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Counter ion Effects in AOT Systems and New Fluorocarbon- based Micro Emulsion Gels Counter Ion Effects in AOT Systems

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Abstract— Micro emulsions have important applications in various industries, including enhanced Oil recovery, reactions, separations, drug delivery, cosmetics and foods. We investigated Two different kinds of water-in-oil micro emulsion systems, AOT (bis(2-ethylhexyl) sulfosuccinate) micro emulsions with various counter ions and per fluorocarbon-based Micro emulsion gels with triblock copolymers. In the AOT systems, we investigated the Viscosity and inter droplet interactions in Ca(AOT)2, Mg(AOT)2 and KAOT Micro emulsions, and compared our results with the commonly-studied NaAOT/water/decane system. We attribute the differences in behavior to different, hydration characteristics of the counter ions, and we believe that the results are consistent with a previously proposed charge fluctuation model. Per fluorocarbons (PFCs) are of Interest in a variety of biomedical applications as oxygen carriers. We have used triblock Copolymer Pluronic® F127 to modify the theology of PFC-based micro emulsions, we Have been able to form the rmoreversible PFOB (perfluorooctyl bromide)-based gels, and have investigated the phase stability, theology, microstructure, interactions, and gelation Mechanism using scattering, reometry, and microscopy. Finally, we attempted to use these data to understand the relationship between reology and structure in soft attractive Colloids.

Keywords—Academy of technology(AOT), Power Finance Corporation(PFC),perfluorooctylbromide(PFOB),Nuclear magnetic resonance(NMR),professional employer organization(PEO),sodium(Na),calcium(Ca)

INTRODUCTION

My topic work explores two different types of water-in-oil micro emulsion systems. The first system involves a charged surfactant, AOT (bis(2-ethylhexyl) sulfosuccinate), which has commonly been used as a model system for the study of water-in-oil micro emulsions. We have investigated the effect of counter ion type on the solution interactions and viscosity, and have used our results to test a previously-proposed charge fluctuation model to describe inter droplet interactions in this system. The second micro emulsion system we investigated utilizes a perfluoro carbon (PFC) as the oil. While other groups have reported stable PFC-based micro emulsions, these systems have all been low-viscosity liquids. We wished to create stable, elastic gels containing PFCs. We used triblock copolymers to modify the theology of the PFC micro emulsion and form thermo reversible gels. We have attempted to use the results on this system to gain an understanding of the relationship between theology and structure in soft attractive colloids.

1.1 Micro emulsions:

Alcohol to a coarse macro emulsion stabilized by an ionic surfactant [2]. One of the best recent descriptions of micro emulsions is given by Attwood [3]: "A micro emulsion is a system of water, oil, and amphiphilic compounds (surfactant and co-surfactant) which is a transparent, single optically isotropic, and thermodynamically stable liquid." The great potential for practical applications of micro emulsions has stimulated a great deal of research in the field, especially for applications in enhanced oil recovery in the 1970s. Schulman and coworkers were the first to investigate these transparent liquids [1, 4-9]. The microstructure, size, shape, theology and dynamics of micro emulsions have been characterized by various techniques such as scattering, viscometry, reometry, X-ray diffraction, ultracentrifugation, cryo-electron microscopy, electrical birefringence and nuclear magnetic resonance (NMR) [10]. One of the most significant developments in the field was a theoretical statistical-mechanical description of micro emulsion systems, and the demonstration that micro emulsions are thermodynamically stable phases because of their ultralow interfacial tension and highly flexible interfacial layer [11-18]. By contrast, emulsion systems are only kinetically stable and often phase separate after a short time.

