

Research on Gemini Surfactant by Chemical Trapping Experiments:
Aqueous Solution Studies

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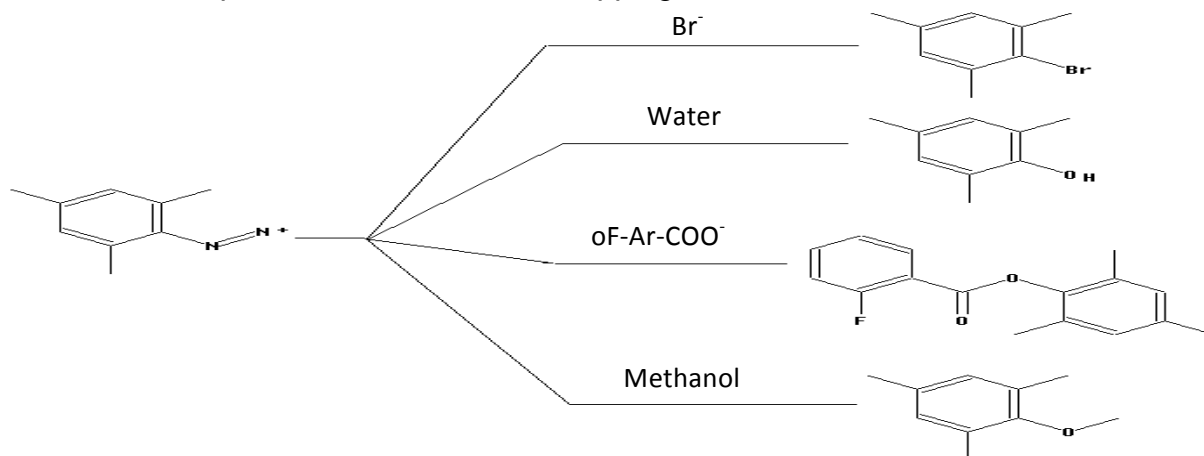
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Abstract:

This research was the first step to study counterion binding to gemini surfactants by the chemical trapping methodology developed by Professor Romsted's research group. There are two steps in the chemical trapping experiments required by method: in aqueous salt solutions and in micellar solutions. Aqueous salt solutions establish the product yields of various counterions and other nucleophiles under controlled conditions and generate calibration curves for the hindered trapping agent 2,4,6-trimethylarene-diazonium tetrafluoroborate. The micellar solution chemical trapping experiments yield the products generated at the micellar interface and the calibration curves established from the aqueous salt solution runs provide a way to calculate the interfacial concentration of the different molecular species. The aqueous salt solutions used in this research were sodium ortho-fluorobenzoate and sodium para-fluorobenzoate since through previous experiments these anions were shown to influence cationic micellar aggregate shape and were quantified through chemical trapping. The 2,4,6-trimethylarene-diazonium tetrafluoroborate trapping agent was reproducibly prepared and the probable products of the fluorobenzoates were also prepared. The trapping experiments were recorded using HPLC. The initial data of a diquatery ammonium gemini surfactant with the ortho-fluorobenzoate as an added counterion was recorded after the preparation of the 12-2-12 gemini

surfactant. The gemini surfactant itself has received some study by the Romsted research group. The investigation provided sufficient evidence to support further study of the substituted benzoate counterions in the presence of the various cationic surfactants.

Figure 1: Possible products from chemical trapping



Introduction:

