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Effect of Hofmeister series salts on Absorptivity of aqueous solutions on Sodium polyacrylate

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Abstract. Sodium polyacrylate (SPA) is a popular super absorbent commonly used in children diapers, sanitary pads, adult diapers etc. The use of SPA is in force from past 30 years and the newer applications like as food preservant are evolving. SPA is recently discovered by our group for improvement of sensitivity of colorimetric agents. Though the discovery of improvement in sensitivity is phenomenal, the mechanism still remains a puzzle. A typical assay reagent contains colorimetric/fluorescent reagents, buffers, salts, stabilizers etc. These chemicals are known to influence the water absorptivity of SPA. If we were to perform chemical/biochemical assays on SPA absorbed reagents effect of salts and other excipients on colorimetric/fluorescence compounds absorbed on SPA is very important. The hofmeister series are standard for studying effect of salts on permeability, stability, aggregation, fluorescence quenching etc. We recently studied affect of urea, sodium chloride, ammonium sulfate, guanidine thiocayanate on fluorescence characteristics of fluorescence compounds and noted that except urea all other reagents have resulted in fluorescence quenching and urea had an opposite effect and increased the fluorescence intensity. This result was attributed to the different water structure around fluorescent in urea solution versus other chaotropic agents.

1. Introduction

Sodium Poly Acrylate (SPA) is a super absorbent used widely in industry [1-3]. The products like children diapers, sanitary pads, food preservatives, stabilizers, drug delivery etc are based on super absorbents [4-9]. The chemical and biochemical applications of superabsorbents is only limited to their use as absorbent pad in lateral flow devices [10, 11]. Our group has reported use of SPA superabsorbents in assay of pesticides for field sample concentration and Isoniazid (INH) assay on the SPA bead [12]. The INH study has posed few questions regarding the intake of borate buffer and colorimetric reagent. Superabsorbents like SPA for thick gels with water locked inside its core. These are neither liquids nor solids. The fluorescent/colorimetric compound intake and behavior of dye solutions in presence of SPA needs to be understood. The previous reports on this topic are non-existent and our two publications are indicative of a certain level of gradient intake of dyes into the SPA core.

Now a days sodium polyacrylate and potassium polyacrylate are used as “solid rain” to provide water to plants grown in drought hit regions and the newer research even suggests delivery of pesticides to the plants through SPA route [13-16]. The understanding of organic compound interaction with SPA hence forms a new field of study. We studied different dye (both colorimetric and fluorescent) solutions in presence of SPA. The study indicated that in the absence of any salts in solution, the dye intake is normal. As the Hofmeister salts are introduced, the SPA has gradient intake of dyes with the highest concentration at the exterior of the bead and it decreases gradually to the core of SPA bead. The presence of urea as chaotropic agent has opposite effect and it facilitated intake of dyes into the SPA core. This result is inline with our previous studies on Hofmeister salts with fluorescent compounds wherein, Urea carrying opposite effects compared to other chaotropic agents [17].

A similar pattern is noticed for the intake of fluorescent solutions in SPA. When a fluorescent compound dissolved in the water containing chaotropic reagents like Urea, Sodium chloride, Guanidine Isothiacyanate, Ammonium sulphate, urea has behaved opposite of the rest of three. The urea seems to be encouraging intake of fluorescent solution to the SPA core where as the other chaotropic agents have resulted in reduction of intake of fluorescent compounds in SPA. The lesser intake of fluorescent compounds into SPA core can be explained because of higher solute concentration in the exterior, the SPA’s super absorbent behavior pulls only water leaving the lesser soluble fluorescent compounds in solution. But urea though a salt seems to showing opposite and penetrating into the SPA core. This observation has significant impact not just from our colorimetric/fluorescence assay perspective but also in the agriculture. There is increased interest in use of super absorbent SPA for delivery of nutrients to plants etc and urea is a significant nutrient for many crops. The mechanism seems to be increased solvation of urea in water and absence of non-charged ions. Urea is technically an organic compound with about 500-600g/liter solubility and rest of the three compounds are ionic in nature. This result is significant and provides a basis why some of the fluorescent/colorimetric compounds are taken in the SPA core and also enablement of similar chemical assays on SPA surface.

