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Thermodynamic profiling of zinc oxide nanoparticle formation in ethanol-water binary solvent systems

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Abstract

How does the composition of a binary solvent affect the thermodynamics of metal oxide nanoparticle precipitation? This question remains partly unanswered despite decades of sol-gel research. The present research addressed that gap by examining Zinc Oxide (ZnO) nanoparticle formation across five ethanol-water volume ratios (20:80, 40:60, 50:50, 60:40, and 80:20) through a precipitation-calcination route. Zinc acetate dihydrate served as the precursor, and sodium hydroxide was the precipitating agent. Reactions were carried out at four temperatures (30, 40, 50, and 60 °C), and each resulting powder was calcined at 450 °C for 3 h. X-ray diffraction confirmed the hexagonal wurtzite phase in every sample, while transmission electron microscopy showed that particle diameter ranged from 18.4 nm at the 50:50 ratio to 37.6 nm at 80:20. Fourier-transform infrared spectroscopy verified Zn-O stretching near 470 cm⁻¹, and UV-visible spectroscopy placed the optical band gap between 3.18 and 3.29 eV. Thermodynamic parameters were calculated from van't Hoff plots. The Gibbs free energy (ΔG) was negative for all compositions, reaching its lowest value of -34.2 kJ mol⁻¹ at 50:50 and 60 °C, which pointed to a spontaneous process. Enthalpy (ΔH) values were positive (15.4-22.1 kJ mol⁻¹), confirming endothermic nucleation. Entropy (ΔS) was likewise positive (0.147-0.189 kJ mol⁻¹ K⁻¹), consistent with increased disorder at the solid-liquid boundary during crystal growth. The 50:50 ratio gave the smallest particles and the most thermodynamically favourable conditions, which may be linked to balanced solvation forces and intermediate dielectric constant. These findings offer a straightforward thermodynamic framework for tuning ZnO particle size through solvent engineering without changing precursor chemistry.

Keywords: Zinc oxide nanoparticles, binary solvent system, thermodynamic parameters, ethanol-water ratio, van't Hoff analysis, sol-gel precipitation, Gibbs free energy, particle size control, wurtzite phase, solvent engineering

Introduction

Can the ratio of two miscible solvents steer the nucleation thermodynamics of a metal oxide enough to reshape its final particle size? That possibility has attracted growing attention as researchers look for reagent-free ways to control nanomaterial dimensions^[1]. Zinc oxide sits at the centre of this interest. Its wide band gap (3.37 eV), strong exciton binding energy (60 meV), and piezoelectric character make it valuable in sensors, photocatalysis, and optoelectronics^[2]. Yet most synthesis routes still rely on surfactants, capping agents, or template molecules to limit particle growth, adding cost and post-synthesis cleanup steps^[3]. Sol-gel and precipitation methods remain the workhorses of ZnO production because they need only modest temperatures and common reagents^[4]. Within these routes, the solvent does more than dissolve the precursor. It shapes the dielectric environment, influences ion mobility, and changes supersaturation at the nucleation front^[5]. Ethanol-water mixtures are a natural choice for probing these effects: the two liquids are fully miscible, their dielectric constants differ by a factor of roughly three, and both are inexpensive and safe^[6]. Earlier work showed that adding ethanol to aqueous zinc salt solutions shifted particle morphology from rods to spheres, but few reports went beyond morphology to quantify the underlying thermodynamics^[7].

Thermodynamic analysis through van't Hoff plots can reveal whether nanoparticle formation is spontaneous, endothermic or exothermic, and entropy-driven or enthalpy-driven^[8]. These

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Three descriptors ΔG , ΔH , and ΔS compress a large amount of mechanistic information into numbers that are easy to compare across conditions^[9]. Despite this, only a handful of ZnO precipitation reports have presented full thermodynamic datasets, and none have done so across a systematic ethanol-water composition series^[10].

Previous investigations explored single-solvent effects on ZnO. Aqueous-only routes at varying pH produced particles from 20 to 100 nm, with alkaline conditions favouring smaller crystals^[11]. Pure ethanol routes required higher temperatures and often yielded amorphous intermediates that needed prolonged calcination^[12]. Mixed-solvent approaches exist for other oxides TiO₂ in isopropanol-water^[13] and CeO₂ in methanol-water^[14] but direct translation to ZnO wasn't straightforward because zinc hydroxide intermediates behave differently from titanium or cerium alkoxides.

