

Amplification of the Index of Refraction of Aqueous Immersion Fluids by Ionic Surfactants.

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Goal and Objective

■ Goals:

The discovery of aqueous systems which has **high RI** in order to improve depth of focus (DOF) in 193 nm **Immersion Lithography**

(1) Higher RI than water at 193 nm ($n=1.44$ at 193 nm)

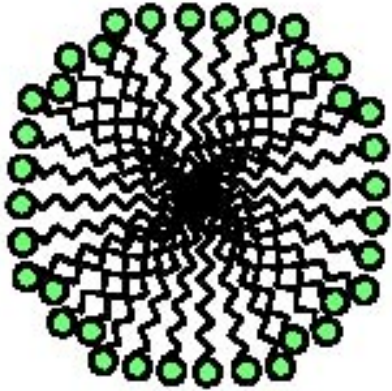
(2) acceptable transparency at 193 nm and compatibility with pertinent photoresist systems employed at 193 nm.
(absorption of water @193 nm $< 0.05 \text{ cm}^{-1}$)

Improvement in depth of focus (DOF)

$$\text{DOF} = k_2 n / (\text{NA}^2)$$

The DOF increased by factor of n (RI)!

Why Surfactants?



Anionic and cationic **surfactants** form aggregates (**micelles**) in aqueous solution above a certain certain critical micelle concentration (cmc) and can stabilize polar or nonpolar compound.

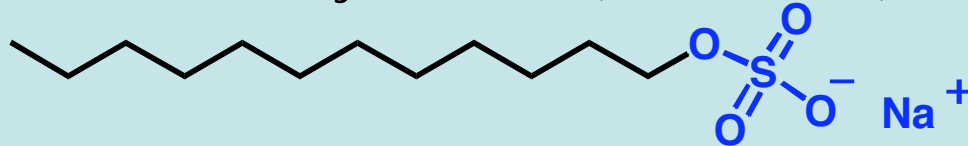
Potential Benefits of Surfactants

- Water based (water has high RI and optical property).
- Resists for 193 nm are know to be compatible with the surfactant systems to be investigated.
- Not photoactive or degradable
- Environmentally benign
- Allow a wide variation of structural modifications
- inexpensive, commercially available materials.

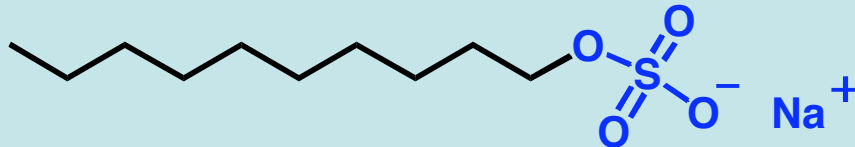
System Selected for Initial Investigation

Surfactants:

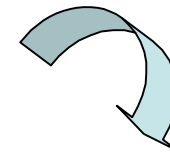
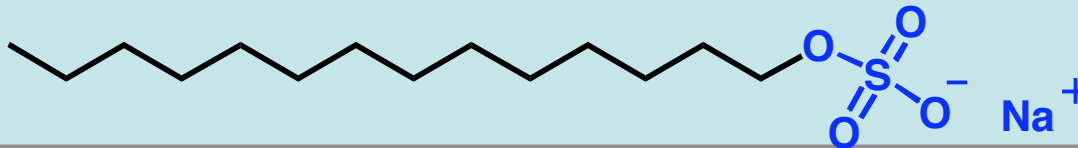
Anionic: sodium dodecyl sulfate (SDS, S12S)



sodium decyl sulfate (S10S)



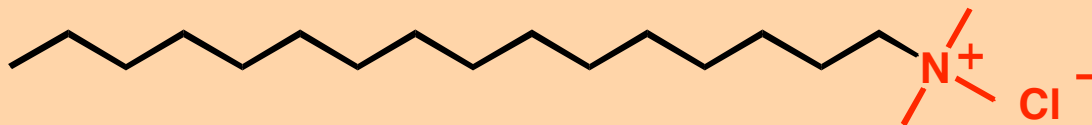
sodium tetradecyl sulfate (S14S)



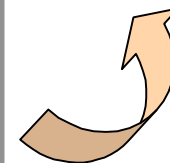
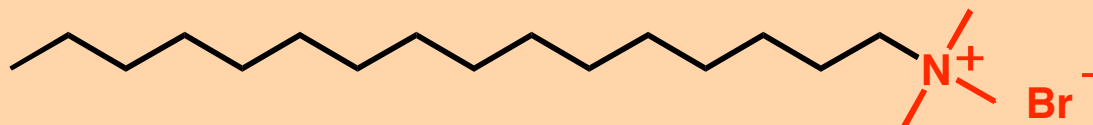
Variation