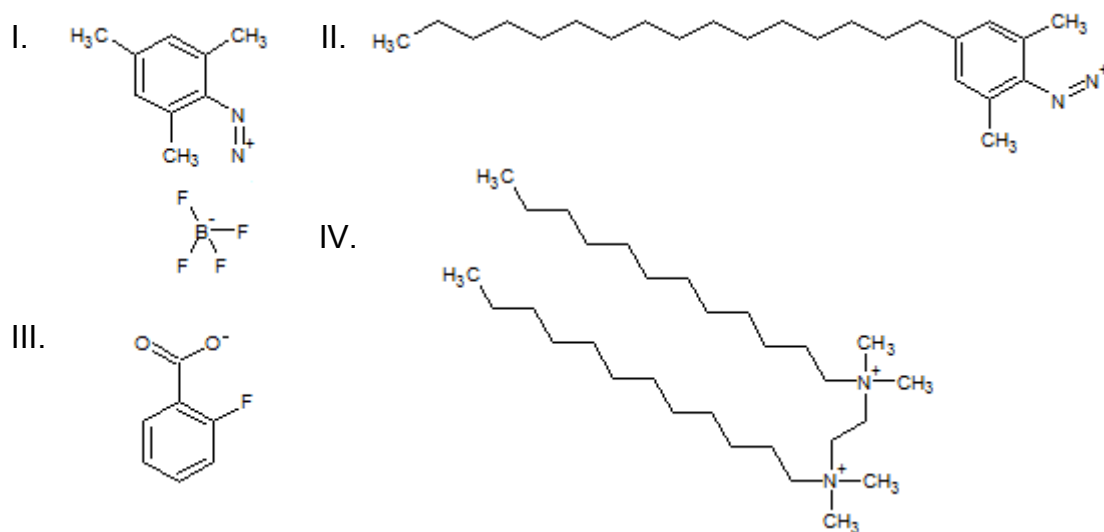
Micelle research is an exciting and versatile field that has been growing and evolving as more discoveries are made.¹ From drug delivery to soaps, new and different applications have been discovered with each passing year. Part of what makes micelles so interesting to different fields is how the aggregate shape of the micelle can change based on changes in head group, tail length, the number of tails, counter ion, and other physical state variables.

Micellized surfactants, which are aggregate colloids, have been of interest to researchers for decades because they have many unusual properties depending on their shape. How to exactly control the aggregate shape changes is still an active area of exploration.^{1,4} Gemini surfactants have double alkyl chain structures and are also of particular interest because they have lower CMC values than single alkyl

chain surfactants.² As a result they form rod-like micelles more easily than single alkyl chain surfactants which could be harnessed for many applications in industry.³

In order to study what happened at the interface, the chemical trapping method was used to probe micelle aggregate structures. This method uses HPLC to quantify products.² Chemical trapping with water was done first to create calibration curves of the product yields, so that the correlation of the chemical trapping with the micelle could yield interfacial concentrations. Though the gemini surfactant experiments are in the literature, the selected counter ions were not yet investigated.^{2,3} The o-fluorobenzoate ion was of particular interest because when the experiment was run with the tetradecyltrimethyl ammonium surfactant, no growth was observed up to 70mM concentration.⁵ Preliminary work with the Gemini suggested that significant growth happened with the orthofluorobenzoate counter ion. Confirmation of this would be another step in learning how to control micelle growth.

Figure 2: Important Compounds I. Short chain arenediazonium salt II. Long Chain arenediazonium salt III. orthofluorobenzoate ion IV. 12-2-12 Gemini surfactant



Experimental:

Preparation of Na⁺ o-Fluorobenzoate Salt³

Weighed out about 6g of 2-fluorobenzoic acid and mixed in 1000mL beaker with 300mL of DI water. Used a pH probe to measure the pH and dripped in 2M NaOH solution until pH was 6. Switched to 1M NaOH and dripped in until pH 7. Put on low heat and let water evaporate away leaving white solid on bottom. (Same procedure for 4-fluorobenzoate Salt. Yield: about 7g collected each time.)

Synthesis of 12-2-12 2Br Gemini Surfactant³

Weighed out 40g 1-bromododecane and added it to 60mL acetone which was stirred. Added 6.3g N,N,N',N'-tetramethylethylenediamine with 15mL more of acetone to the reaction mixture. Refluxed for 24 hours. When taken off heat a white solid formed and was washed with acetone. Recrystallized in warm acetone. (¹H NMR was found to agree with the reported values in Yan Geng's thesis.)

Preparation and Isolation of Esters³

Weighed out 1g mesitol and added to 10mL of 10% NaOH solution. Stirred until solid dissolved. Slowly added in 1.6mL 2-Fluorobenzoylchloride, and the solution turned opaque. Let stir on high for 4 hours. Put in vial with 3mL ice cold DI water and pipeted off the white opaque oil. Let sit on ice for 15 minutes and added 3mL of pet. ether and shook until oil dissolved. Washed with DI water and a drop of 1%NaOH.