The other main differences between micro emulsions and emulsions are the size and the shape of dispersed phase. Micro emulsion droplets are nano scale, typically 10-200 nm, much smaller than emulsion particles (1-20 μm) and also smaller than the wavelength of visible light, so that the micro emulsions systems are transparent. The microstructure of micro emulsions can evolve from droplet-like to bicontinuous structures, whereas emulsions consist of large coarse spherical droplets [19]. Due to these unique properties and

characteristics, micro emulsions have been used in various industries. Research on micro emulsion-based flooding techniques in enhanced oil recovery began in 1970s; however the potential of their use was overestimated because of the high expense of surfactant and current low oil prices [20-25]. Cheaper production of surfactants was needed to make this technique affordable [26-29]. Micro emulsions can solubilize both hydrophilic and hydrophobic reactants at high concentration, so they have been used as a novel medium for chemical synthesis as micro reactors" or "nano reactors", distinct from reactions in a bulk solvent [10].

The reaction parameters and chemical reactivity can be determined by the microstructure of micro emulsion, the properties of solvent, surfactant and cosurfactant [30-35]. Micro emulsion reaction systems have been used for spectroscopic analysis, preparations of mesoporous structure materials [36-38], synthesis of polymeric particles [37, 39-41], synthesis of ultrafine metal, metal oxide, and semiconductor particles [42-47], and even used in supercritical fluids [48-50] and enzyme-catalyzed reactions [51-53]. Due to their thermodynamic stability, bioavailability and topical penetration of poorly soluble drugs enhanced by the amphiphiles, micro emulsions have gained an important role as drug delivery vehicles [19, 54-56] and in cosmetics [57-59]. This application has inspired research on the use of novel highly efficient and nontoxic surfactants and cosurfactants. The transparent nature and ability to solubilize large amounts of volatile organic compounds, like alcohol in fragrance formulations, make micro emulsions an important precursor in cosmetic formulations, where they are sometimes referred to as micro emulsion gels [60-62]. Some foods contain micro emulsions naturally, and the preparation of foods nearly always requires the incorporation of lipids which exist as micro emulsions in foods. Micro emulsions can also be used as liquid membranes for separation due to their significantly large interfacial area and fast spontaneous separation, extracting organic substances, metal, or proteins from 3 dilute streams [63-69]. The ultralow interfacial tensions and the high solubilization power of both hydrophilic and hydrophobic substances make micro emulsion an excellent medium in textile detergency [70-73].

In the above application processes, the rheological properties and structure are important factors. These impact the stability, reactivity, bioavailability, penetration, separation efficiency, fine particle quality, and so on. Viscosity is a macroscopically observable parameter, very important in oil recovery, drug delivery, reaction, cosmetics, and separations. The rheological properties, shape and size of micro emulsion structure are basically determined by the surfactant and solvent. So the selection of surfactant and solvent is very important, attracting enormous interest of researchers on the factors of theology and structure like chain length of solvent, ion size and charge of surfactant.

1.2 Per fluorocarbons and Fluorinated Amphiphiles

1.2.1 Per fluorocarbons (PFCs)

When the hydrogen atoms in hydrocarbons are replaced by fluorine completely, the products are called per fluorocarbons (PFCs), or simply fluorocarbons [74-76]. Hydrogenated amphiphiles can also be fluorinated fully or partially to form per fluorinated amphiphiles or partially fluorinated amphiphiles [74]. Due to its strong electronegativity, fluorine shows an unusually high potential of ionization and very low polarizability. Because the C-F bond is among the most stable single covalent bonds and its atom radius is much larger than hydrogen atom, most fluorocarbons are very stable and inert thermally, chemically and biologically [75, 76]. They also have a larger volume, a larger density and a much more stiff chain than their hydrogenated counterparts [74-79].Because of the low polarizability of fluorine, both the van der Waals interactions between fluorinated chains and the cohesive energy densities in liquid fluorocarbons are very low, resulting in many valuable properties, such as high fluidity, low surface tension, low boiling point, low refractive indexes, low dielectric constant, high gas solubility, excellent spreading property, high vapor pressure, and high compressibility [75]. The high density, anti-friction properties, and magnetic susceptibility values close to that of the water in PFCs also are useful in biomedical applications [75]. Additionally, the per fluorinated chain offers larger surface area to enhance the hydrophobicity so that the chain is both hydrophobic and lipophobic. Fluorocarbons are even immiscible with their hydrogenated counterparts because of their different chain conformations. This phenomenon is still pending to be explained successfully and completely [75, 78].

