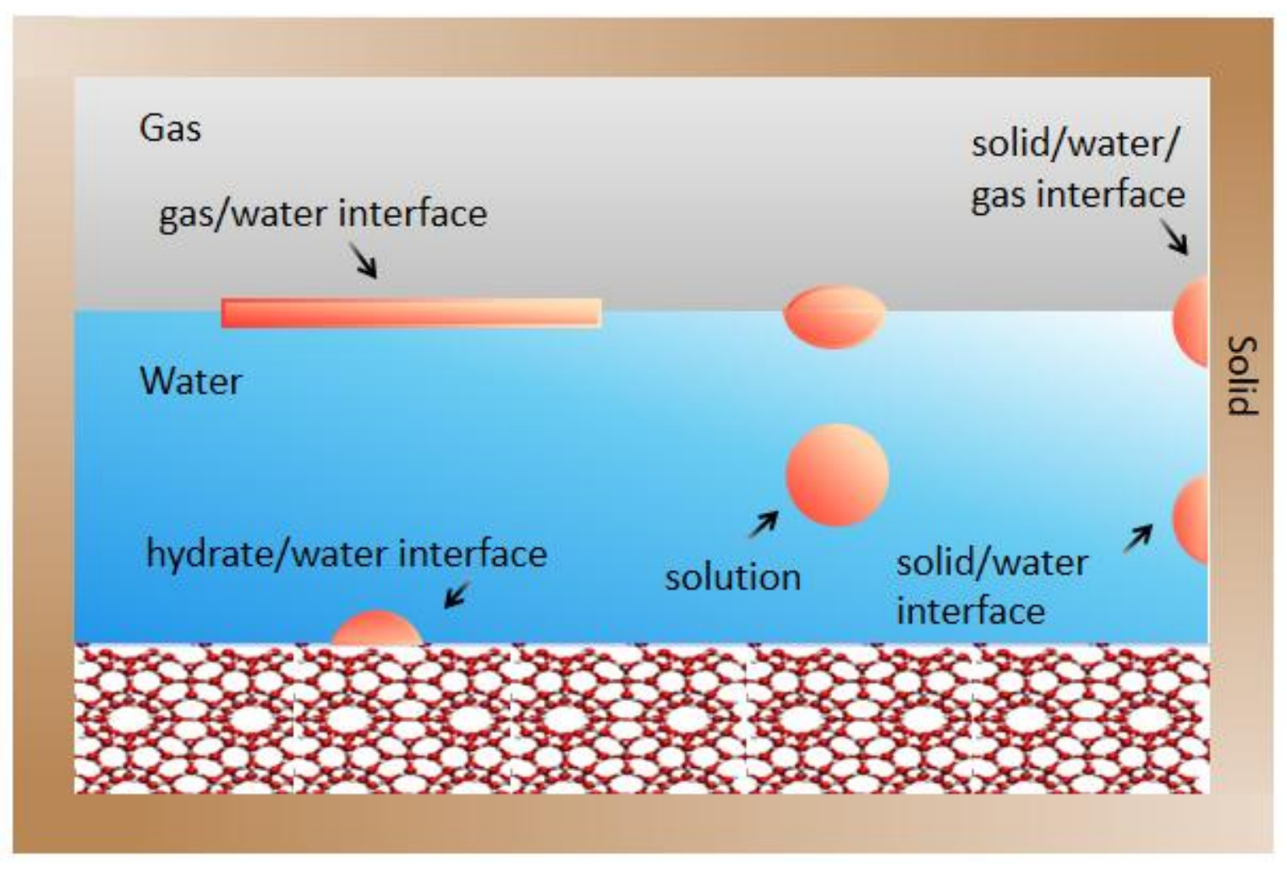
INTRODUCTION & AIM

Hydrate-based cold energy storage is a promising technology for peak-load shifting in air-conditioning systems. However, slow and unpredictable nucleation remains a critical bottleneck that prevents practical deployment.

