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Stabilization of oil in water emulsions by compositions of oil soluble surfactants and water soluble polyelectrolytes

In order to create new effective emulsifiers of oils influence of compositions of oil soluble surfactants and water-soluble polyelectrolytes on stability of emulsions was studied. It was shown that new composition emulsitifiers provides high stability of emulsions. The investigations of interfacial tensions of this systems showed that this phenomenon occurs due to high surface activity of compositions.

Keywords*: emulsion, interfacial tension, polyelectrolyte, surfactant.*

Introduction

New and improved techniques for stabilizing oil-in-water emulsions are being developed but virtually in all the cases the stabilizing agent has been soluble in either the aqueous phase or the oil phase. However, there have been many studies in relation to the polymer-surfactant interaction; they were never used for stabilizing an oil-in-water emulsion. It was discovered recently by Stamkulov et al [1] that by using a combination of oil soluble surfactant and water soluble polymer, an emulsion that is stable over a period of month can be formed. This surfactant-polymer pair is oppositely charged. The principle assumed here is that, an oppositely charged system of water-soluble-polymer and oil-soluble-surfactant should produce a reasonably stable emulsion. Whether this principle is a general effect, or specific to the Hexadecylamine-Polyacrylic Acid system, forms the purpose of this paper.

Emulsions are a special kind of colloidal dispersion in which there are two immiscible liquids and where one of them is dispersed in the other [2]. Nevertheless, it is a well-known fact that the dispersed phase tends to coalesce and as a result, two distinct immiscible phases are formed [3]. Becher [4] describes emulsions as, "A heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets." Therefore, in order to prevent this coalescence, surface stabilizing agents are generally employed. [1]

Figure 1 - An oil droplet in water; the drop is prevented from contacting and coalescing with other droplets by the presence of an adsorbed layer of surfactant.

Mechanism of stabilizing an emulsion The distance between the droplets of the dispersed phase, must be large enough to overcome the Van der Waals force of attraction [5]. Once these drops are far apart and are uniformly distributed, the time for phase separation is also increased. This is achieved by either of the following [6]: Charge stabilization, Steric stabilization and Particle Stabilization. Charge stabilization: As the name suggests, the droplets of the dispersed phase, are covered by the same charge, such that when two droplets come together they experience a repulsive force and hence, stay apart.

Steric Stabilization: Here, a mechanical barrier, generally a copolymer that is attached to dispersed droplets surface, separates the droplets from the dispersed phase. This barrier would extend away from the surface of the droplets, to a distance where it can prevent Van der Waals force of attraction. Particle stabilization: This mechanism is not different from steric stabilization as both the mechanisms employ a mechanical barrier but in this case, the barrier, rather than being formed by a polymer, is formed by solid particles. Charge and steric stabilization usually involve usage of surfactants and polymers respectively. The mechanisms are explained in detail in the discussion of surfactants and polymers.

Novel method of stabilizing an Oil-in-Water Emulsion

Stamkulov et al. in 2009 reported ofa report a novel way for preparing oil-in-water emulsion. Here unlike, what was discussed previously, the surfactant and polyelectrolyte are not soluble in the same phase. The surfactant used here is Hexadecylamine and the polyelectrolyte is Polyacrylic acid. Hexadecylamine is oil soluble and positively charged. Polyacrylic acid is water-soluble and is negatively charged. Hexadecylamine in toluene and Polyacrylic acid in water is taken in equal portions and emulsified. The resulting emulsion was found to be stable for around a month [4].