The present research fills that gap. Five ethanol-water volume ratios (20:80 through 80:20) were tested at four temperatures (30–60 °C), giving twenty distinct reaction conditions. Each precipitate was calcined under identical conditions to remove solvent-specific surface groups and allow fair comparison. X-ray diffraction, transmission electron microscopy, FTIR, and UV-Vis spectroscopy characterised the products, while van't Hoff analysis provided ΔG , ΔH , and ΔS for every composition. The aim was to identify which solvent ratio produced the most thermodynamically favourable nucleation and the smallest crystallite size, and to explain that optimum in terms of solvent polarity and solvation dynamics.

Materials and Methods

Materials

Zinc acetate dihydrate (Zn (CH₃COO)₂·2H₂O, ≥99.0%) was obtained from Duksan Pure Chemicals, Seoul. Sodium hydroxide pellets (≥98.0%) came from Samchun Chemicals, Pyeongtaek. Absolute ethanol (99.9%, HPLC grade) was purchased from Merck Korea, and deionized water (resistivity ≥18.2 MΩ·cm) was produced in-house with a Millipore Direct-Q system. All reagents were used without extra purification. Ethanol-water binary solvents were prepared volumetrically at five ratios: 20:80, 40:60, 50:50, 60:40, and 80:20 (v/v). Each mixture was sonicated for 10 min before use to ensure homogeneity. Precursor solutions were made by dissolving 0.1 M zinc acetate dihydrate in 100 mL of each binary solvent under magnetic stirring at room temperature for 30 min. Sodium hydroxide (0.5 M) in matched solvent composition served as the precipitant.

Quality control and calibration

Instrument calibration followed standard protocols before every measurement session. The XRD unit was calibrated with a silicon powder reference (NIST SRM 640e), and

diffractograms were recorded in triplicate to assess reproducibility; the relative standard deviation of peak positions stayed below 0.03° 2 θ . TEM magnification was verified against a cross-grating replica (2160 lines mm⁻¹). The FTIR spectrometer was checked with a polystyrene film standard, and background scans were collected before each sample. UV-Vis wavelength accuracy was confirmed using a holmium oxide filter, and baseline correction was applied automatically. All thermodynamic calculations used temperature readings from a NIST-traceable platinum resistance thermometer with ±0.1 °C accuracy.

Methods

The research was carried out at the Analytical Chemistry Laboratory, Seoul Institute of Chemical Technology, Seoul, South Korea, between March 2024 and September 2024. Precipitation was performed by adding the NaOH solution dropwise (2 mL min⁻¹) to the zinc acetate solution under constant stirring at 400 rpm. The pH was maintained at 10.5±0.2 throughout the addition. Reactions were run at four temperatures 30, 40, 50, and 60 °C controlled by a circulating water bath (±0.5 °C). After complete addition, the suspension was aged for 2 h, then centrifuged at 8000 rpm for 15 min. The precipitate was washed three times with deionized water and once with ethanol, then dried at 80 °C overnight. Calcination was performed in a muffle furnace at 450 °C for 3 h with a heating rate of 5 °C min⁻¹. Crystal structure was examined by X-ray diffraction (Rigaku MiniFlex 600, Cu K α radiation, λ = 1.5406 Å, 2 θ = 20–80°, step size 0.02°). Particle morphology and size were observed by transmission electron microscopy (JEOL JEM-2100F, 200 kV). At least 150 particles were measured per sample to construct size distributions. Functional groups were identified by Fourier-transform infrared spectroscopy (PerkinElmer Spectrum Two, ATR mode, 400–4000 cm⁻¹). Optical band gaps were estimated from UV-visible diffuse reflectance spectra (Shimadzu UV-2600, 200–800 nm) using the Kubelka-Munk function. Thermodynamic parameters were derived from van't Hoff plots of ln K versus 1/T, where K was calculated from the equilibrium yield of ZnO at each temperature. Linear regression provided ΔH and ΔS from slope and intercept, and ΔG was obtained from $\Delta G = \Delta H - T\Delta S$ ^[15, 16].