The pet ether layer was put on water bath and drove off all but 1mL. Put into freezer overnight. Volatilize excess liquid with $N_2(g)$ and got an off white crystalline solid. (o-fluoro ester- IR-Characteristic C=O Bond 1737 cm^{-1} ; $H^1\text{NMR}$ - ($CDCl_3$) δ 0.844, δ 3.120 (9H), δ 7.747 (2H), δ 8-9 (4H); MP- $55-58^\circ\text{C}$) (p-fluoro ester- IR- Characteristic C=O Bond 1728 cm^{-1} ; $H^1\text{NMR}$ - ($CDCl_3$) δ 0.841, δ 3.121 (9H), δ 7.739 (2H), δ 8.139 (2H), δ 9.062 (2H); MP- $49-51^\circ\text{C}$)

Synthesis of Ar-diazonium³

Added 15mL anhydrous THF to 250mL round bottom flask with stirring, under $N_2(g)$. Put into IPA/dry ice bath and let cool for 10 minutes (less than -20°C). Injected 1.7mL $BF_3 \cdot Et_2O$ and stirred for 5 minutes. Added 12mL 2,4,6-trimethylaniline which had been vacuum distilled and 15mL THF and let it drip in over 5-10 minutes keeping the temperature at -20°C or less. Washed dropping funnel with 5mL THF then added 1.3mL n-butyl nitrite with 10mL THF and let drip in over 2 minute period. Let stir for 15 minutes at -20°C and it turned steadily golden from clear and continued to darken. Switched to an ice/water bath (0°C) and let stir for 5 hours (solid appeared after 20 minutes). The brownish-orange solid and remaining liquid was poured into beaker with 100mL cold hexane and vacuum filtered. Washed with cold acetonitrile to dissolve and added cold, dry Et_2O to crystallize out the product which was vacuum filtered. Repeated washing with acetonitrile and Et_2O until sample was white. (IR- Characteristic $N \equiv N$ Bond 2251 cm^{-1})

Preparation of Ether Product⁶

Mixed 2.98g tetraethylammonium fluoride with 1.3g mesitol in 10mL DMF under vacuum (20torr) and in a boiling water bath for 10 minutes (clear). Let cool and it turned dark green. Added 1.6mL methyl iodide to 20mL DMF at normal pressure and boiling water in a closed system (yellow). Let stir for 12 hours. Wash with 200mL ether and 100mL water. Wash aqueous layer twice with 100mL ether and combine ether layers. Wash ether layers three times with 100mL water. Dry with magnesium sulfate and roto-vap to give orange oil. Purify on basic alumina column with n-hexane. ($^1\text{H NMR}$ - (CDCl_3) δ 0.006, δ 2.238 (9H), δ 3.681 (3H), δ 6.797 (2H))

HPLC Conditions:

The Agilent 1100 Series HPLC with phenomenex zorbax column was used in all product yield quantifications. The mobile phase used was 80:20 methanol: 0.5% acetic acid in water.

Results and Discussion

From trial runs on the HPLC, the approximate retention times for each possible product were obtained (Table 1).

Table 1: Retention Times (minutes) of Possible Products

	o- Fluorobenzoate	p- Fluorobenzoate
Mesitol	Ester	Ester
5.867	14.342	16.702

Calibration curves of each product were created in order to quantify dediazonation products. The resulting linear regression equations were used to find the calculated

concentration of each product and each standard concentration was recorded in triplicate.

The mesitol standards were run before each dediazonation run in order to check for instrument reproducibility. The calibration curve was made by averaging all runs and the linear regression equation that was $y=41537x + 321$ with a R^2 value of .9972 (Figure 3). This was then used to calculate mesitol concentration in all runs both sodium o-Fluorobenzoate and p-Fluorobenzoate salt solutions.

The o-Fluoro ester standards were then run for the same purpose as the mesitol standards. Linear regression analysis yielded a good fit line of $y=40186x + 231.95$ and a R^2 value of .9990 (Figure 4). This was used in all o-Fluorobenzoate salt solutions to find the calculated concentration of o-Fluoro ester. The same was done for the p-Fluoro ester standards. Linear regression analysis yielded a good fit line of $y=52321x + 44.099$ and a R^2 value of .9996 (Figure 5).