2. Material and Methods

Sodium Polyacrylate powder, fluorescein, Rhodamine-B, Fluorescein Isothiacyanate (FITC), Sodium chloride, Guanidine Isothiacyanate, Urea, Ammonium sulphate were purchased from Sigma-Aldrich, India. Sodium Polyacrylate beads, deionized water are procured locally.

2.1 Preparation of Chaotropic salt solutions

The four chaotropic salts used in the study are Urea, Sodium chloride, Guanidine Isothiacyanate and Ammonium sulphate. The concentrations optimized for the study is 1M. The molar equivalents of respective salt is added to one litre of deionized water and stirred for 15 minutes and filtered through a 10 micron filter and used.

2.2 Preparation of Fluorescent compounds

The three fluorescent compounds for the study are fluorescein, Rhodamine-B and Fluorescein Isothiacyanate. The concentrations studied for intake of fluorescent solutions in SPA are 1mM and 10mM. For fluorescent solutions with chaotropic salts, 1M of chaotropic salt and 1mM or 10mM of fluorescent compound is stirred for 15 minutes and passed through a 10μm filter are used.

2.3 Testing of water absorption of SPA in presence of different test chaotropic agent containing fluorescent solutions

10mg of SPA (2 SPA beads) are placed for 30 minutes in 1mL of a solution. The weight of the swollen bead and the remaining test solution post absorption are calculated. Based on the values an estimate is made on the intake of fluorescent solution to SPA bead. A cross sectional view is also done by cutting the SPA bead to half to check for intake of fluorescent compounds in SPA core. The scope of the study is only to understand the intake of fluorescent compounds in SPA core and the extent of influence of chaotropic agents on absorptivity of fluorescent solutions by SPA.

3. Results and Discussion

3.1. Choice of chaotropic agents and fluorescent compounds

Protein and nucleic acid precipitants and denaturants are commonly used to explore the extreme behaviours and stability of biomolecules. Our recent study of Hofmeister salts on fluorescent compounds has suggested that fluorescent compounds are a new class of compounds with the chaotropic agents having some peculiar affects. For example, we discovered that Urea has opposite effect compared to other chaotropic agents like Sodium chloride, Guanidine Isothiacyanate, and Ammonium sulphate. For this study we chose to use Urea and other above mentioned chaotropic agents for studying fluorescent solutions with SPA. Regarding the fluorescent compounds, our previous Hofmeister salt study included over nine compounds of different fluorescein class and discovered that certain functionalizations have unique affects on the quantum yield, fluorescence and absorbance spectra [17]. For this study we used three fluorescent compounds namely fluorescein, Rhodamine B, Fluorescein Isothiacyanate which are also considered to be best molecules for different fluorescent studies in literature.

3.2. Choice of SPA bead verses SPA powder and reason why the SPA bead is chosen

SPA occurs as powder and bead. For diaper and sanitary pad applications, SPA powder is used due to its increased surface area and the pace at which it can lock the water and other biological and chemical components. The SPA powder has rapid absorbing ability and matches or realizes the 500 times water absorption relative to its weight. But due to rapid absorption, the SPA powder disrupts the fluorescent solution structure. On the other hand SPA bead has relatively slower water absorption rate and has the gradient structure with respect to surface area. When we look at SPA bead from the axis of exterior to core the surface in contact with fluorescent solution and has layered structure for water locking. This property prevents rapid precipitation of fluorescent compound at the SPA surface and enables use of SPA bead for chemical or biochemical assays. **Figure 1** shows of difference in fluorescent compound absorption in bead verses powder.