- *THF hydrate forms at atmospheric pressure and ~277.6 K, making it ideal for laboratory-scale cold storage research.*
- *Classical Nucleation Theory (CNT) predicts that heterogeneous nucleation on solid surfaces lowers the free energy barrier via the geometric factor φ:*

$$\Delta G_{\text{crit}}^{\text{het}} = \phi \cdot \Delta G_{\text{crit}}^{\text{hom}}, \quad \phi = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

- *However, how surfactants interact with metal surfaces to modulate θ and γ_hl has not been systematically investigated.*



Research gap: Prior studies focused on either solid surfaces or surfactants independently; no study has quantified their synergistic effects under rigorously controlled static conditions with large-N parallel experiments.
Aim: To explain the mechanistic basis for how solid/liquid interfacial thermodynamic parameters effect hydrate nucleation.

METHOD

Experimental System:

Solution: 19 wt% THF / 81 wt% deionized water (stoichiometric for structure II hydrate)
Metal substrates: Al (99.996%), Cu (99.99%), Zn (99.99%) — polished prior to each experiment
Surfactants: SDS, SDBS (anionic); DTAC (cationic) — all at 0.05 wt%
Water Bath Experiments (for direct observation of nucleation phenomenology)

Reactor: Glass test tubes (15 mm ID × 150 mm), sealed with rubber stoppers
Temperature control: DC-3050 thermostatic bath (±0.1 K); set to 273.2–274.2 K
Detection: PT100 RTDs + Agilent 34901 data acquisition; nucleation identified by sharp exothermic temperature spike
10 parallel samples per condition; glassware rinsed with DI water between runs (eliminate memory effect)
High-speed camera imaging for visual observation of nucleation onset and morphology

Interfacial Parameter Measurement

Hydrate-liquid interfacial tension: spinning drop tensiometry
Substrate-liquid interfacial tension and contact angle: sessile drop method on polished metal surfaces with/without surfactant
Solid-hydrate interfacial energy: estimated via Berthelot combining rule

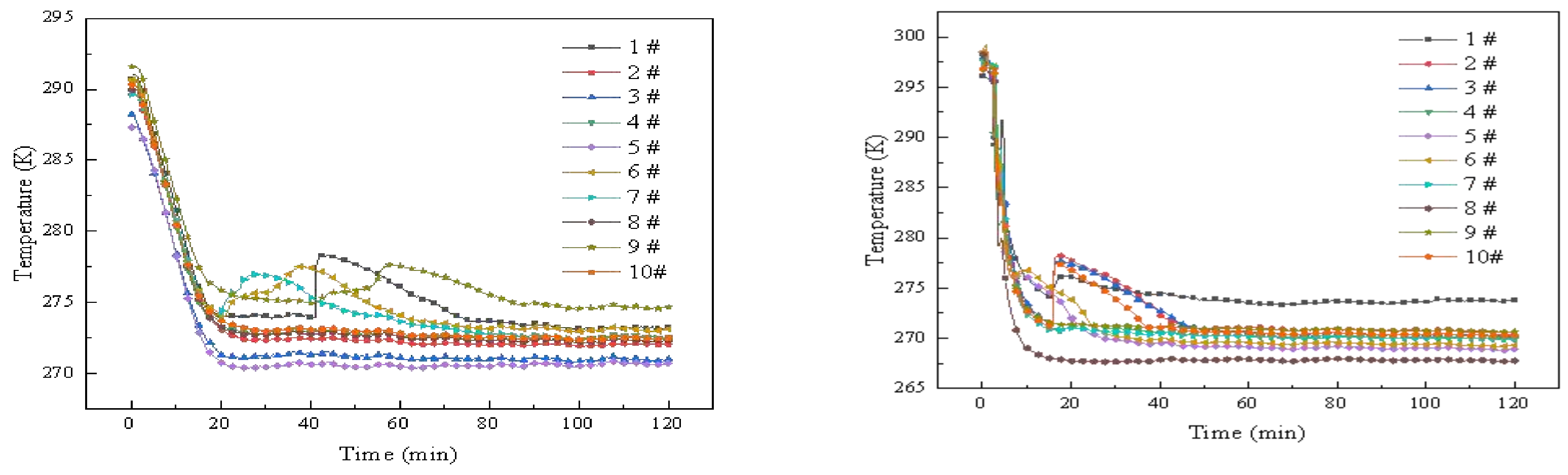
RESULTS & DISCUSSION

Table 1 Experimental system in water bath

Research focus	Experimental group	Solid surface	Surfactant concentration (wt%)	Surfactant type	Water bath temperature (K)	Number of parallel tests
Surfactant type	E1	Aluminum	0.05	SDS	275.2	10
	E2	Aluminum	0.05	SDBS	275.2	10
	E3	Aluminum	0.05	SDSN	275.2	10
	E4	Aluminum	0.05	DTAC	275.2	10
	E5	Aluminum	0.05	Tween 20	275.2	10
Solid surface	E6	Copper	0.05	SDBS	275.2	10
	E7	Zinc	0.05	SDBS	275.2	10
	E8	None (no solid)	0.05	SDBS	275.2	10
Temperature	E9	Aluminum	0.05	SDBS	273.3	10