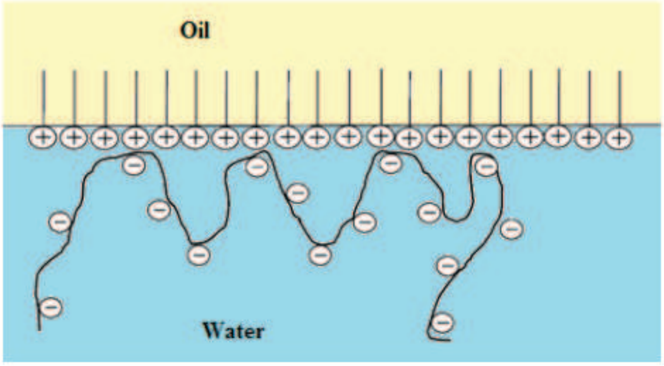

Figure 2 – A schematic representation of the mechanism for the adsorption of polyelectrolyte at the oil-water interface has an adsorbed layer of surfactant of opposite charge. From Ref. [4]

Here, the stabilization owes to the opposite charges on the two molecules (Hexadecylamine and Polyacrylic acid) and that they form a bridge between oil and water. Oil attached-Hexadecylamine arranges itself onto to the chain of Polyacrylic acid, which in turn, is attached to water molecules. It was also shown by interfacial measurements that in the absence of either Polyacrylic acid or Hexadecylamine, the emulsion was not as stable as in the presence of both. Literature for similar work is extremely scarce and it is safe to say that, perhaps this is the first method of its kind.

Preparation methods

Recent research has improved techniques for preparation of double emulsions [10], [11]. However almost all of them seem to refer to two methods as standards for comparison. The methods are simply referred as one-step and two-step methods. The one-step method involves either, phase inversion of an already prepared emulsion or by simply putting in all the ingredients together and giving a „mechanical treatment [12]. The two-step method involves preparing an emulsion and then adding the emulsion to the final continuous phase.

Material

All materials obtained from the manufacturers were used without further purification.

Methodology

The following polyelectrolyte-surfactant combinations were tried.

Table 1 - Combinations used for preparing oil and water emulsions

	Surfactant (oil soluble)	Polymer (water soluble)	Water/ Oil Ratio
1	Hexadecylamine	Sodium Polystyrene sulphonate	50: 50
2	Stearic acid	Poly (Dimethyl Diallyl Ammonium Chloride)	50: 50
3	Hexadecylamine	Carboxy methyl cellulose	50: 50

From here forth, the chemical names would be denoted with their abbreviation shown above. It should be noted that, for molality calculations, the molecular weight of the polyelectrolyte correspond to that of its monomer. To state an example, the molecular weight of Sodium Polystyrene sulphonate is 1,000,000 but for molality calculation, the monomer molecular weight of 206 g/mol is used. In this case, 10^{-3} concentration of Sodium Polystyrene sulphonate to 206 x 10^{-3} M of the monomer. The surfactant and polyelectrolyte are dissolved in their respective phases in a volumetric flask. They are then added together and emulsified using a high shear mixer for 60 seconds. The dynamic interfacial tension measurements are measured using a Kruss instruments K100 tensiometer with a Whilhelmy plate, to measure the interfacial tension at the oil-water interface. Interfacial tension measurements were recorded every 8 seconds, and were started within 2 minutes of the toluene-water interface being formed.

Results

After a series of trails, based on previous work [4], it was found that only one of the three combinations of surfactant-polymer systems formed a stable emulsion. The Hexadecylamine, HDA and Sodium Polystyrene sulphonate, SPSS (2), alone gave stable emulsions, which was stable against coalescence for more than 5 weeks. In all cases, an oil-in-water emulsion is formed. A wide range of concentrations of Hexadecylamine, HDA and Sodium Polystyrene sulphonate, SPSS (2), gave stable emulsions which were between the molality intervals of 10^{-2} to 3 x 10^{-3}. The emulsions were initially prepared using a low molecular weight version of Sodium Polystyrene sulphonate, SPSS (1). Later, new Sodium Polystyrene Sulphonate, SPSS (2) was used which had a molecular weight of 1,000,000. The reason perhaps is the fact that the low molecular weight of Sodium Polystyrene sulphonate, SPSS (1) gave a stable emulsion with Hexadecylamine, HDA at a concentration of 10^{-2}. Even though, this value of concentration is not high, we wanted to test whether higher molecular weight used in lower concentrations would achieve the same. In fact, most of the other emulsions that were stable were made using this higher molecular weight Sodium Polystyrene sulphonate, SPSS (2). However, the lowest concentrations of Hexadecylamine, HDA and Sodium Polystyrene sulphonate, SPSS-2 that were able to form a stable emulsion was 5.5 x 10^{-3} M of Hexadecylamine and 4.85 x 10^{-3} M of Sodium Polystyrene sulphonate (MW:1,000,000). In addition, in all the trials with either of them absent (HDA or SPSS (2)) a poorly stable emulsion was formed that was stable for a few hours.