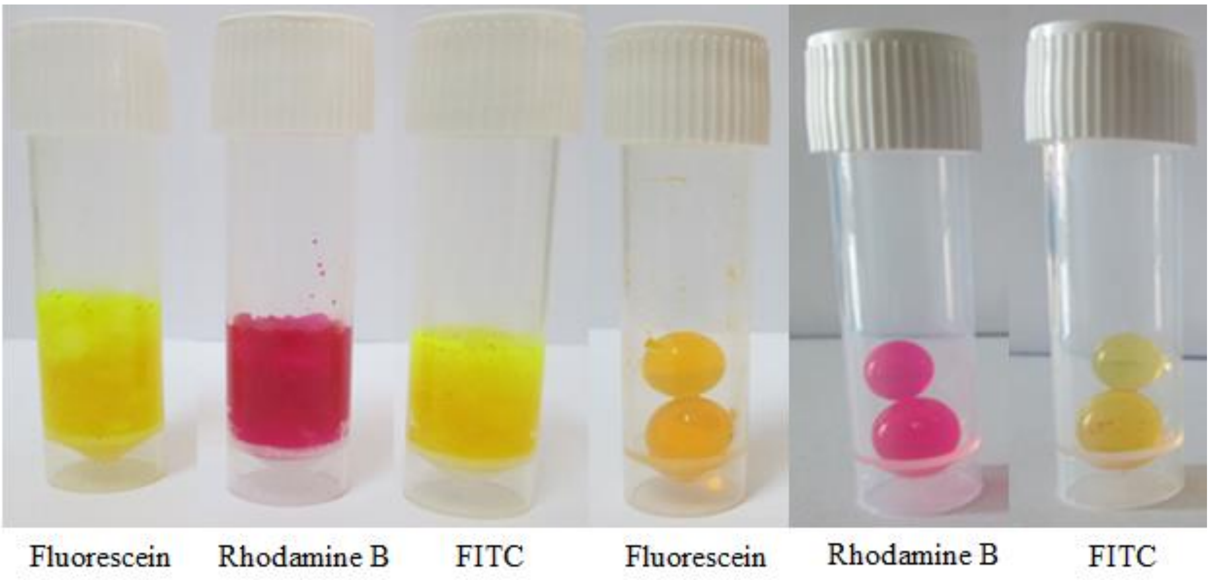


Figure 1: The three fluorescent compounds absorption in SPA powder verses SPA bead.

3.3. Absorption of fluorescent compounds by SPA bead

As such SPA is known to work as 'solid rain' a property by which water is locked in its interstitial structure and delivered water to a plant as and when needed. Almost from past five years even pesticides and other nutrients are reported delivered through 'solid rain' route. We hypothesized that in a way pesticides are similar to colorimetric dyes and fluorescent compounds and have minimal solubility in aqueous solutions and agglomerate at higher concentrations. Hence, we assumed that at the study concentration of 1mM and 10mM, we should observe normal intake of fluorescent compound in SPA core and the **Figure 2** shows the before and after intake of different fluorescent compounds with SPA bead.

Figure 2: SPA bead absorption with 5 different fluorescent compounds with water as a control.

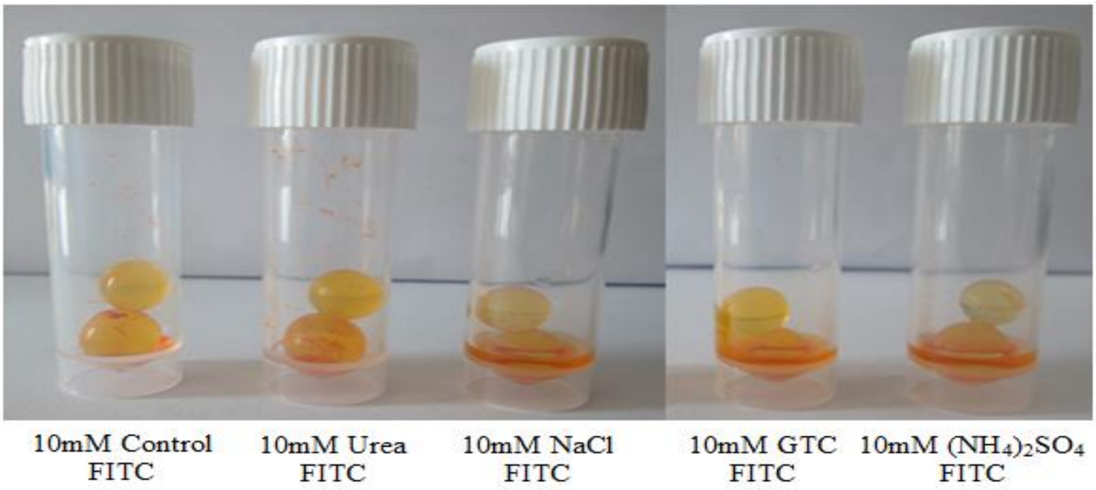
3.4. Affect of presence of Hofmeister (chaotropic) salts on intake of fluorescent compounds in SPA bead structure