Concentration
Size of surfactants
Temperature
Additives

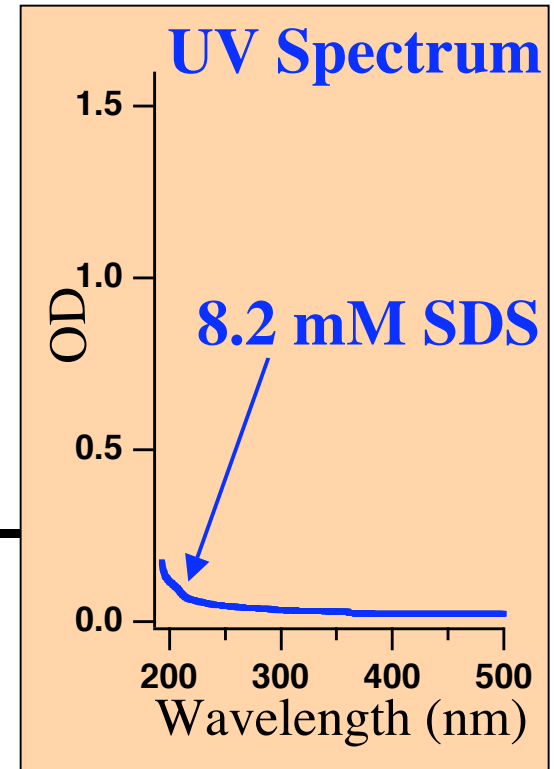
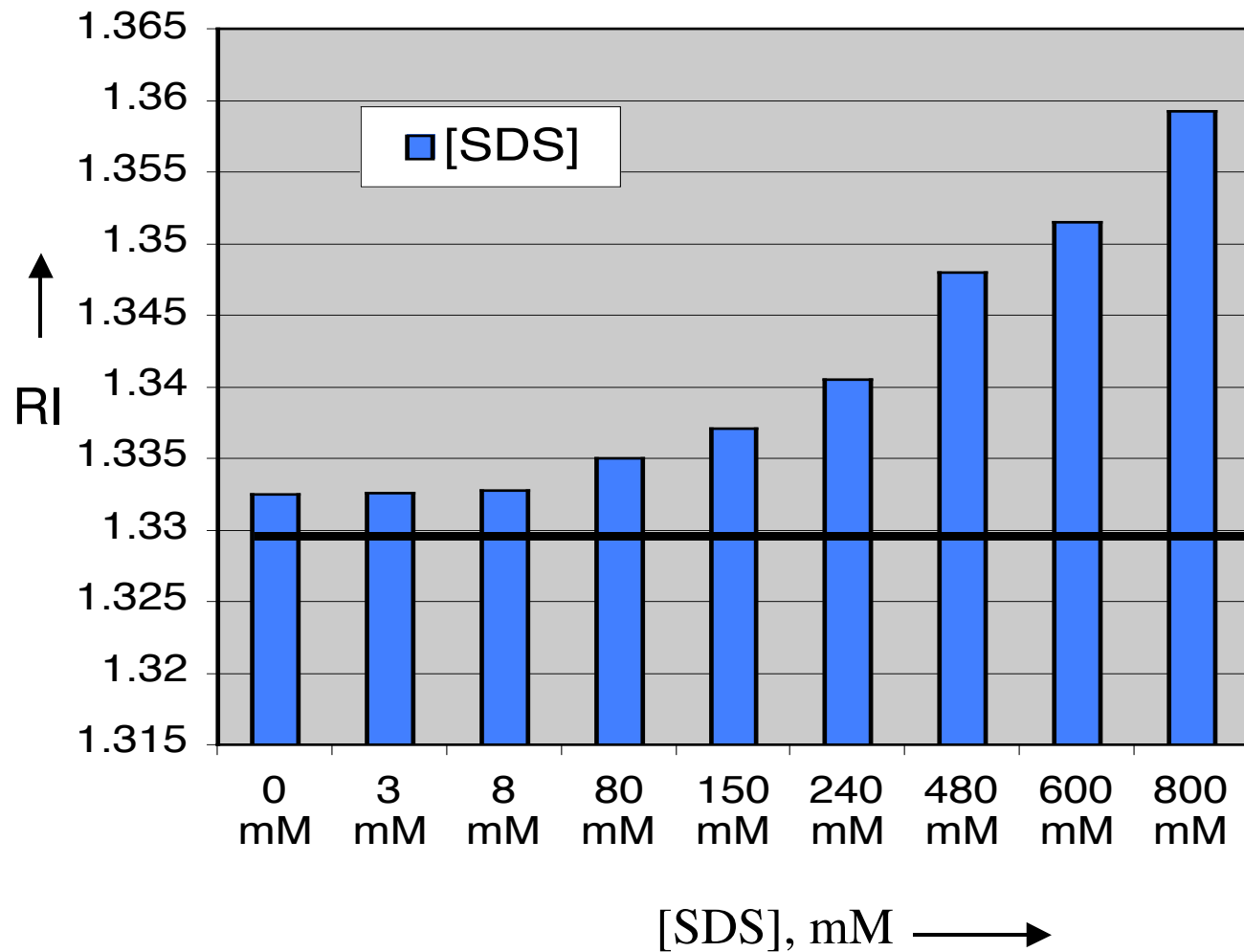
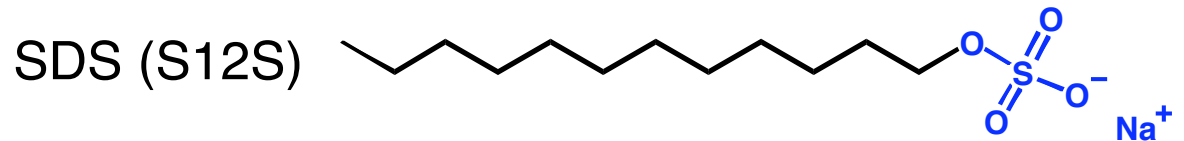
Cationic: cetyl trimethyl ammonium chloride (CTAC)



cetyl trimethyl ammonium bromide (CTAB)



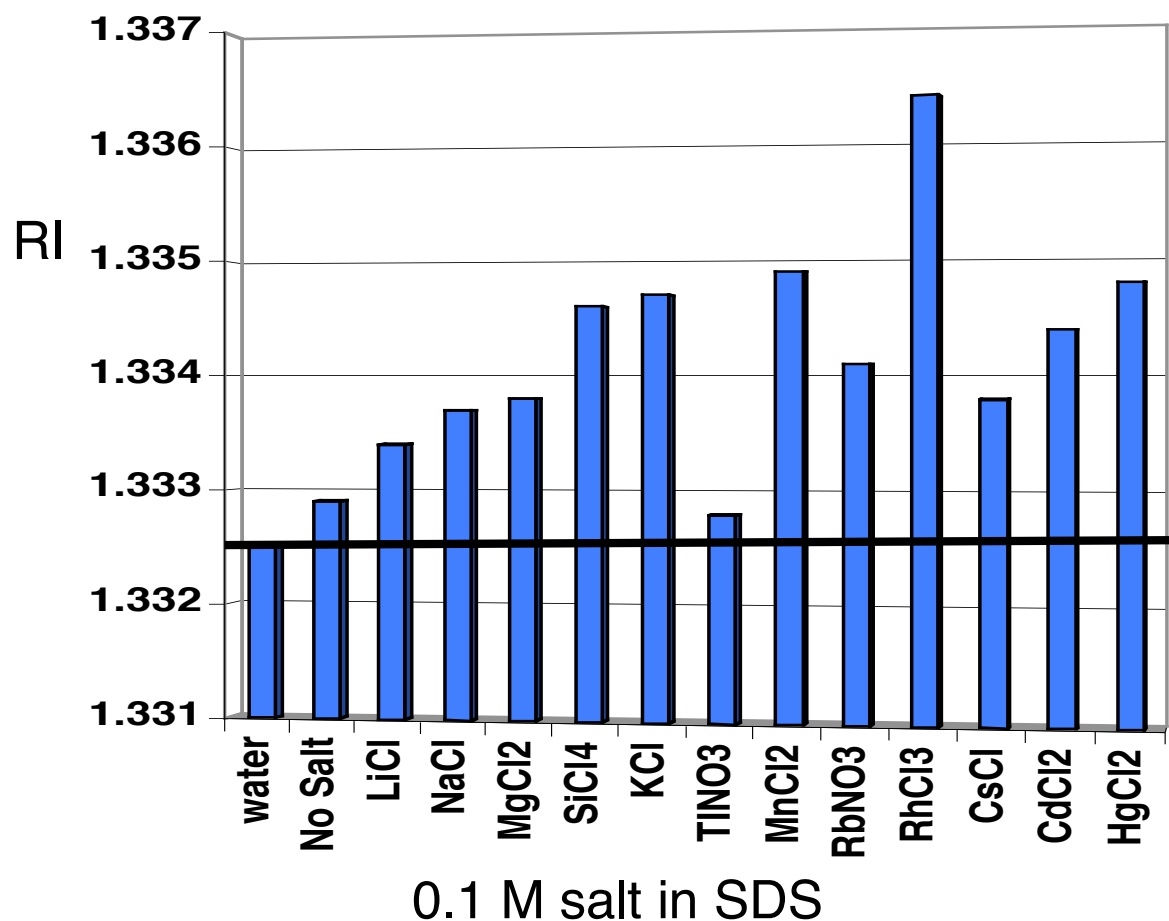
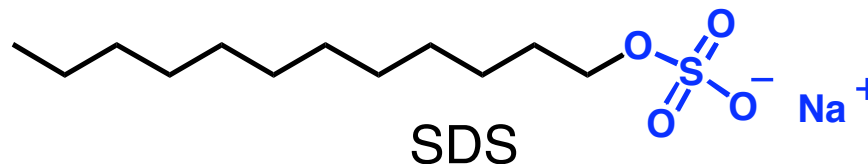
Effect of [SDS] Surfactant on the RI



