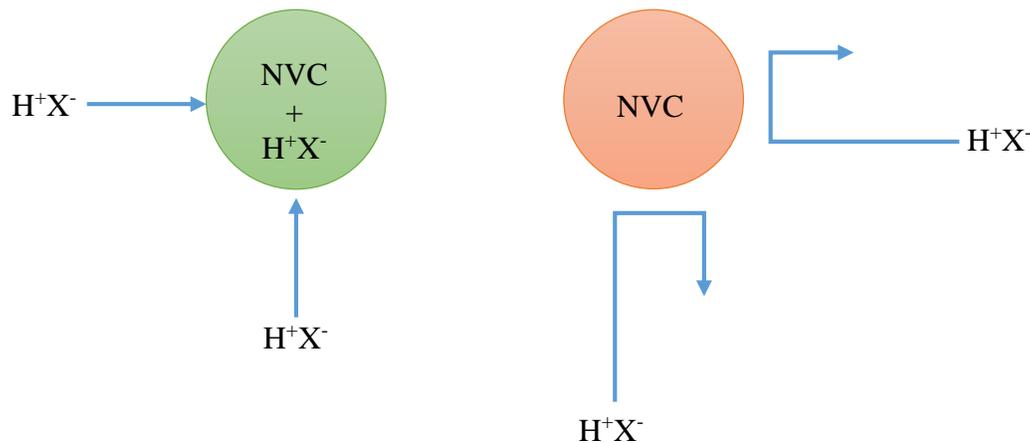


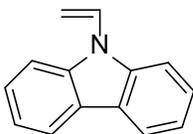
Surfactant Control of Ionic Reactions in Emulsions

Innovative Science Corp. has recently discovered unusual behavior in context to ionic reactions conducted in emulsion. During the course of studies on aqueous cationic polymerizations employing heteropoly acids (H^+X^-) as the initiator, Dr. Lewis hypothesized that reaction resulted from acid entering the monomer droplet from the aqueous phase (Figure 1). This process is somewhat favored by the mutual solubility of certain heteropoly acids in both water as well as oxygenated organic compounds, the latter being insoluble in water. It was witnessed that no polymerization occurred when oxygenated components capable of dissolving heteropoly acids were absent. For example, the aqueous polymerization of N-vinylcarbazole (NVC) using phosphotungstic acid does not occur when the monomer is dissolved in toluene, which is a non-solvent for the acid initiator (Figure 1, Red Droplet). On the other hand, when NVC is dissolved in anisole (a solvent that can dissolve the heteropoly acid and/or its aqua adducts) polymerization does occur (Figure 1, Green Droplet).



● = Good solvent for H^+X^- (polymerization)

● = Non-solvent for H^+X^- (no polymerization)



N-vinyl(carbazole) (NVC)

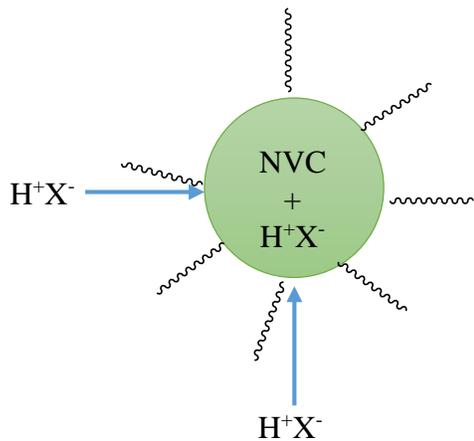
Figure 1. Influence of solvent on outcome of polymerization.