Figure 3: Mesitol Calibration Curve

Figure 4: o-Fluoro Ester Calibration Curve

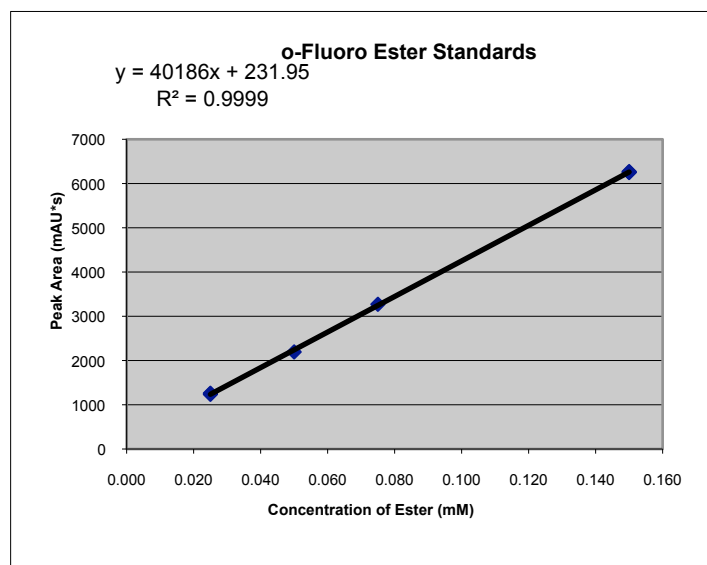
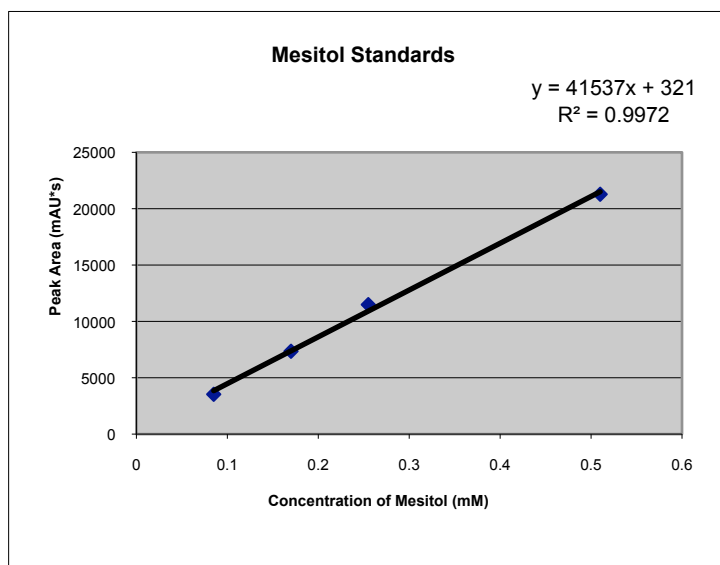
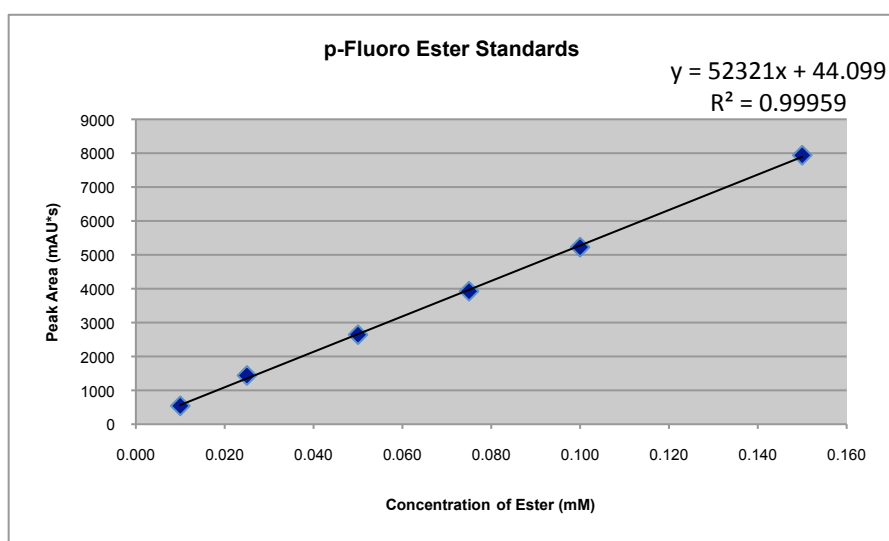


Figure 5: p-Fluoro Ester Calibration Curve



It was expected that the blank would be quantified as being 100% conversion of the diazonium in product; however, this was not the case in the o-fluoro runs and in most of the p-fluoro runs. With few exceptions the percent conversion of the concentration of the diazonium equivalent was well over 100% and often greater than 110% in the o-fluoro runs (Tables 2 and 3). This begs the question of whether using the blank as 100% is really the best way to quantify the diazonium. There is also the question of whether the water blank is at the same pH as the salt solutions which can direct the dediazonation reaction to make other products; however, the reproducibility of the predicted yields for all the salt solution runs were shown to be

fairly close. Actually calculating the concentration of the amount of diazonium each sample could solve the problem of getting such a high percent conversion.