Figure 3 shows intake of Hofmeister salts with two different fluorescent compounds into SPA bead and **Table 1** gives the quantitative picture of quantum of intake. It was observed that among the chaotropic salts studied, Urea was unique. As reported with other salt solutions, water absorptivity of SPA bead is minimized as the salt concentration of Ammonium sulphate, Guanidine Isothiacyanate and Sodium chloride are increased. But Urea has not displayed any such behaviour and the fluorescent compound absorptivity is normal upto 2M of Urea. This was inline without previous observation of Hofmeister salts on fluorescent and colorimetric dyes wherein Urea displayed increase in fluorescence quantum yield where as other chaotropic salts have resulted in decrease of quantum yield and is shown below [17]. We hypothesized that the Urea is an organic compound and not an ionic compound to have rapid precipitating effects when concentrated at the SPA surface. Also the water structure in solvated form of Urea is definitely different other study compounds because of the shear solubility ratios. **Table 2** shows the water solubility ratios and it can be clearly observed that Urea is soluble in water as a high molar solution and it could be the reason for odd man behavior of Urea among chaotropic agents.

Quantum yields of fluorescein under different buffer conditions

	Urea	**$(NH_4)_2SO_4$**	**NaCl**	**Guanidine Isothiocyanate**
Quantum yield	1.024	0.762	0.887	0.097
Standard deviation	0.034	0.024	0.028	0.003

10mM Control Rhodamine | 10mM Urea Rhodamine | 10mM NaCl Rhodamine | 10mM GTC Rhodamine | 10mM $(NH_4)_2SO_4$ Rhodamine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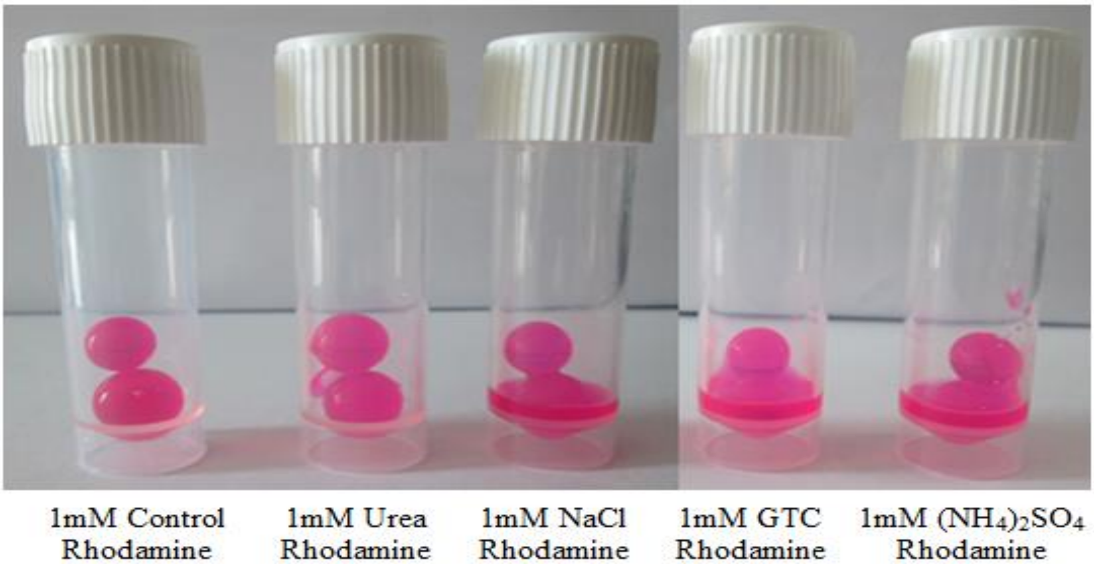
10mM Urea FITC
10mM NaCl FITC
10mM GTC FITC
10mM $(NH_4)_2SO_4$ FITC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1mM Urea Rhodamine
1mM NaCl Rhodamine
1mM GTC Rhodamine
1mM $(NH_4)_2SO_4$ Rhodamine

