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Research exercise: Solution Structures of Amphiphiles

Solution Structures of Amphiphiles

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Goal

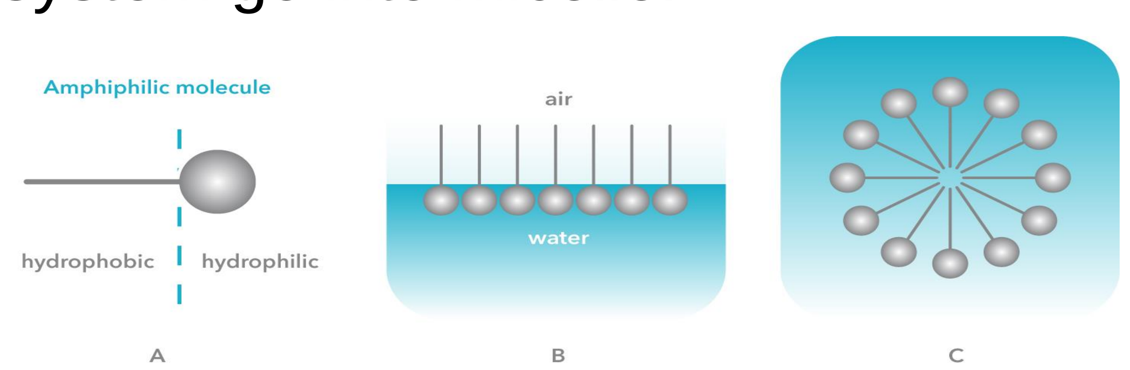
To determine amphiphile solution structure(s) at very small concentrations using electrochemical and transport measurements.

Introduction

•A better understanding of the interaction and solubilizing properties of micelles before critical micelle concentration(cmc) is reached is important.

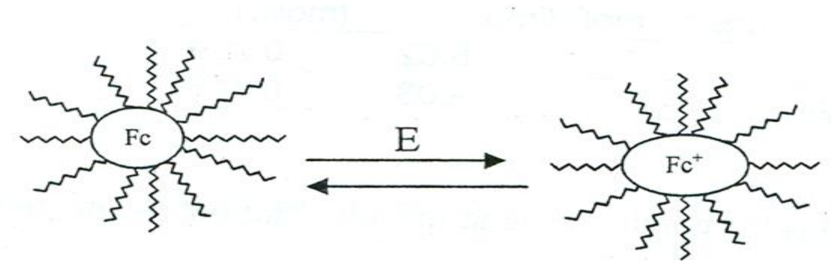
•The ionic radii of SDS structures yield insights about the types of interactions that occur between SDS molecules before cmc is reached.

•Critical Micelle Concentration(cmc): concentration of surfactats above which micelles form and almost all additional surfacants added to the system go into micelle.



•Ferrocene (Fc) was used as an electrochemical probe since it demonstrates good solubility, invariant redox potentials, and excellent chemical and electrochemical reversibility in organic electrolytes.

•Fc should interact with the hydrophobic portions of the amphiphilic structures.



Experimental

•0.08mM Fc and 17mM SDS solution prepared in a 500ml volumetric flask.

•The ratio of SDS to Fc was kept around 210 to ensure there was no more than one Fc per SDS aggregate.

•The solution was diluted by a factor of 0.1;each concentration was tested.

•CV Technique used to obtain the peak current of the Fc-SDS dilutions.

•Scan rate set at 4 V/s.

•Viscosity measurements taken on each dilution using a 50 Canon Capillary Viscometer.

Results

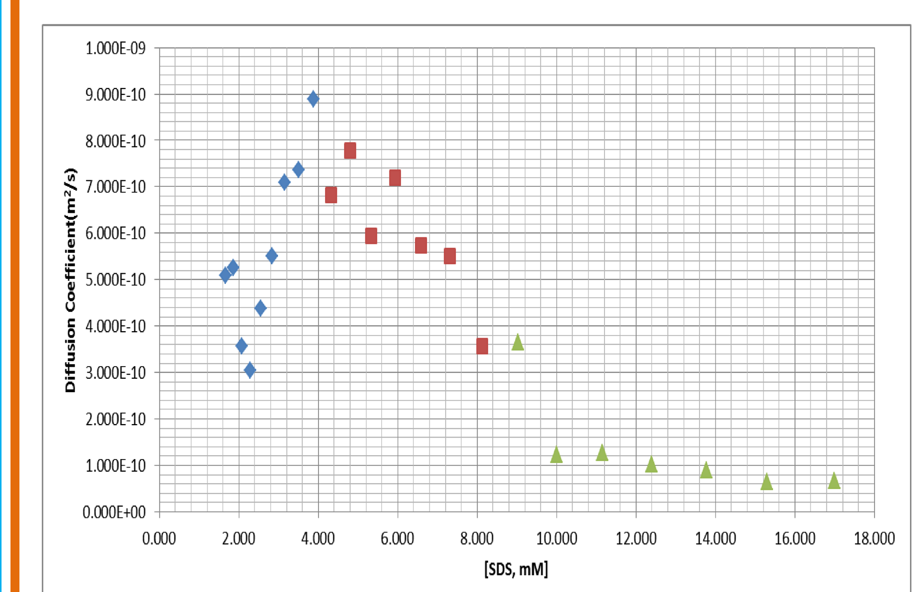


Figure 1. Calculated Diffusion Coefficient at Concentrations of SDS Less Than and Above cmc at 25°C, [SDS]/[Fc]=212.5