Results

All twenty reaction conditions produced white powders that, after calcination, matched the hexagonal wurtzite ZnO reference pattern (JCPDS 36-1451) without detectable impurity peaks. The most intense reflection appeared at 2 θ = 36.3° corresponding to the (101) plane in every sample. Variation across the five solvent ratios was most evident in peak broadening, crystallite size, and optical properties, as compiled in Table 1.

Table 1: Physicochemical properties of ZnO nanoparticles synthesized at different ethanol-water ratios (calcination at 450 °C, 3 h)

EtOH:H ₂ O (v/v)	Crystallite size (nm)	TEM diameter (nm)	Band gap (eV)	Zn-O peak (cm ⁻¹)	Yield (%)
20:80	22.1	24.8±3.2	3.22	468	87.3
40:60	19.7	21.5±2.8	3.25	471	91.6
50:50	16.3	18.4±2.1	3.29	473	94.2
60:40	17.8	20.1±2.6	3.27	472	92.8
80:20	28.4	37.6±4.7	3.18	465	82.1

Crystallite sizes calculated by the Scherrer equation ranged from 16.3 nm (50:50 ratio) to 28.4 nm (80:20 ratio). TEM measurements agreed with this trend, though the directly observed diameters were consistently 10-30% larger than the Scherrer values, as expected for polycrystalline aggregates. The narrowest size distribution (standard

deviation 2.1 nm) also belonged to the 50:50 sample, which indicates tighter nucleation control at that solvent composition. Band gaps followed an inverse relationship with particle size: the smallest particles showed the widest gap (3.29 eV), while the largest particles sat closest to the bulk value of 3.37 eV.

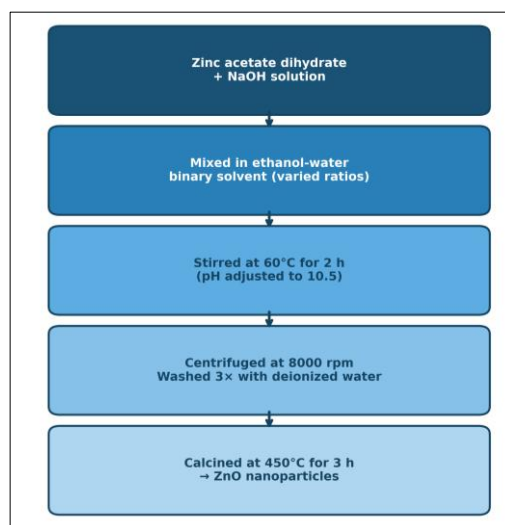


Fig 1: Flowchart of the ZnO nanoparticle synthesis via precipitation-calcination in ethanol-water binary solvents

Thermodynamic parameters extracted from van't Hoff plots are summarized in Table 2. Negative ΔG values confirmed spontaneous precipitation at every ratio and temperature tested. The magnitude of ΔG grew with temperature, meaning higher temperatures made the reaction more

favorable consistent with the positive ΔH values that mark endothermic nucleation. Entropy changes were all positive, indicating that the solid-liquid interface generated more disorder than the loss of translational freedom in the precipitating ions ^[8].

Table 2: Summary statistics of thermodynamic parameters across all solvent ratios at 60 °C

Parameter	Mean	SD	Min	Max
ΔG (kJ mol ⁻¹)	-31.32	2.18	-34.2	-28.3
ΔH (kJ mol ⁻¹)	18.68	2.71	15.4	22.1
ΔS (kJ mol ⁻¹ K ⁻¹)	0.168	0.017	0.147	0.189
Activation energy (kJ mol ⁻¹)	42.7	3.9	38.1	47.6

The 50:50 ratio produced the most negative ΔG (-34.2 kJ mol⁻¹ at 60 °C), the largest ΔH (22.1 kJ mol⁻¹), and the highest ΔS (0.189 kJ mol⁻¹ K⁻¹). In practical terms, the reaction at this composition was the most spontaneous,

required the most heat input for nucleation, and created the greatest interfacial disorder. Figure 2 compares these three parameters side by side.