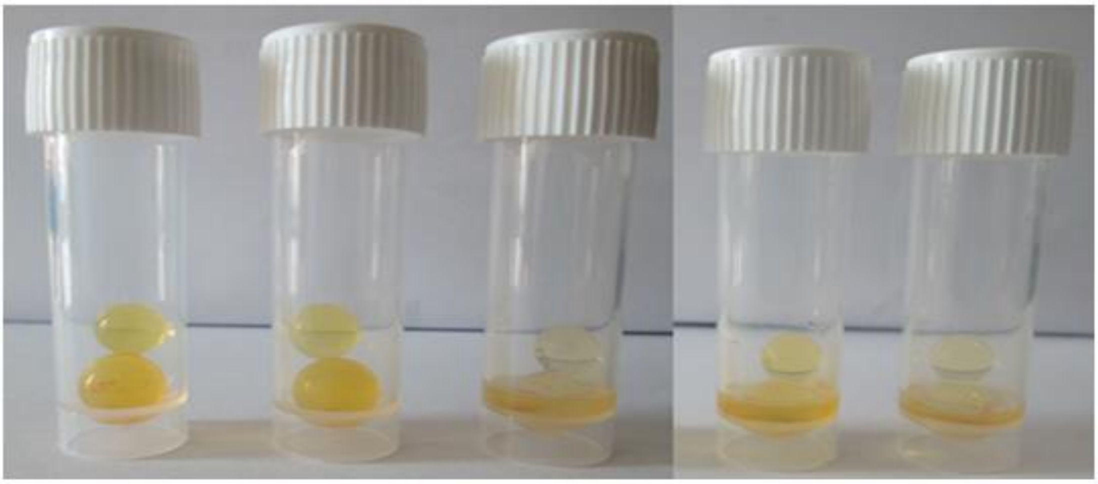

Figure 3: Urea, Ammonium sulphate, Guanidine Isothiacyanate and Sodium chloride (Hofmeister series salts) absorption capacity with 1mM and 10mM FITC and Rhodamine B solutions in SPA bead.

Table 1: Table 1 shows the absorption quantity of Hofmeister series salts taken by SPA beads.

Hofmeister Series salts (Chaotropic agents)	SPA Bead Absorption Concentration
UREA	1M
SODIUM CHLORIDE	600µM
AMMONIUM SULFATE	550µM
GUANIDINE ISOTHIOCYANATE	400µM

Table 2: Hofmeister series salts (Chaotropic agents) solubility proportions in Water.

Hofmeister Series salts	Solubility(Gram/Litre)H_20
UREA	500
SODIUM CHLORIDE	360
AMMONIUM SULFATE	75
GUANIDINE ISOTHIOCYANATE	100

4. Conclusion

The observation that Urea facilitates intake of fluorescent compounds has far reaching applications and we discovered a new agent which can compensate for ill effects of salts on the SPA water absorptivity. The fluorescent compound intake in absence of any salts (neat solution) is inline with other reported publications of use of non-polar pesticides via solid rain route. The Urea and salt combination studies will be interesting with respect to bioassay and realizing optimum combinations of different assay components for bioassay studies and is beyond the scope of this study.

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