NOTES ON TECHNIQUES TO DETERMINE CMC

Category	Technique / Method	Principle of CMC Determination	Key Features / Special Characteristics	Advantages	Limitations / Disadvantages
Surface & Physicochemical Methods	Surface Tension (Tensiometry)	Surface tension decreases with increasing surfactant concentration until interface saturation occurs; the breakpoint in the surface tension vs concentration plot corresponds to the CMC.	Usually performed using Du Nouy ring or related methods. Measures adsorption at the air–water interface rather than direct bulk micellization.	Applicable to ionic, non-ionic, cationic, anionic, and zwitterionic surfactants. Direct and widely used method.	Tedious and time-consuming. Sensitive to impurities and temperature fluctuations. Surface saturation may occur below the true CMC due to highly surface-active impurities. Cannot reliably distinguish CAC from true CMC.
	Density Measurement (Densimetry)	Density changes with surfactant aggregation state because micellization changes hydration and partial molar volume. Breakpoint in density vs concentration indicates CMC.	Micellization is associated with dehydration and release of bound water molecules.	Useful for studying hydration behaviour of surfactants.	Poor sensitivity at very low concentrations (<1 mM). Not reliable for many non-ionic surfactants because density variation is too small.
	Viscosity Measurement	Viscosity changes as micelles form;	Usually measured using capillary	Applicable to most surfactant systems,	Lower sensitivity near dilute

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		breakpoint in viscosity vs concentration plot corresponds to CMC.	viscometers.	especially non-ionic surfactants.	concentration regions.
	Refractive Index (RI)	Formation of micelles changes refractive index due to altered turbidity and optical density. CMC obtained from slope change in RI vs concentration plot.	Sensitive to transition between monomers and micelles.	Simple and rapid method.	Sensitive to temperature and low concentration effects.
	Floating Density Bottle / Buoyant Force Method	Apparent weight or buoyant force of a floating density bottle changes because interfacial tension differs below and above CMC.	Based on concentration-dependent buoyant force/interfacial tension variation.	Simple and low-cost experimental setup.	Lower precision compared with standard methods.
Spectroscopic Methods	UV–Visible Spectroscopy (Direct Method)	Absorbance of surfactant solution changes with concentration; breakpoint in absorbance vs concentration	Does not necessarily require an external probe.	Simple and rapid.	Limited sensitivity unless measurable spectral change occurs.

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	UV–Visible Spectroscopy (Indirect / Probe-Based Method)	Probe molecules exhibit different absorption behaviour in water and inside micelles. Changes in absorbance intensity or wavelength indicate micellization.	Includes dye solubilization, spectral shift, tautomerism, ion pairing, donor–acceptor interactions, and nanoparticle-based effects.	Applicable to ionic and non-ionic surfactants under varying electrolyte conditions.	Requires addition of a probe which may alter the true CMC. Probe concentration must be minimized.
	Benzoylacetone (BZA) Tautomerism Method	Keto–enol equilibrium of BZA shifts upon incorporation into micelles. Increase in enol absorbance (~312 nm) and decrease in keto absorbance (~250 nm) indicate CMC.	Micellar interior stabilizes the enolic form because of lower polarity.	Applicable to anionic, cationic, and non-ionic surfactants.	Not suitable for very low CMC surfactants (< ~5 × 10^{-4} mol/L). Small premicellar aggregates may not provide sufficient hydrophobicity for spectral transition.
	Curcumin Tautomerism Method	Micellization shifts equilibrium between diketo and keto–enol forms of curcumin, changing absorbance at 360 and 428 nm.	Probe is highly sensitive to medium polarity.	Simple UV-based approach for CMC determination.	Probe–surfactant interactions may influence micellization.
	Dye Solubilization	Water-insoluble dye	Uses dyes such as	Applicable to a	Dye may perturb

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	Method	dissolves only after micelles form, causing sudden increase in absorbance.	eosin, rhodamine, methyl orange, crystal violet, etc.	broad range of surfactants.	micellar structure. Weak solubilization may produce poor absorbance signals, especially for low-CMC systems.
	Fluorescence Spectroscopy (Indirect Method)	Fluorescent probes experience different environments below and above CMC. Breakpoint in fluorescence intensity or spectral ratio indicates micellization.	Most common probe is pyrene using the I_1/I_3 intensity ratio.	Highly sensitive, precise, rapid, and suitable for low CMC systems.	Requires fluorescent probe which may interact with surfactant. Interpretation may be affected by excimer formation, partition equilibrium, or probe localization.
	Fluorescence Spectroscopy (Direct Method)	Intrinsic fluorescence of surfactant changes with concentration.	Example given: Triton X-100.	No external probe required.	Limited applicability because most surfactants are not intrinsically fluorescent.
	THP-T1 Fluorometric Titration Method	THP-T1 remains non-emissive inside micelles but forms fluorescent aggregates near CMC during titration.	Based on aggregation-induced emission (AIE).	Fast, simple, highly sensitive, and suitable for different surfactant classes.	Requires specialized fluorescent indicator. Relatively less established compared with pyrene methods.