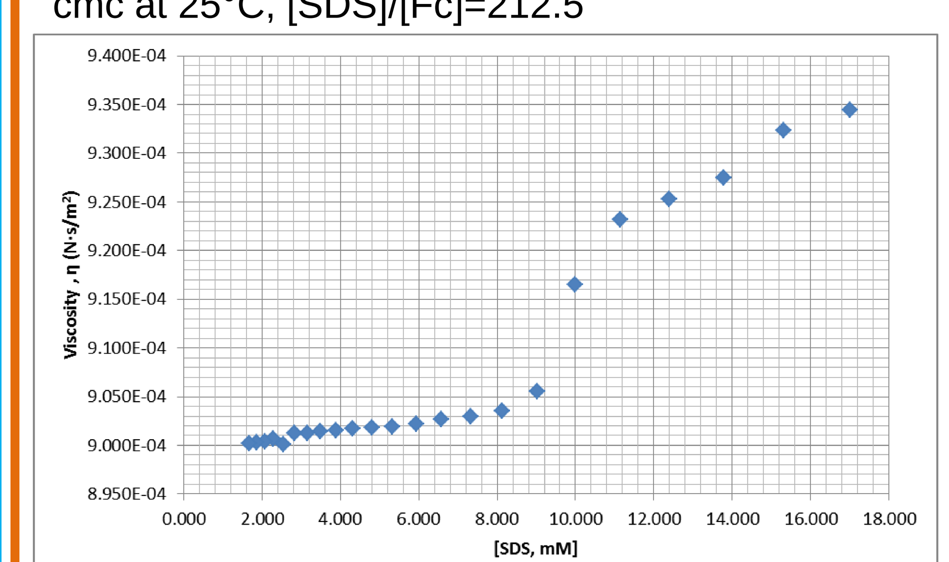


Figure 2. Relationship Between Varying Concentrations of SDS and Calculated Viscosity, 25°C, [SDS]/[Fc]=212.5

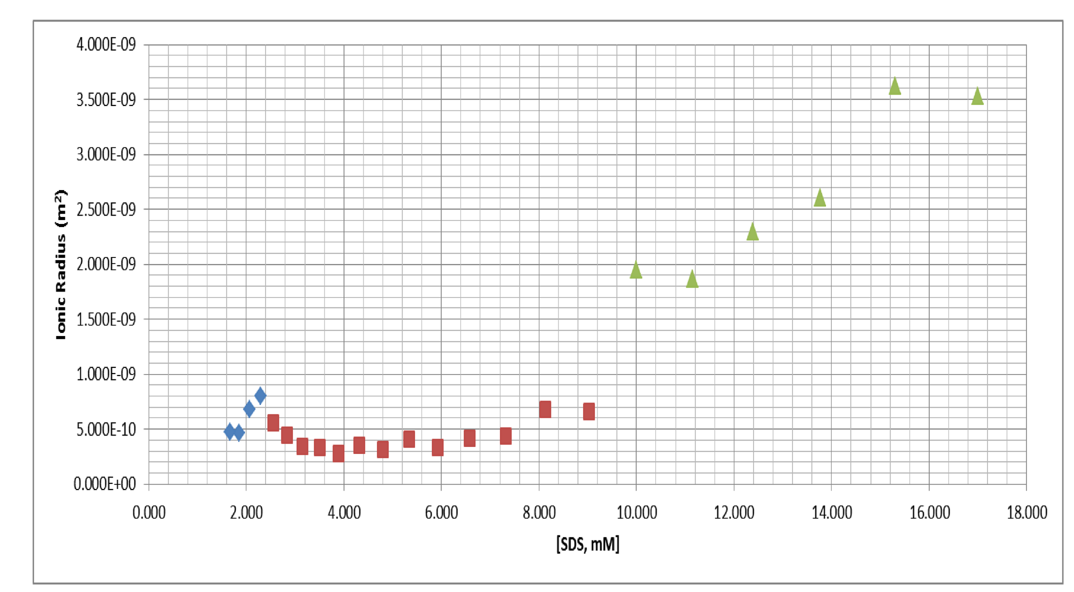


Figure 3. Calculated Ionic Radii for Concentrations of SDS Above and Below Determined cmc, 25°C, [SDS]/[Fc]=212.5