Interfacial tension

As previously done [1], the interfacial tension measurements were measured at the oil-water interfaces in the presence of Hexadecylamine, HDA, and Sodium Polystyrene Sulphonate, SPSS (2) complexes. It is necessary to record these measurements as these give insight to the mechanism of stabilization of the emulsion. Stamkulov [1] indicated that when Hexadecylamine is used without Poly Acrylic Acid, a poorly stable emulsion is formed and measured the interfacial tension for pure Hexadecylamine that is absorbed at the oil water interface. It was observed that at very low concentrations of Hexadecylamine, typically in the range of 10^{-4} to 10^{-5}, the interfacial tension was very high – around 35 mN/m, which is close to the interfacial tension between pure toluene and water. However, as the concentration of Hexadecylamine was increased by a factor of 10, the interfacial tensions dropped to 2.6 mN/m and similar results were observed with the polymer, Polyacrylic acid. Expecting similar patterns, interfacial tension measurements were taken for pure Polystyrene Sulphonate, SPSS (2) absorbed at the oil-water interface. So far, we have seen from previous work [1], and present experimental result that neither Hexadecylamine, nor Sodium Polystyrene Sulphonate lowers the interfacial tension of the oil water interface when used at concentrations in the order of about 10^{-3}. Interfacial tension measurements were not as problematic as Stamkulov [1] found. It was a alittle surprising that a thick layer between Hexadecylamine in Toluene and Sodium Polystyrene Sulphonate was not formed, given that they are oppositely charged. Also, unlike with Stamkulovs work, the interfacial tension reached a constant value much quicker. In Stamkulovs case, it was in a few hours and sometimes extended to days. Here, it reached thatstate within two hours and with some cases, less than an hour. Therefore, it is likely that Sodium Polystyrene Sulphonate reaches the interface quicker that Polyacrylic acid.

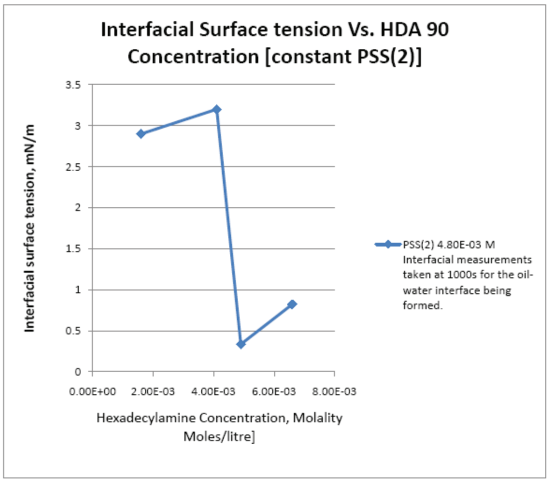

Figure 3 - Interfacial tension as a function of HDA concentration at the oil-water interface.