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Light Scattering & Structural Methods	Dynamic Light Scattering (DLS)	Micelle formation increases turbidity and scattered light intensity. Breakpoint in scattering intensity vs concentration indicates CMC.	Sensitive to aggregate size and size distribution.	Non-invasive and highly sensitive for low CMC systems.	Extremely sensitive to dust particles and impurities.
	Small-Angle X-ray Scattering (SAXS / SR-SAXS)	Scattering profiles reveal aggregate size, shape, and morphology above CMC.	Provides morphology information such as spherical, elongated, lamellar, or vesicular structures.	Excellent structural characterization method.	Not primarily used for direct CMC determination. Requires sophisticated instrumentation and model fitting.
	High-Resolution Ultrasound Spectroscopy (HR-US)	Sound velocity and attenuation change upon micellization because of altered compressibility and hydration.	Measures sound speed and ultrasound attenuation.	Non-destructive and useful for studying structural transitions.	Limited sensitivity below ~1 mM and unsuitable for many low-CMC non-ionic surfactants.
Electrochemical Methods	Conductometry / Electrical Conductivity	Ionic surfactants show different conductivity slopes below and above CMC due to partial ionization of micelles.	Degree of micellar ionization (α) can be estimated from slope ratios.	Simple, mature, reliable, and inexpensive for ionic surfactants.	Applicable mainly to ionic surfactants. High electrolyte concentrations and ion exchange effects interfere with measurements. Weak breakpoints

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					may occur for low-CMC systems.
	Carpena Conductivity Model	Conductivity data are fitted using a Boltzmann-type sigmoid equation instead of graphical intersection.	Reduces subjectivity associated with two-line intersection methods.	Improves accuracy when conductivity transition curvature is weak.	Requires computational fitting and model assumptions.
	Streaming Potential Method	Micellization alters streaming potential generated when electrolyte solution flows through a capillary.	Measured using capillary electrophoresis instrumentation.	Sensitive electrokinetic technique.	Requires electrolyte addition for non-ionic surfactants.
	Zeta Potential Method	Surfactant adsorption changes interfacial charge density and zeta potential until micellization occurs.	Measures electrical potential at the liquid–air interface.	Useful for ionic surfactant systems.	Limited applicability to non-ionic systems.
	Potentiometry	Ion-selective electrodes detect electrochemical potential changes caused by micellization.	Based on ion-selective electrode response.	Rapid and selective electrochemical analysis.	Sensitive to temperature and electrode interferences. Poor electrode response may affect accuracy.
	Electrical	Transformation	Frequency-	Sensitive to	Requires specialized

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	Impedance Spectroscopy (EIS)	from monomers to micelles changes electrical impedance and frequency response.	dependent electrochemical characterization.	structural transformations.	instrumentation and interpretation.
	Voltammetry	Micellization changes diffusion coefficient and limiting current of an electroactive probe.	Boron-doped diamond electrodes can eliminate need for reporter probes.	Applicable to ionic and non-ionic surfactants.	Electroactive probes may alter the system. Residual current correction affects accuracy.
Capillary Electrophoresis-Based Methods	Micellar Electrokinetic Chromatography (MEKC)	Solute retention factor or electrophoretic mobility changes with surfactant concentration until micellization occurs.	Based on surfactant-assisted electrophoretic separation.	Useful for studying charged surfactant systems.	Unreliable when unpredictable solute–micelle interactions occur.
	Electrophoretic Mobility Method	Mobility of tracer molecules changes upon micelle formation.	Uses CE instrumentation.	Sensitive to aggregation state.	Requires suitable tracer selection.
NMR-Based Methods	NMR Diffusometry (DOSY / PGSE NMR)	Self-diffusion coefficients change as monomers aggregate into micelles.	Can distinguish CAC from true CMC and detect slow exchange processes.	Provides aggregation number and polydispersity information.	Expensive, technically demanding, and less sensitive at very low concentrations.
	NMR Chemical	Chemical	Can be globally	Useful for studying	Requires advanced

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	Shift Method	environment changes upon micellization cause proton chemical shift variations.	fitted with diffusion data.	premicellar aggregation and molecular interactions.	NMR instrumentation and complex analysis.
Theoretical / Mathematical Methods	Model-Based Analytical Approaches (e.g., Al-Soufi Model)	Experimental data fitted to analytical concentration models; CMC defined objectively via derivative analysis.	Applicable to conductivity, surface tension, diffusion, and NMR data.	Eliminates subjective graphical interpretation and provides physically meaningful fitting parameters.	Depends strongly on model assumptions and may not adequately describe highly polydisperse systems.