✓ RI increase upon higher [SDS]

Effect of cations on RI of aqueous SDS

[SDS]= 8.2 mM (cmc), 25 °C
RI measured at 589 nm



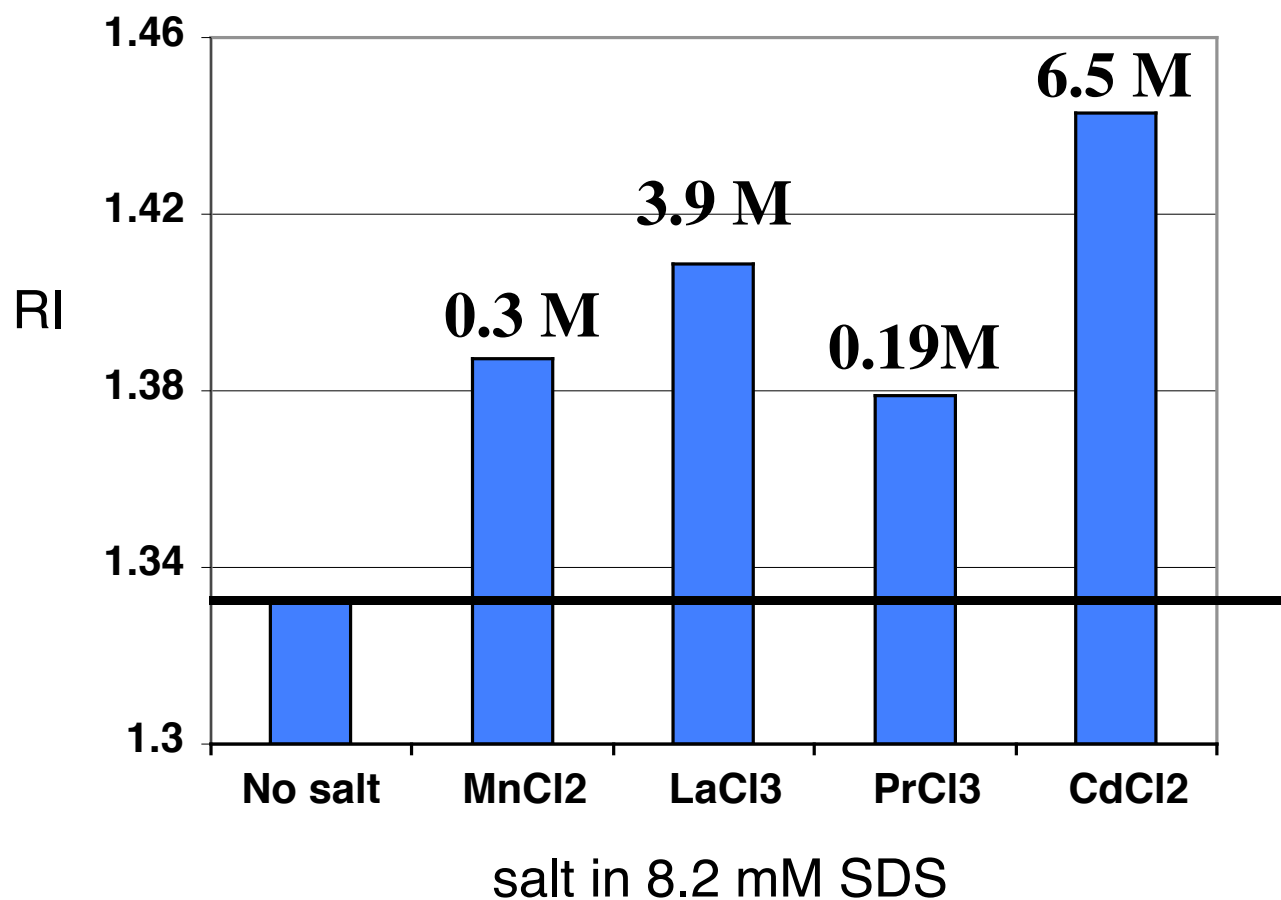
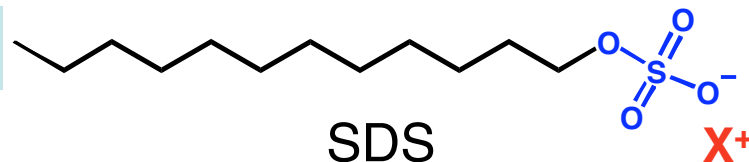
other salts tested

TlNO ₃	NbCl ₅
LaCl ₃	CeCl ₃
PrCl ₃	NdCl ₃
SmCl ₃	EuCl ₃
KI	Gd(NO ₃) ₃
TbCl ₃	HoCl ₃
LuCl ₃	TaCl ₅
PbCl ₂	GdCl ₃
TlF	TlI
Ba(SCN) ₂	

✓ RI increase upon adding salts

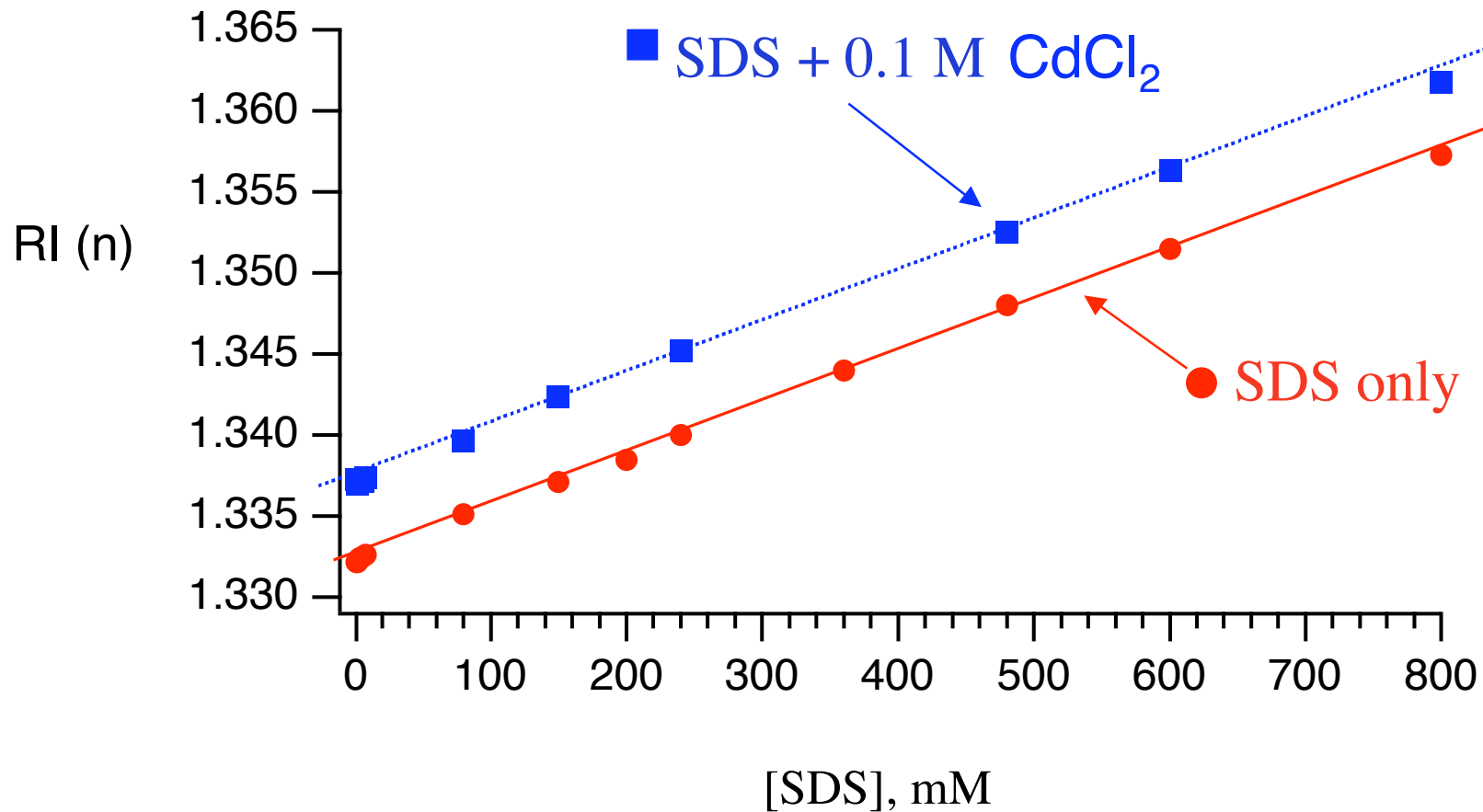
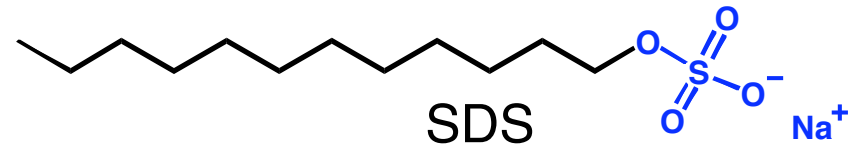
Salts are also selected based on their solubility