Table 2: o-Fluorobenzoate Salt Runs Normalized Product Yields

Run #	Salt Concentration (M)	Mesitol	o-Fluoro Ester	Percent Conversion
1	0.8	82.3%	17.7%	112%
1	1.0	78.8%	21.2%	115%
1	1.5	72.0%	28.0%	119%
2	1.5	77.9%	22.1%	100%
3	1.5	71.3%	28.7%	119%
1	1.8	68.1%	31.9%	119%
2	1.9	69.5%	30.5%	114%
1	2.0	66.3%	33.7%	118%
2	2.0	68.4%	31.6%	81%
3	2.0	68.9%	31.1%	118%
1	2.2	66.0%	34.0%	119%
2	2.2	71.4%	28.6%	104%
2	2.3	65.5%	34.5%	110%
1	2.4	64.3%	35.7%	118%
2	2.5	60.6%	39.4%	91%
3	2.5	61.6%	38.4%	118%

The average retention time of the mesitol and o-Fluoro Ester can be found in table 1.

Table 3: p-Fluorobenzoate Salt Runs Normalized Product Yields

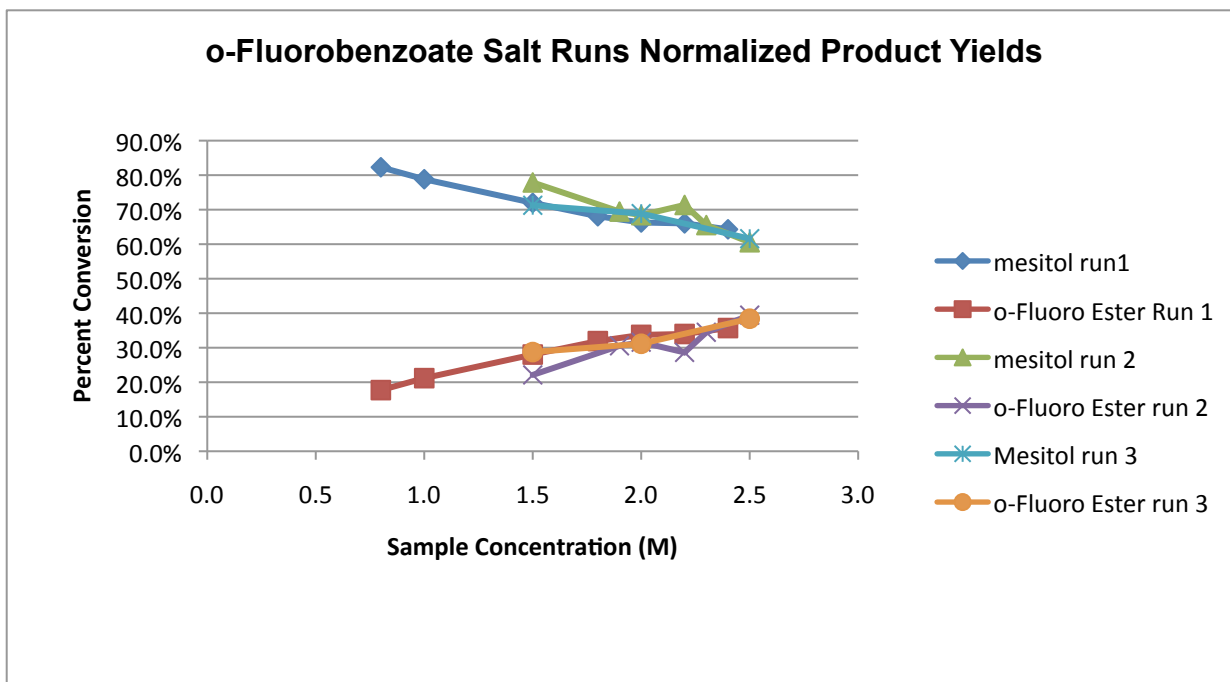
Run #	Salt Concentration (M)	Mesitol	p-Fluoro Ester	Percent Conversion
1	0.25	97.2%	2.8%	106%
1	0.50	94.6%	5.4%	104%
1	0.60	93.2%	6.8%	103%
1	0.90	91.2%	8.8%	102%

2	0.90	92.0%	8.0%	102%
1	1.00	90.2%	9.8%	88%
2	1.00	92.5%	7.5%	98%
2	1.10	90.4%	9.6%	100%
2	1.20	91.5%	8.5%	95%
2	1.30	91.9%	8.1%	91%

The average retention time of mesitol and p-Fluoro ester can be found in table 1.