Lewis then hypothesized that transport of heteropoly acid from the aqueous to the organic phase could be prevented by inclusion of an anionic surfactant. The rationale behind this hypothesis is that soap molecules with negative termini would impart a negatively charged protective-shell around the monomer droplet that would repel the negatively charged heteropoly anion (i.e., repulsion of like charges) of the heteropoly acid and prohibit its access to the monomer droplet. It is theorized that transport of H^+ is not encumbered greatly by surfactant molecules and the solubility of X^- in the organic phase (i.e., monomer droplet) drives the transport behavior (and drags H^+ into the monomer droplet). This phenomena would (in theory) apply to all charged acids (i.e., those that are dissociated in water) that have partial solubility in organic media. According to this model, nonionic and cationic surfactants should have little impact on the ability of the heteropoly anion to transit from the aqueous phase into monomer swollen micelles (Figure 2, A and B). On the other hand, anionic surfactants should prohibit the heteropoly anion from entering the monomer swollen micelle and thus prevent polymerization (Figure 2, C).

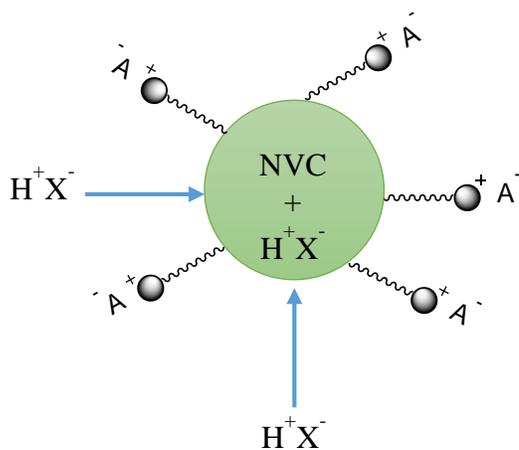
A series of experiments have been conducted for aqueous polymerization of N-vinylcarbazole (dissolved in anisole) using phosphotungstic acid as the initiator in the presence and absence of surfactants. In the absence of surfactant (Figure 1, Green Droplet), polymerization is rapid and reaches a steady state of conversion within a few hours. Cationic surfactants undergo reaction with heteropoly acids to form insoluble alkylammonium salts of the heteropoly acid and as such could not be explored for this type of acid initiator since they consume it. In the presence of a nonionic surfactant polymerization proceeds unimpeded (Figure 2, A) whereas essentially no conversion of monomer is obtained when an anionic surfactant is employed (Figure 2, C)!

We believe that these findings will have much broader implications in the future as the green chemistry field continues to flourish. *In particular, for reactions conducted in emulsion that require transport of an anion from the aqueous phase to the organic phase either cationic or nonionic surfactants must be used. In contrast, when similar reactions require the transport of a cation from the aqueous phase into the organic phase only anionic or nonionic surfactants can be implemented.*

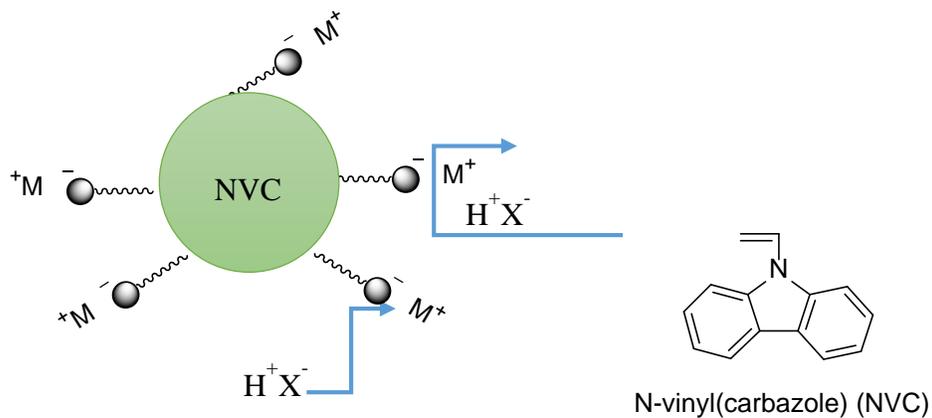
A. Nonionic surfactant does not prohibit transport of X^- . Polymerization occurs.



B. Cationic surfactant does not prohibit transport of X^- . Polymerization occurs.



C. Anionic surfactant prohibits transport of X^- . No polymerization.



● = Good solvent for H^+X^-

Figure 2. Effect of solvent on outcome of transport of X^- .