[SDS] = 8.2 mM (cmc), 25 °C, [salt] ~ 0.1 M

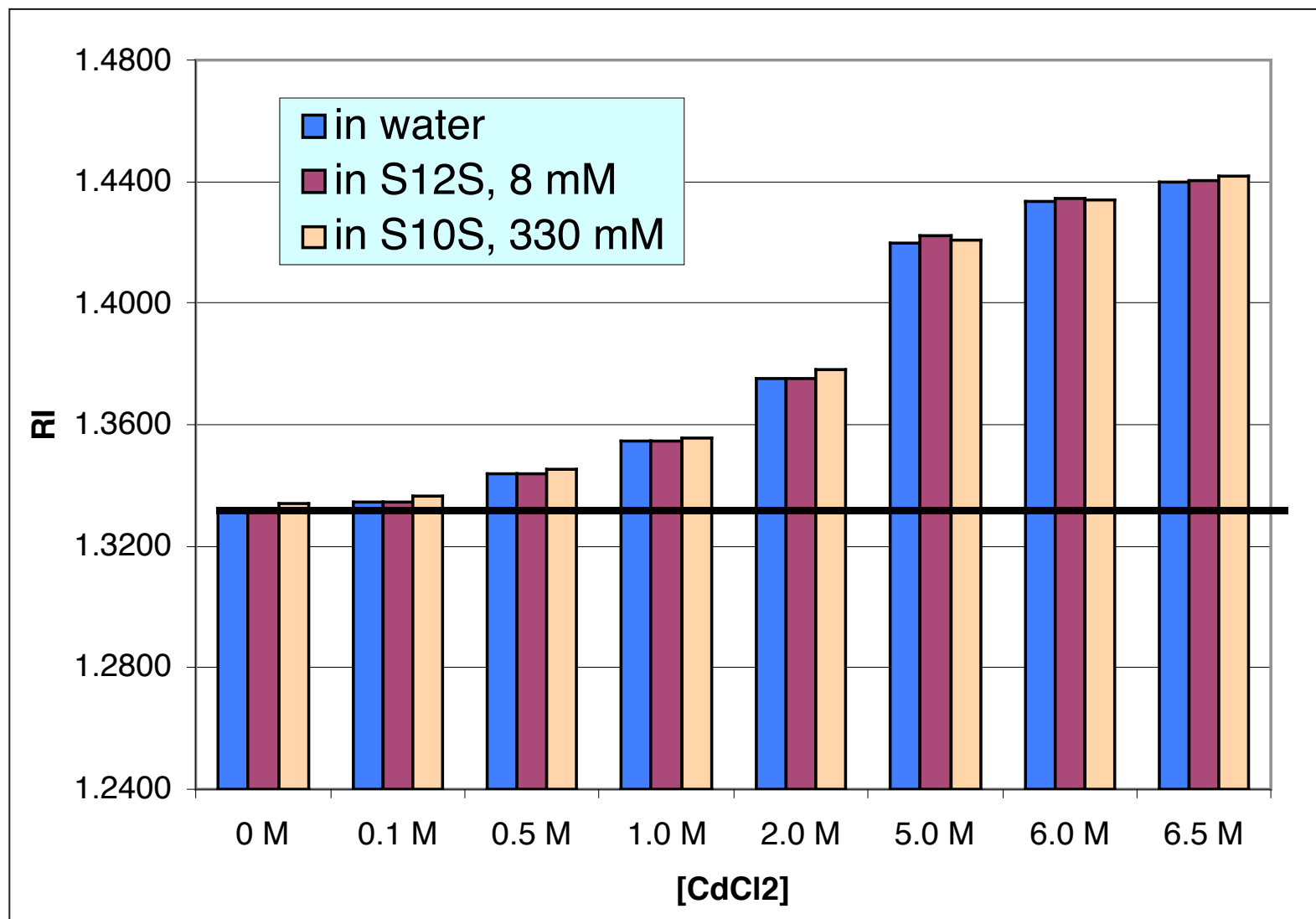


✓ **CdCl₂ show the highest RI & selected for further study**

Effect of [Surfactant] on the RI



Effect of $[\text{CdCl}_2]$ on RI

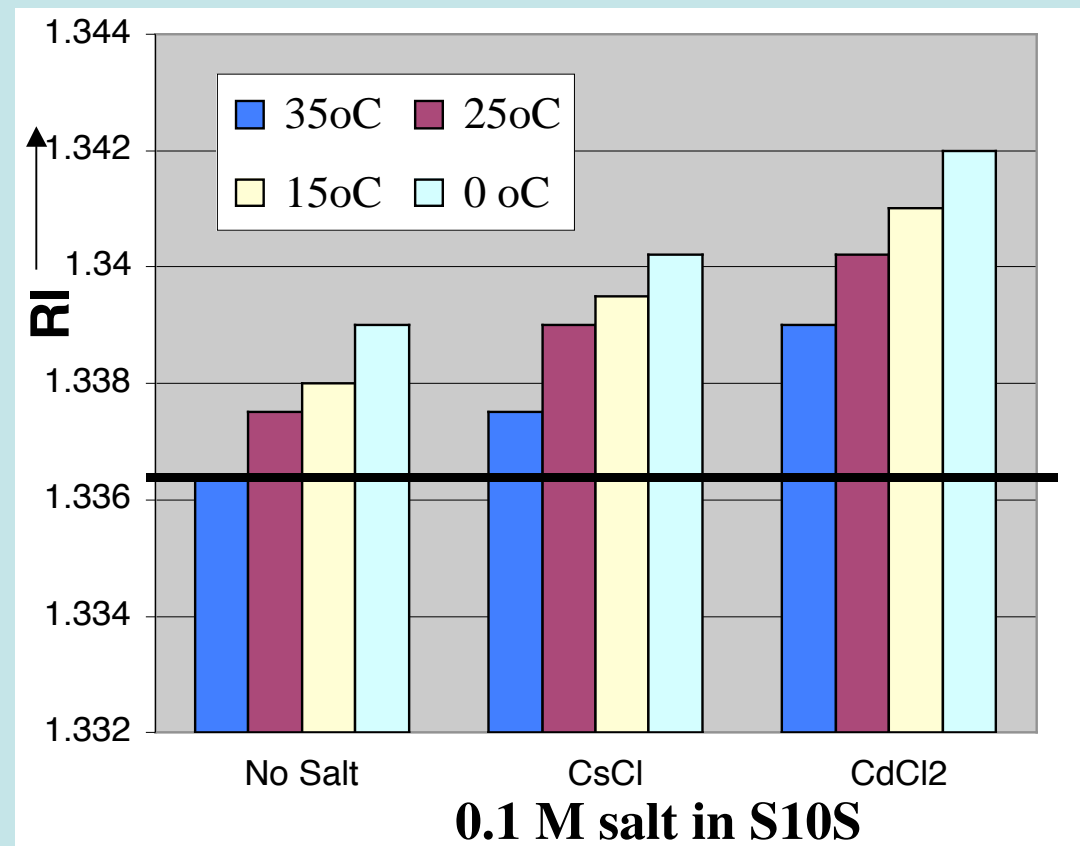