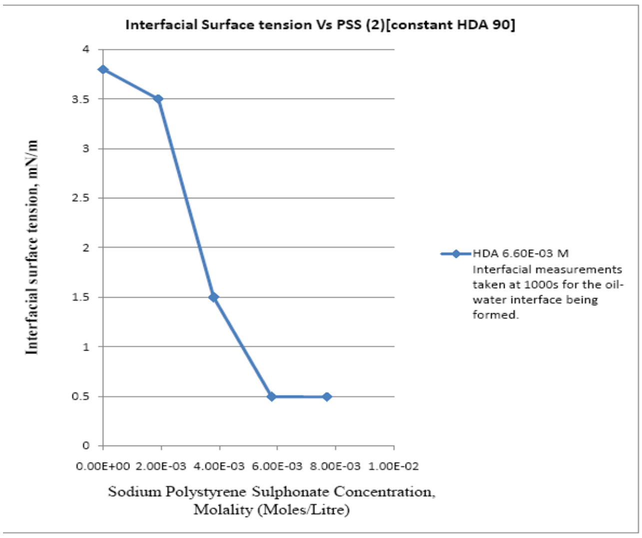

Figure 4 - Interfacial tension as a function Sodium Polystyrene concentration at the oil-water interface.

Graphs show the interfacial tension as a function of concentration of Hexadecylamine and Sodium Polystyrene Sulphonate respectively. It is easy to note that in both the cases, the interfacial tension drops drastically after a certain concentration threshold. This happens maybe at lower concentrations, the polymer fails to provide the necessary viscosity of the continuous phase to prevent the oil droplets from coalescing. At higher concentrations of Hexadecylamine, micelle formation becomes much easier.

It is also rather surprising that the interfacial tension drops to a minimum and rises again as seen in Graph 3. Stamkulov [1] observed this exact phenomenon. We were also able to reproduce this feature. Previously [1], it was explained that the polyelectrolyte was extending away from the oil water interface. It can also be explained that initially, there is a strong attraction between the Hexadecylamine-Toluene and Sodium Polystyrene Sulphonate-water phase. As Sodium Polystyrene Sulphonate starts to attach Hexadecylamine, they form a complex. This complex would have the Sodium Polystyrene Sulphonate extending into the water phase on one side and the other side attached to Hexadecylamine. The strong interaction between the two might lead to what might be seen in associative phase separation [10]. In associative phase separation, oppositely charged surfactant-polyelectrolyte in aqueous solutions tend to associate into one viscous phase containing both and another empty clear aqueous phase. Here it might be that initially, Hexadecylamine tries to pull Sodium Polystyrene Sulphonate and keep it in the oil phase. However, since Sodium Polystyrene Sulphonate is oil insoluble, it might be pulled back into the aqueous phase again. All this would be seen happening in the first 500 seconds of the interfacial tension recordings.

Conclusion

The results clearly show that stable emulsions can be formed with oppositely charged oil soluble surfactant and water-soluble polymer systems. So far two such systems have been successful namely the Hexadecylamine - Polyacrylic acid combination and the Hexadecylamine - Sodium Polystyrene sulphonate combination. It is also to be noted that these combinations give stable emulsions at various concentrations, which remain stable for more than a month. However, other than poor attraction between the surfactant – polymer systems in the other cases, no other explanation can be given at this stage. Though, the aim of this project was not the analysis of new methods of preparing double emulsions, it does appear to have achieved it. All the previous literature and research indicate [7]-[10], that the double step process of preparation of double-emulsion is universally accepted. This involves preparing one emulsion first and then pouring that to another phase being the next step [10]. Here, an extremely simple step has been discovered where, the entire process of preparing just involves merely homogenization. Though, only two concentration ranges of the surfactant-polymer were observed forming stable double emulsions, other concentrations are likely to give the same result. It needs to be emphasized that none of the emulsions showed any confirmatory images of double emulsions immediately after shear mixing. They have to be left undisturbed for weeks to get such clear images. The dip of the interfacial surface tension also, cannot be clearly explained and involves around a lot assumptions due to lack of literature regarding the interaction between an oil soluble surfactant and water soluble polyelectrolyte that are oppositely charged.