High-energy metal surfaces lower ΔG by improving wettability with the hydrate phase (reducing θ), consistent with CNT. Notably, Zn showed the strongest promotion despite having lower bulk surface energy than Cu, suggesting additional chemical activation effects (e.g., surface oxide chemistry) that are currently under further investigation.

System	Nucleation behavior
No solid substrate	No nucleation observed (within observation window)
Al surface	Slowest among metals; longest induction times
Cu surface	Intermediate promotion
Zn surface	Strongest promotion; shortest induction times



(a) E2 (b) E9

Fig. T-t profiles of THF hydrate nucleation at different water bath temperatures

Table 2 Induction time of THF hydrate nucleation in different systems

system	1# (min)	2# (min)	3# (min)	4# (min)	5# (min)	6# (min)	7# (min)	8# (min)	9# (min)	10# (min)
E1	3.00	9.16	29.17	27.33	33.67	98.50	27.17	>120	>120	>120
E2	7.33	9.17	29.00	28.33	>120	>120	>120	>120	>120	>120
E3	16.50	22.83	68.50	83.33	>120	>120	>120	>120	>120	>120
E4	7.17	22.67	10.50	29.17	29.50	22.83	74.17	84.50	>120	>120
E5	5.83	7.00	2.50	20.67	41.83	43.00	>120	>120	>120	>120
E6	51.83	69.33	115.3	>120	>120	>120	>120	>120	>120	>120
E7	10.50	3.67	5.83	2.33	32.83	78.00	33.50	>120	>120	>120
E8	93.00	>120	>120	>120	>120	>120	>120	>120	>120	>120

Water bath experiments with surfactants revealed fundamentally different behaviors depending on surfactant charge:

Anionic surfactants (SDS, SDBS) — Inhibition:

Adsorb onto metal surfaces via van der Waals forces, with hydrophobic C_{12} chains lying flat against the substrate, forming surface hemicelles (~5 nm)
This surface passivation shields high-energy metal sites, reduces effective surface energy, and increases the solid-hydrate contact angle θ

Net effect: elevation of ΔG, inhibiting nucleation
The detrimental contact angle increase outweighs any beneficial reduction in γ_{hl}

Cationic surfactant (DTAC) — Promotion:

Does not adsorb significantly onto positively charged metal surfaces
Forms micelles in the bulk phase, reducing γ_{hl} from ~35 mJ/m² to ~20 mJ/m²
Decreases both the critical nucleus radius r and ΔG without passivating the metal surface*
Net effect: promotion of nucleation through bulk interfacial modification

CONCLUSIONS

- *THF hydrate nucleation under static conditions is inherently stochastic and heterogeneous: no nucleation occurred without a solid substrate in any of the parallel samples within the observation period*
- *Metal surfaces promote nucleation following a clear hierarchy: Zn > Cu > Al, attributed to their wettability-mediated reduction of the CNT free-energy barrier*
- *Surfactant effects are mechanism-dependent, not charge-direction-dependent:*
  Anionic SDS/SDBS inhibit nucleation via metal surface passivation (↑θ ↑ΔG)
  Cationic DTAC promotes nucleation via bulk micellization (↓γ_{hl} ↓ΔG)

FUTURE WORK/ REFERENCES/ACKNOWLEDGMENT

- *Surface characterization (AFM, XPS) to quantify surfactant adsorption layer thickness and surface energy modification on each metal*
- *Optimization of substrate geometry (surface area, roughness) to further enhance nucleation promotion efficiency*
- *Scale-up validation in pilot-scale cold storage units for air-conditioning applications*
- *Extension of model to mixed surfactant systems and nanoparticle-modified surfaces*

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