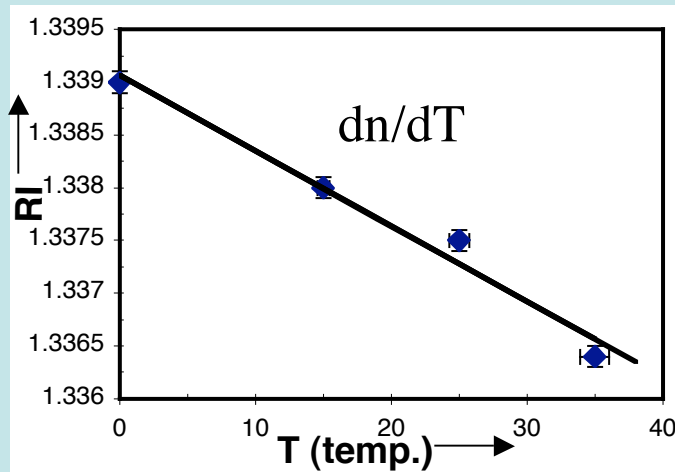


✓ S12S: sodium dodecyl sulfate, S10S: sodium decyl sulfate

✓ RI measured at 589 nm

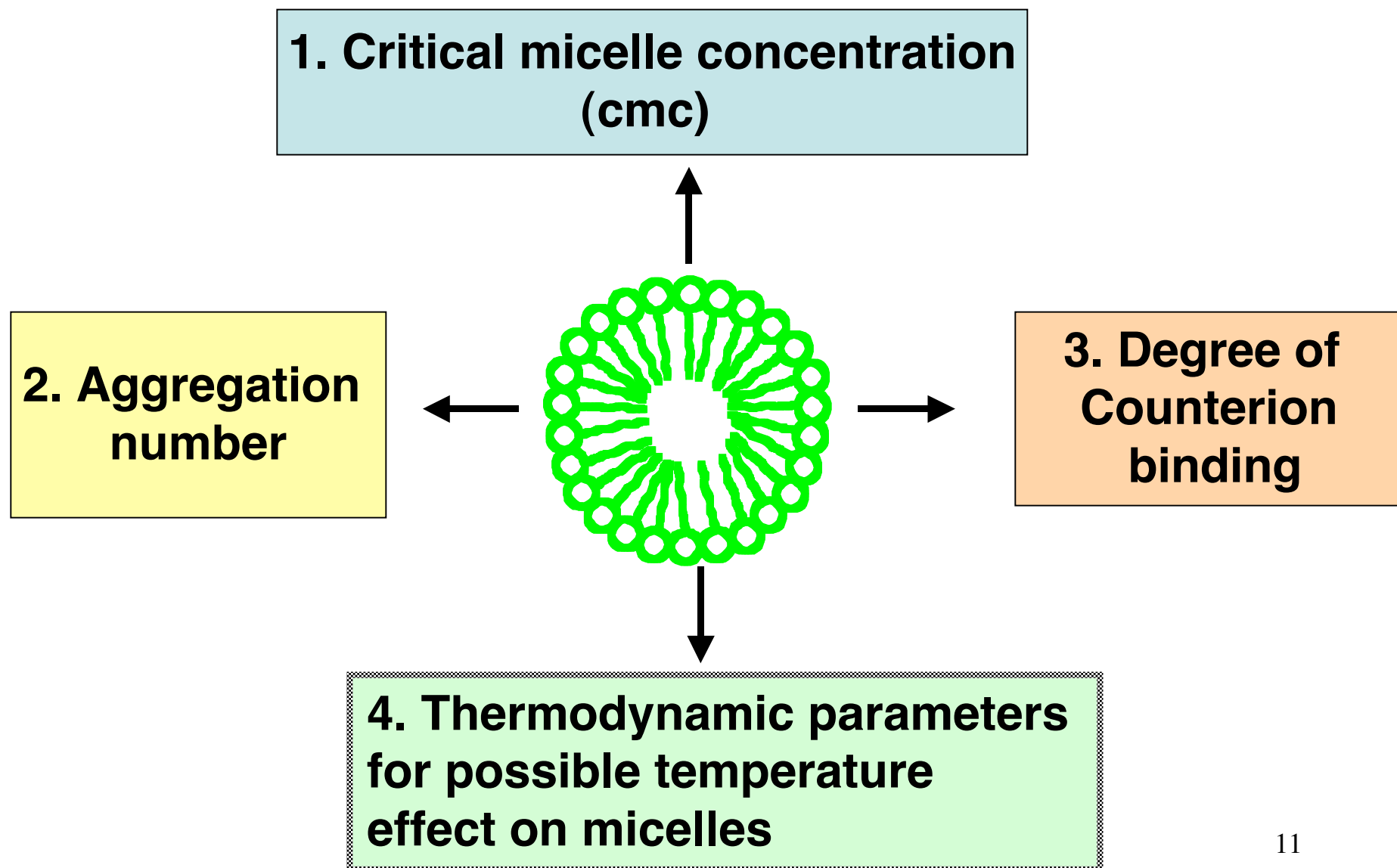
Effect of Temperature on RI

RI of Sodium Decyl Sulfate (S10S)