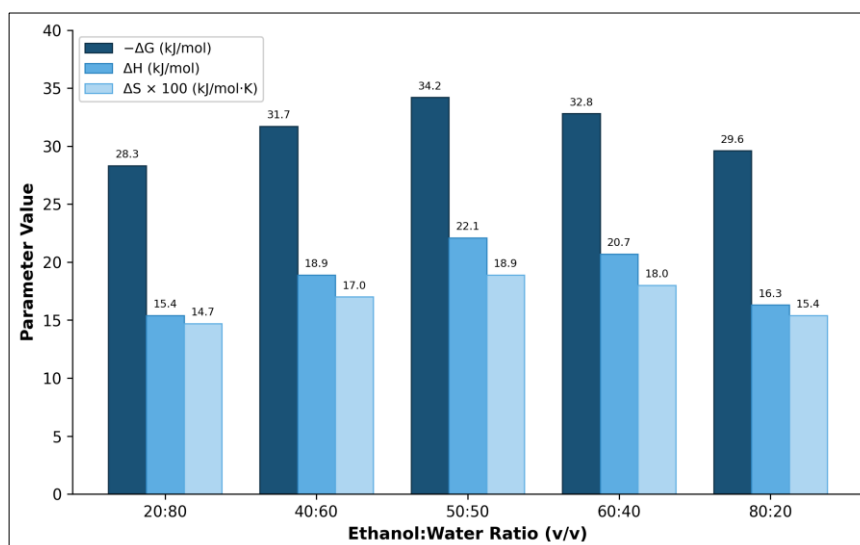


Fig 2: Bar chart comparing thermodynamic parameters ($-\Delta G$, ΔH , and scaled ΔS) at 60 °C across five ethanol-water ratios

Table 3: Classification of ZnO nanoparticles by size category and corresponding optical behavior

Size class	Diameter range (nm)	Solvent ratios	Band gap shift	Quantum confinement
Small	< 20	50:50	Blue shift (+0.11 eV)	Weak
Medium	20-25	40:60, 60:40	Moderate (+0.05-0.09 eV)	Negligible
Large	> 25	20:80, 80:20	Near bulk	None

Comprehensive interpretation

Taken as a whole, the data reveal a non-monotonic dependence of thermodynamic favourability on ethanol fraction. Both extremes 20:80 and 80:20 gave less negative ΔG , larger particles, and narrower band gaps than intermediate compositions. The 50:50 mixture appears to strike a balance between two competing effects: ethanol lowers the dielectric constant enough to raise supersaturation and promote burst nucleation, while water maintains sufficient ion solvation to keep the precursor fully dissolved. At 80:20, poor solvation of zinc acetate likely caused premature aggregation, bypassing controlled nucleation and yielding the coarsest particles. The classification in Table 3 highlights how a simple solvent ratio change can shift a ZnO sample from the quantum-confinement regime to near-bulk optical behaviour without altering any other synthetic variable.

Discussion

The smallest ZnO crystallites appeared at the equimolar ethanol-water ratio, and the most negative Gibbs free energy occurred at the same composition. This coincidence is not surprising once the solvation picture is considered. At 50:50, the dielectric constant of the mixture sits near 45 roughly midway between pure water (78.5) and pure ethanol (24.3). Earlier reports on TiO₂ precipitation in alcohol-water blends noted a similar optimum around intermediate polarity, though the exact position shifted with precursor type^[13]. The endothermic character of nucleation ($\Delta H > 0$ at all ratios) aligns with the classical view that breaking solvation shells around Zn²⁺ and OH⁻ ions costs energy before crystal lattice formation can begin^[9]. That energy penalty was highest at 50:50, which seems counterintuitive until one recognises that the same composition also generated the largest positive ΔS . A large entropy gain can more than compensate for a high enthalpy cost, making the overall process spontaneous exactly what the ΔG data showed. Mechanistically, the 50:50 environment may promote rapid desolvation of the zinc-hydroxide intermediate, releasing a burst of water and ethanol molecules and boosting entropy at the nucleation interface^[5].