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Майда еритін баз-ың және суда еритін полиэлектролиттердің композициясын қолдану арқылы тура эмульсияларды тұрақтандыру

Мұнайдың тиімді эмульгаторларын даярлау мақсаты үшін тура эмульсияның тұрақтылығына майда еритін БАЗ-ар мен суда еритін полиэлектролиттің композицияларының әсері қарастырылды. Анықталған композициялық эмульгаторлар эмульсияның жоғары тұрақтылығын қамтамасыз етеді. БАЗ-дың майдағы ерітіндісі - полиэлектролиттің су ерітіндісі шекарасындағы фаза аралық керілудің өлшемі, анықталған эффект фаза аралық керілудің күшті төмендеуімен шартталғанын көрсетті.

Кілттік сөздер: *эмульсиялар, беттік керілу, полиэлектролит, БАЗ.*

Н.Ш. Стамкулов, К.Б.Мусабеков, С.Б.Айдарова, П.Лукхам, С.Ш.Кумаргалиева, А.Кенжебеков

Стабилицазия прямых эмульсий с помощью композиции маслорастворимого пав и водорастворимого полиэлектролита

С целью разработки эффективных эмульгаторов нефтей изучено влияюние композиции маслорастворимого ПАВ и водорастворимого полиэлектролита на устойчивость прямых эмульсий. Установлено, что новые композиционные эмульгаторы обеспечивают высокую устойчивость эмульсий. Измерение межфазного натяжения на границе масляный раствор ПАВ - водный раствор полиэлектролита показало, что обнаруженный эффект обусловлен сильным снижением межфазного натяжения.

Ключевые слова: *эмульсии, поверхностное натяжение, полиэлектролит, ПАВ.*

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Коллоидно-химические характеристики золя, приготовленного на основе нанопорошка γ-Al_2O_3

Исследованы электроповерхностные свойства и агрегативная устойчивость γ–Al_2O_3*, (Alu C, «Degussa») в растворах NaCl. Определены оптические характеристики золя – волновой экспонент и относительный коэффициент рассеяния частиц. Сделано заключение, что коагуляция золя протекает преимущественно по безбарьерному механизму в потенциальном минимуме, обусловленном преобладанием сил дисперсионного притяжения над силами структурного отталкивания на относительно больших расстояниях между частицами.*

Ключевые слова*: нанопорошки, синтез, агрегаты частиц, устойчивость, коллоидно-химические характеристики золя.*

Введение

Разработка современных конструкционных и оптических материалов с заданными функциональными свойствами предполагает необходимость детального изучения физико-химических и коллоидно-химических свойств дисперсий (золей и суспензий), полученных на основе нанопорошков различного происхождения и кристаллической модификации. В последнее время большой интерес вызывает получение функциональных материалов на основе наноструктурированных систем оксидов металлов с заданными физико-химическими свойствами. В большой степени это относится к системам на основе Al_2O_3.

Экспериментальная часть

В работе были исследованы золи γ-Al_2O_3, приготовленные на основе коммерческого нанопорошка, полученного методом плазмохимического синтеза (Alu C, фирма Degussa). Порошок отличался высокой чистотой, содержание Al_2O_3 составляло 99,8 %. Удельная поверхность порошка равна 100±15 $м^2/г$, исходные частицы оксида алюминия в порошках и золях агломерированы, средний размер структурной единицы агрегата, согласно электронно-микроскопическим данным) составлял $\approx$ 26 нм.

Результаты и их обсуждение

Потенциометрическое титрование дисперсии γ - Al_2O_3 проводили в интервале pH=3.5–9.0 с концентрацией фонового электролита NaCl 10^{-3}, 10^{-2}; 10^{-1} и 1М. Результаты приведены на рисунке 1. Видно, что точка нулевого заряда (ТНЗ) с ростом концентрации фонового электролита смещалась в