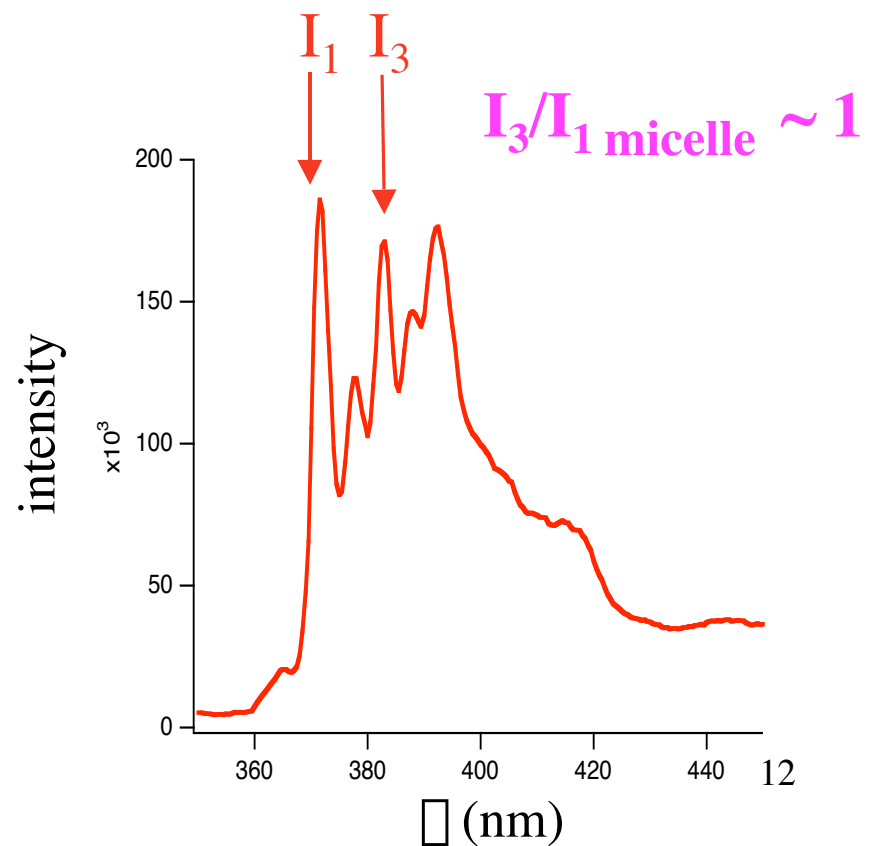
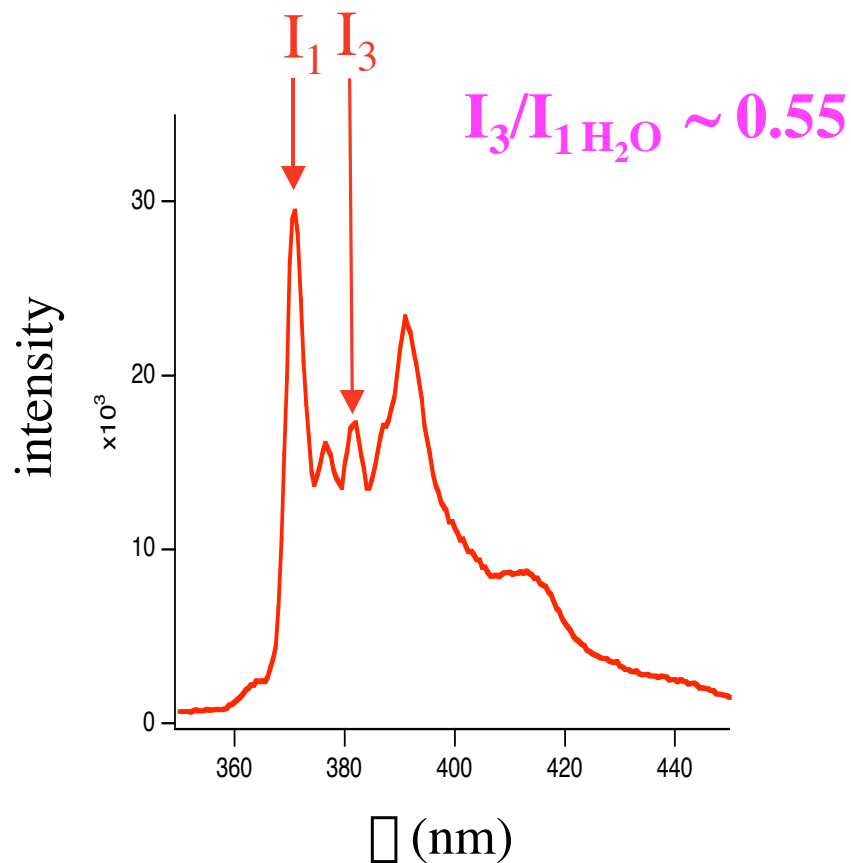
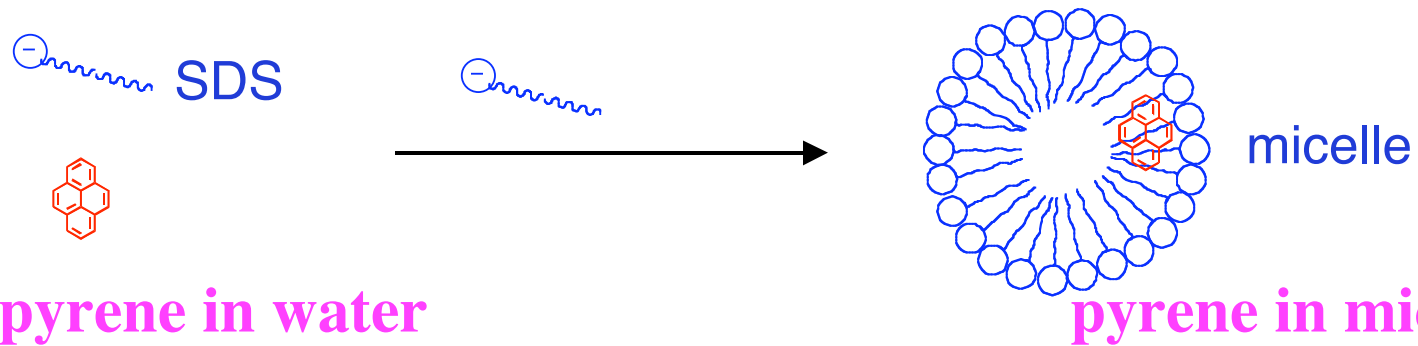


✓ RI increase upon temperature decrease

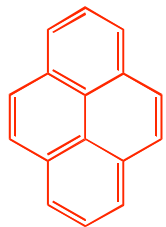
Changes in micellar properties by adding salt



Pyrene as fluorescence probe for micelle formation



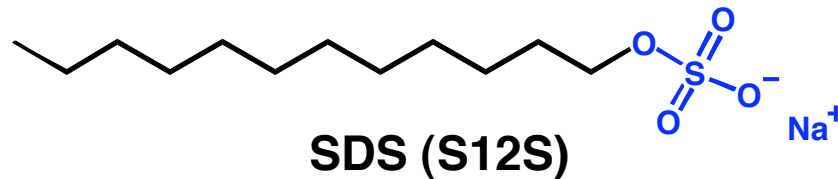
Determining CMC of SDS/CdCl₂



pyrene
(probe)