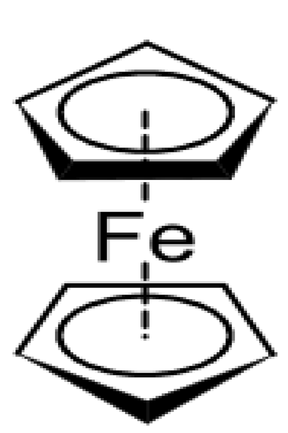
Table 1. Ferrocene in Sodium Dodecyl Sulfate at 25°C at a sweep rate of 0.06V/s, [SDS]/[Fc]= 212.5

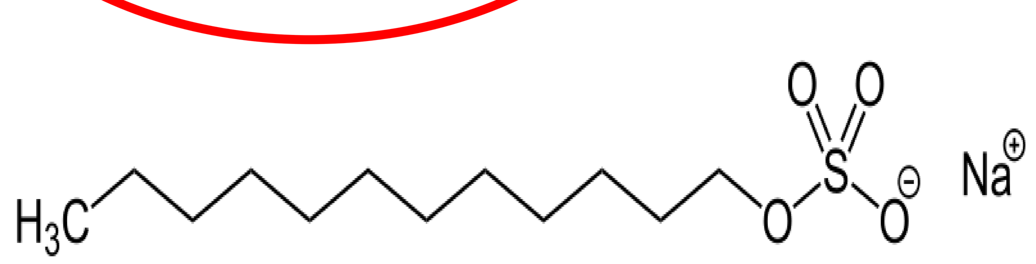
[FC,mM]	[SDS, mM]	$D(m^2/s)$	$\eta(N \cdot s/m^2)$	$a(m^2)$
8.000E-02	17.000	6.621E-11	9.313E-04	3.288E-09
7.200E-02	15.300	6.469E-11	9.282E-04	3.377E-09
6.480E-02	13.770	9.035E-11	9.253E-04	2.425E-09
5.830E-02	12.393	1.027E-10	9.228E-04	2.138E-09
5.250E-02	11.154	1.265E-10	9.205E-04	1.741E-09
4.724E-02	10.000	1.223E-10	9.185E-04	1.804E-09
3.252E-02	9.034	3.646E-10	9.127E-04	6.092E-10
3.826E-02	8.131	3.562E-10	9.150E-04	6.220E-10
3.444E-02	7.318	5.497E-10	9.135E-04	4.037E-10
3.099E-02	6.586	5.739E-10	9.121E-04	3.873E-10
2.789E-02	5.928	7.188E-10	9.109E-04	3.096E-10
2.511E-02	5.335	5.948E-10	9.098E-04	3.746E-10
2.259E-02	4.801	7.771E-10	9.088E-04	2.870E-10
2.203E-02	4.321	6.828E-10	9.086E-04	3.268E-10
1.830E-02	3.889	8.896E-10	9.072E-04	2.512E-10
1.647E-02	3.500	7.359E-10	9.064E-04	3.039E-10
1.482E-02	3.150	7.102E-10	9.058E-04	3.151E-10
1.334E-02	2.835	5.499E-10	9.052E-04	4.072E-10
1.201E-02	2.552	4.381E-10	9.047E-04	5.115E-10
1.081E-02	2.296	3.039E-10	9.042E-04	7.377E-10
9.727E-03	2.067	3.566E-10	9.038E-04	6.291E-10
8.753E-03	1.860	5.245E-10	9.034E-04	4.278E-10
7.878E-03	1.674	5.083E-10	9.031E-04	4.416E-10

Reactions

$Fc_{*} \leftrightarrow Fc^{+}_{*} + e^{-}$

$Fe^{2+} \leftrightarrow Fe^{3+} + e^{-}$





Conclusions

1) Viscosity increases with concentration

2) Diffusion coefficient:

•Most dilute concentrations, D increases with concentration until it reaches a maximum

•D decreases with increasing concentration until cmc

•Above cmc, D stays relatively constant

3) Ionic radii increases with concentration, at most dilute concentrations, implying more complex/larger structures

Equations

•**The Randles-Sevcik:** Cyclic Voltammetry(CV) Technique used to obtain the peak current of the SDS structures; the diffusion coefficient of the structures was then obtained.

$$i_p = 2.69 \times 10^8 n^{3/2} A D^{1/2} C v^{1/2}$$

•**Stokes-Einstein:** Computes ionic radii after obtaining measured solution viscosities and diffusion coefficients

$$a = k_b T / D 6 \pi \eta$$

References:

Mandal, A.B."Self-Diffusion Studies on Various Micelles Using Ferrocene as Electrochemical Probe."*Langmuir* 7 9.1993: 1932-1933. Print.

C. O. Laoire et al. "Electrochemical Studies of Ferrocene in a Lithium Ion Conducting Organic Carbonate Electrolyte." *Electrochemical Acta* 54 2009. 6560-6564. Print.