In the o-fluoro runs, the data is reproducible with a few slight anomalies. The graph of the percent conversions of the mesitol and ester concentrations the data behaves as was expected. It can be seen in figure 6 that as the concentration of the salt increases the concentration of mesitol decreases and the concentration of the ester product increases. More runs and replications of the different data points would help to get better overall data.

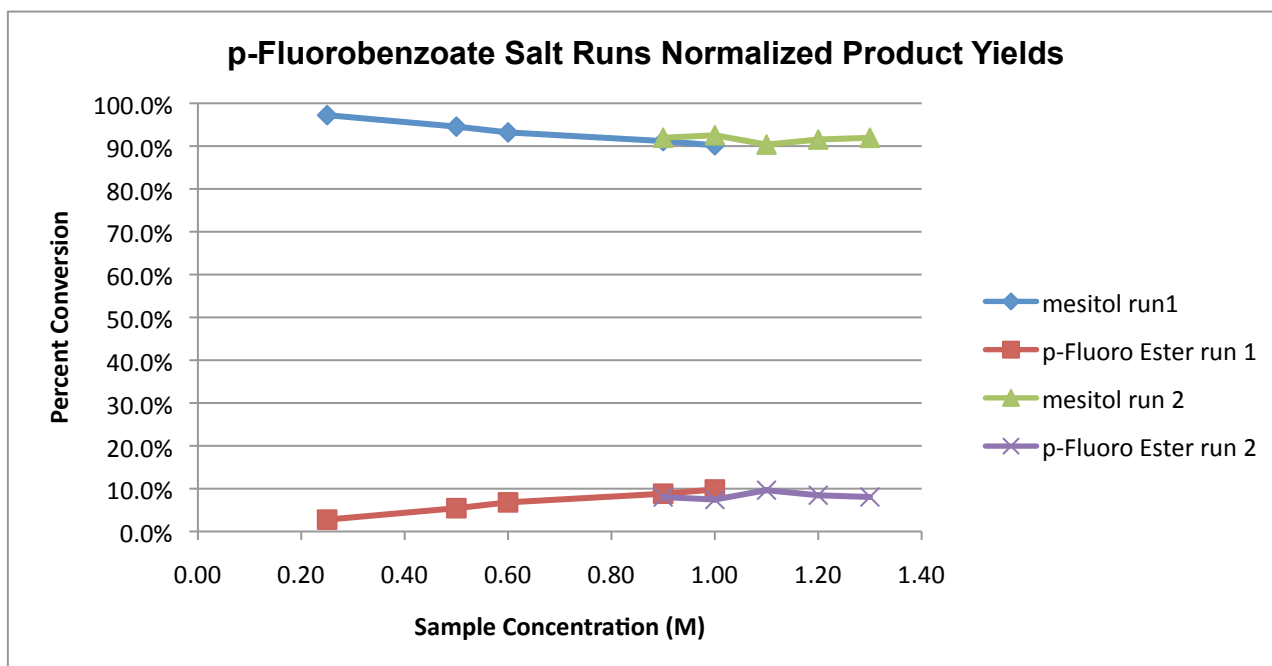
Figure 6: o-Fluorobenzoate Salt Normalized Product Yields



The same graph was made for the p-fluorobenzoate salt runs as well with similar, but less dramatic results. More runs should be done with replicates of the data points

already taken to further demonstrate that good replication of data was achieved. However, as can be seen in figure 7 there is very minimal decrease in mesitol concentration and increase in ester concentration. The p-fluorobenzoate salt is not very water soluble and because of that only low concentrations could be used. Small concentrations of methanol could be added to the flask to get higher concentrations of salt into solution, but then there is the possibility of getting the ether product which would need to be quantified as well as the ester and mesitol products.