(2×10^{-6} M)

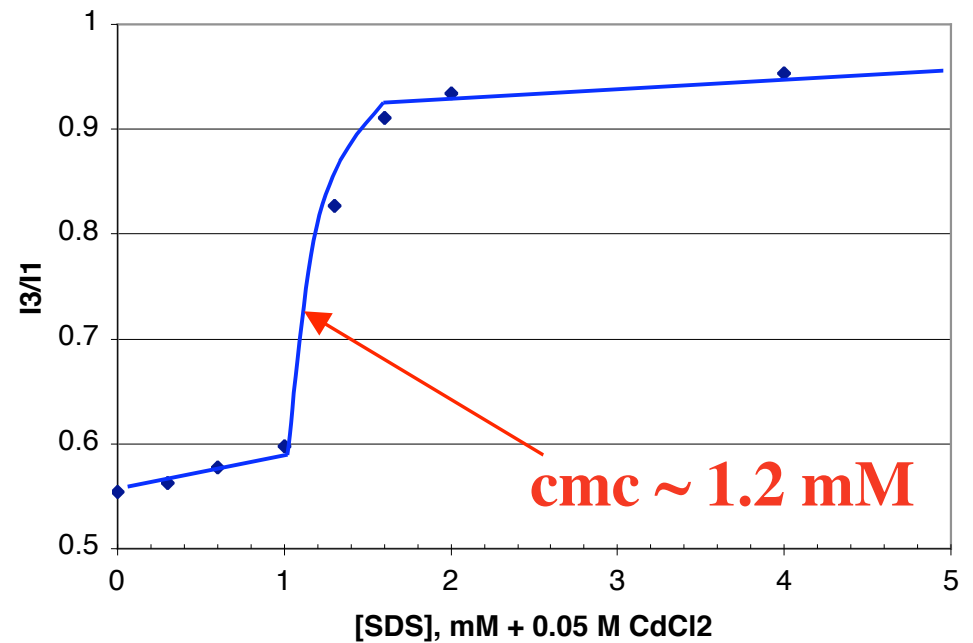
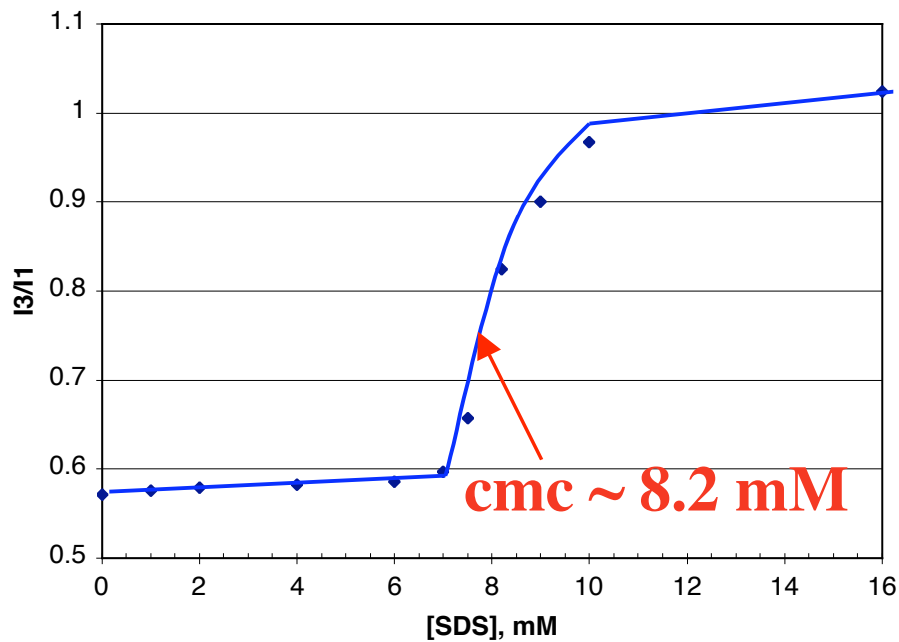
+



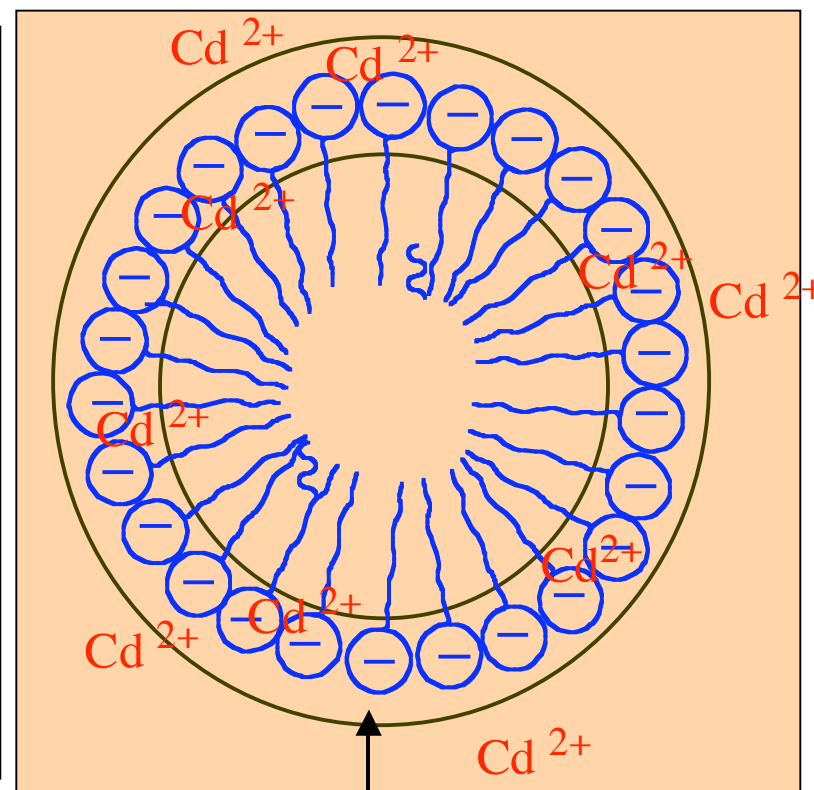
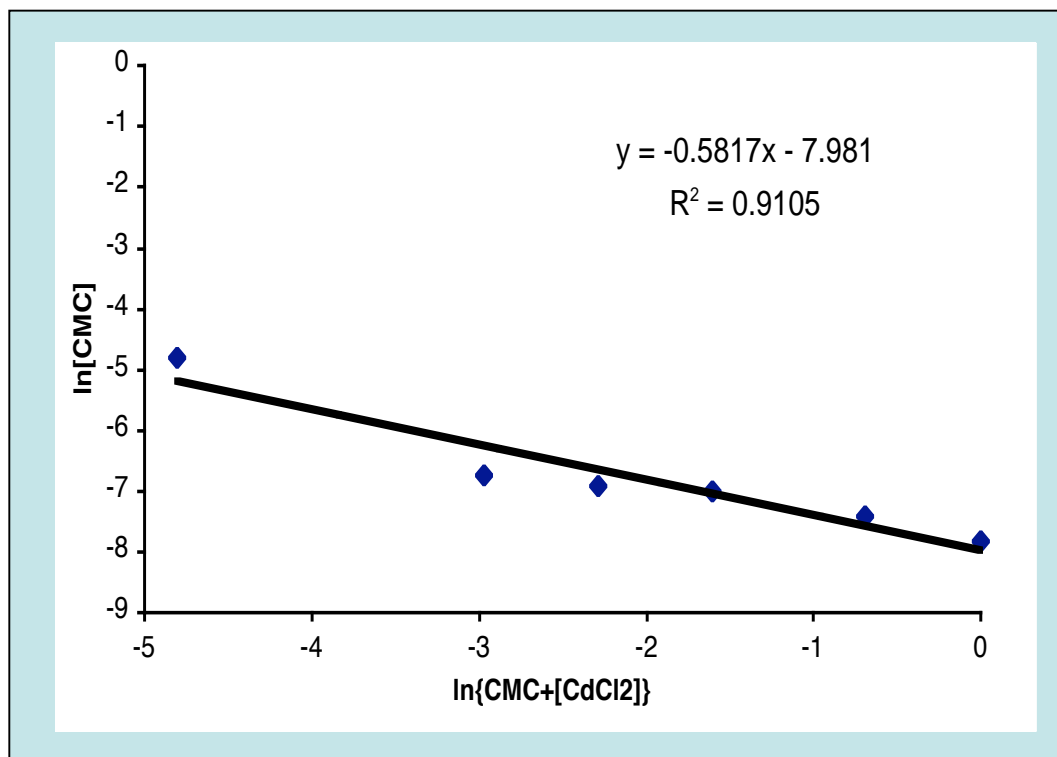
SDS (S12S)