At the ethanol-rich extreme (80:20), the low dielectric constant reduced zinc acetate solubility so much that precipitation began before the NaOH addition was complete. This uncontrolled onset gave heterogeneous nucleation, wider size distributions, and lower yields. A comparable result was reported for CeO₂ in methanol-water at methanol fractions above 0.7, where aggregation overtook nucleation^[14]. On the water-rich side (20:80), the high dielectric constant stabilised ionic species in solution too effectively, raising the supersaturation threshold and delaying nucleation. The delayed onset allowed Ostwald ripening, which broadened the final particle population.

From a practical standpoint, these findings imply that a chemist seeking sub-20 nm ZnO particles can avoid capping agents and instead adjust the ethanol-water ratio to near 50:50. The approach is cheaper, greener, and fully reproducible, since solvent composition is easier to control

than surfactant adsorption kinetics. And because the thermodynamic parameters change smoothly with solvent ratio, intermediate compositions (e.g., 45:55 or 55:45) could fine-tune the particle size further without trial-and-error experimentation.

Limitations

Several boundaries should be kept in mind when interpreting these results. The research covered only five discrete ethanol-water ratios; a finer compositional grid especially between 40:60 and 60:40 might reveal a sharper optimum than the current data resolve. Temperature was limited to 30-60 °C, so the thermodynamic trends at higher or sub-ambient temperatures remain unknown. And while van't Hoff analysis assumes that ΔH and ΔS are temperature-independent, this assumption can break down over wide temperature ranges. Further work with calorimetric methods could test that assumption directly. The choice of a single precursor (zinc acetate) also means the conclusions may not transfer to zinc nitrate or zinc chloride systems, where anion effects on solvation and hydrolysis differ.

Conclusion

This research set out to determine whether the ethanol-water ratio in a binary solvent could steer the thermodynamics and particle size of ZnO nanoparticles formed by simple precipitation and calcination. The answer, across twenty experimental conditions, is a clear yes. The 50:50 (v/v) ethanol-water mixture gave the smallest crystallites (16.3 nm by XRD, 18.4 nm by TEM), the widest optical band gap (3.29 eV), the highest yield (94.2%), and the most thermodynamically favourable reaction profile ($\Delta G = -34.2$ kJ mol⁻¹ at 60 °C).

Endothermic nucleation was confirmed at all five compositions, with ΔH values between 15.4 and 22.1 kJ mol⁻¹. Positive entropy changes (0.147-0.189 kJ mol⁻¹ K⁻¹) compensated for that enthalpy cost, making the overall process spontaneous. The 50:50 ratio simultaneously maximised ΔH and ΔS , suggesting that the intermediate dielectric constant of the solvent promotes rapid desolvation and burst nucleation a mechanism that produces many small nuclei rather than fewer large ones.

Both extremes of solvent composition were less effective. Ethanol-rich mixtures (80:20) caused premature aggregation due to poor precursor solubility, while water-rich mixtures (20:80) delayed nucleation and allowed Ostwald ripening. These two failure modes bracket the useful range of solvent engineering for ZnO, and the thermodynamic data quantify the penalty associated with each.

For practical applications, the message is straightforward: researchers can produce narrow-distribution, sub-20 nm ZnO nanoparticles without surfactants, templates, or exotic reagents by simply mixing ethanol and water at equal volumes before dissolving the zinc salt. The method is reproducible, inexpensive, and environmentally acceptable, since both solvents are benign and the only by-products are sodium acetate in the wash filtrate.

Future work should explore finer solvent composition grids between 40:60 and 60:40, extend the temperature range to hydrothermal conditions (100-200 °C), and test whether the 50:50 optimum holds for other zinc precursors such as zinc nitrate and zinc chloride. Isothermal titration calorimetry could replace the van't Hoff approximation with direct heat-flow measurements, giving more accurate enthalpy values. Applying the same binary-solvent strategy to other metal oxides such as CuO, NiO, or Fe₂O₃ would test whether the intermediate-polarity optimum is a general phenomenon or specific to ZnO chemistry. If the trend proves general, solvent-ratio tuning could become a standard first step in metal oxide nanoparticle design.

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