Figure 7: p-Fluorobenzoate Salt Normalized Product Yields

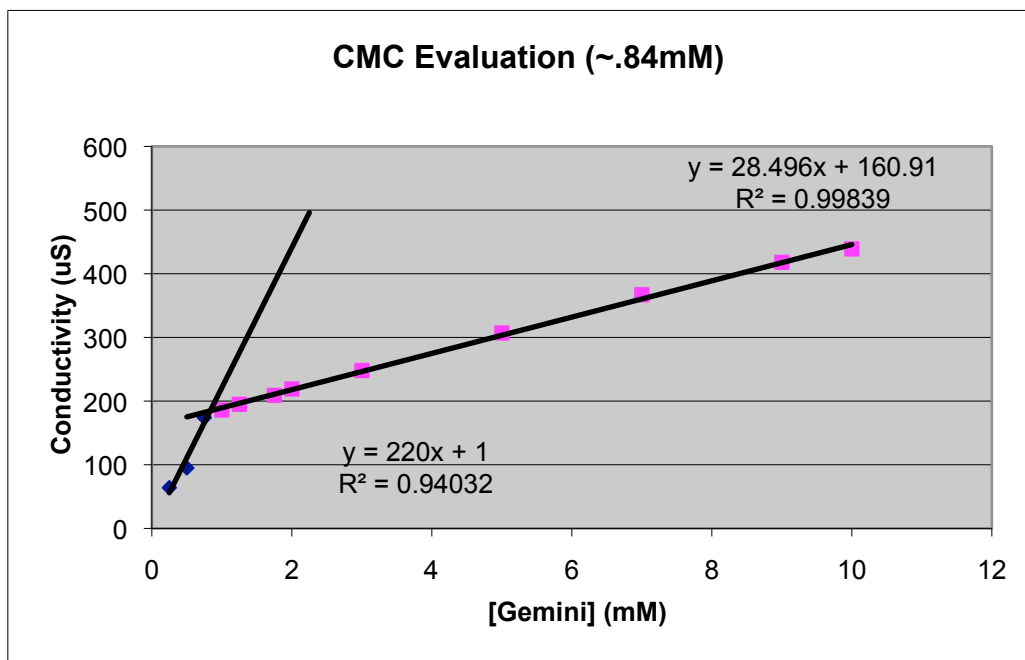


For further quantification, in each diazonium reaction the concentration of water was calculated to see how much the salt was affecting the water concentration. It was seen that the higher the concentration of salt, the lower the water concentration. The blank averaged about 56M while the highest salt concentration

had a water concentration of only 42M. The data as a whole appears to be adequate enough to support micelle trapping experiments in the future.

Preliminary investigations into characteristics of the gemini surfactant were begun. The 12-2-12 cationic gemini was prepared following the method outlined in Yan Geng's thesis. To find the critical micelle concentration (CMC), a series of samples were prepared and their conductivity was measured. The CMC for the 12-2-12 gemini surfactant was found to be 0.835mM surfactant by plotting the specific conductance against the surfactant concentration and determining the change in slope upon micelle formation (figure 8).

Figure 8: Determination of CMC for 12-2-12 Gemini Surfactant



The surfactant was then tested with added sodium o-fluorobenzoate salt to address whether the aromatic counter ion promotes aggregate growth by taking viscosity readings. The more a gemini surfactant grows (from sphere to rod) the more

viscous the solution is. The time it took for solutions of 10mM gemini surfactant by itself and with 0.5mM NaBr and 0.5mM sodium o-fluorobenzoate salt respectively were measured by running the solutions through a viscometer. The 10mM gemini surfactant took 232.33 seconds, the 10mM gemini with 0.5 mM NaBr salt took 234.67 seconds , and the 10mM gemini with 0.5 mM orthofluorobenzoate salt took 241.67 seconds. This shows that the orthofluorobenzoate counterion was encouraging micellar growth because it took the longest. Adding just more Br⁻ as the counterion did increase viscosity, but not to the degree that orthofluorobenzoate did. Even with a tiny amount of the counterion there was a significant change in viscosity which provides further incentive to continue research with this counterion.

There is still much to do to get a complete picture of how these counterions work. The next most important piece would be to do chemical trapping experiments in the presence of the gemini surfactant to quantify the products at the micellar interface. Future research is encouraged by the successful and useful information gathered from the chemical trapping of the aqueous salt solutions.

References

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