+

CdCl₂



Degree of counterion binding of SDS /salt A



Stern layer

- **58 % counterion binding**
- **42 % ionization of micelles**

Empirical equation for the index of refraction

$$n(S, T, \lambda) = n_0 + (n_1 + n_2 T + n_3 T^2) S + n_4 T^2 + \frac{n_5 + n_6 S + n_7 T}{\lambda} + \frac{n_8}{\lambda^2} + \frac{n_9}{\lambda^3}$$

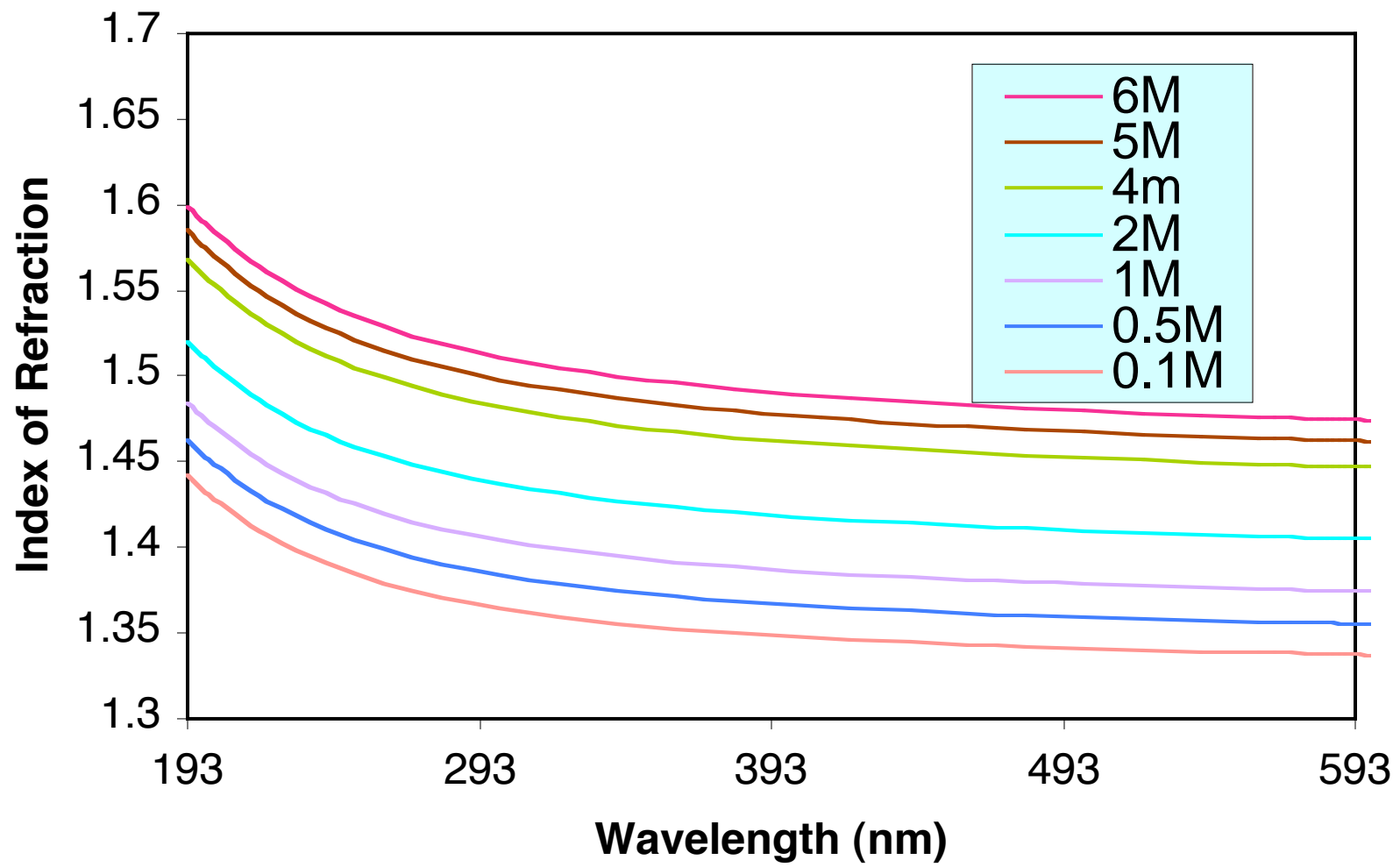
S: the salt concentration in parts per thousand (‰),
T: temperature (°C), **λ:** wavelength (nm)

Coefficients n :

$$n_0 = 1.31405, n_1 = 1.779 \times 10^{-4}, n_2 = -1.05 \times 10^{-6}, \\ n_3 = 1.6 \times 10^{-8}, n_4 = -2.02 \times 10^{-6}, n_5 = 15.868, n_6 = 0.01155 \\ n_7 = -0.00423, n_8 = -4382, n_9 = 1.1455 \times 10^6$$

Applied Optics, 34, 3477, 1995

Wavelength dependence of RI of CdCl₂ solutions from theory



Summary of results ...

- ✓ In order to find out the fluids which has refractive index (RI) higher than that of water, RIs of aqueous alkyl sulfate surfactants were examined.
RIs of aqueous alkyl sulfate surfactants were significantly increased at:
 - **higher surfactant concentration**
 - **addition of selected inorganic salts**
 - **lower temperature**
 - **lower number of chain length (smaller the size)**
- ✓ We tried to understand experimental data using theory in order to predict and identify appropriate salts (molar refraction concept).
- ✓ Model predicts that RI of aqueous surfactants could be increased **> 1.6** (@ 193nm) based on our preliminary results.¹⁷