1.2.2 **Fluorinated Amphiphiles:** Fluorinated amphiphiles can be classified into four types according to their functional groups on the backbone: anionic, cationic, amphoteric, and nonionic [74].

Because of strong hydrophobic interactions and low van der Waals interactions from the fluorinated chain, fluorinated amphiphiles tend to self-assemble in water and collect at interfaces, showing strong surface activity. They have much lower critical micellar

concentrations (cmc) than their hydrogenated counterparts [74, 75]. An increase of the chain length will decrease the cmc, and branching of the backbone will increase the cmc [74]. Per fluorinated amphiphiles also have smaller cmc than their partially fluorinated counterparts [74, 75].

1.2.3 Applications of Fluorocarbons and Fluorinated amphiphiles

Because of their unique properties, fluorocarbons and fluorinated amphiphiles have a lot of applications in both biomedical research and industrial research. In biomedical research, typical applications involve oxygen transport, because of the exceptional oxygen solubility and biocompatibility displayed by PFCs [75, 76, 78]. It is reported that fluorocarbon-based systems can act as "liquid ventilation," temporary blood substitutes, and injectable oxygen carriers during surgery [74-76, 78]. Fluorocarbons can dissolve a large amount of gases, much more than hydrocarbons and water, displaying gas solubilities up to 25% higher than water [75, 76, 78]. The oxygen in fluorinated oil is not bound chemically to the fluorinated chain, so it may be easily transported to tissues. The fluorocarbon brings no risks of infection to tissues and body because there is no metabolite-related toxicity. Thus, fluorinated blood substitutes are very important in cases of blood shortage, rare blood type groups, on-site rescue, and so on [74-76, 78]. After Creutzfeldt-Jacob disease, also called "mad cow syndrome", was found, fluorinated micro emulsions become more popular and competitive than the blood substitutes from bovine hemoglobin derivatives [78]. Fluorinated gels and micro emulsions also have strong potentials for use in pulmonary drug delivery, controlled drug delivery, and ointments in pharmacy and ophthalmology to maintain gas exchange and acid-base status [74-76, 78]. They also work very well in retinal repair, replacement of the vitreous liquid, and treatment of articular disorders such as osteoarthritis and rheumatoid arthritis [75, 78]. Because of their unique properties, fluorocarbons and fluorinated amphiphiles have a lot of applications in both biomedical research and industrial research.

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1.3 polymer Adsorption and Triblock Copolymers

Polymer adsorption has been a very effective tool to control and adjust the phase behavior and rheological properties of colloidal suspensions. Triblock copolymers, which consist of two end blocks and one midblock, are a significant class of macromolecules that have such attractive applications. Intuitively, the formation of bridges absorbing two surfaces on each end of the polymer will induce inter particle attractions, and the formation of loops or brushes absorbing single surface on both of the ends will induce interparticle repulsion (Figure 1-1).

Figure 1-1. The triblock copolymers form loops and bridges on micro emulsion droplets. Dark double circles indicate surfactant layer between two immiscible liquids.

These interactions lead to unusual phase behavior and rheological properties of emulsion systems containing triblock copolymers [80-88]. To understand the structure, dynamics, phase behavior and rheological properties of adsorbed layers of polymer or surfactant molecules in colloidal systems, numerous techniques have been used, such as scattering, magnetic resonance, spectroscopic, hydrodynamic and rheological techniques [82, 84-95]. For example, poly(ethylene oxide)/polyisoprene/poly(ethylene oxide) triblocks (PEO-PI-PEO) were investigated in micro emulsion systems of AOT/water/decane [80, 81] and AOT/water/isooctane [89-95], forming highly associated solutions [80, 81, 89-95]. The phase behavior of AOT/water/decane is unusual with a gas-liquid transition due to an entropic gain with the conversion of loops to bridges. The viscoelastic moduli depend on concentration or volume fraction, conforming to theories of reversible networks or flowerlike micelle solutions [80]. SANS results of these systems showed that the equilibrium spacing of the droplets is independent of molecular weight and the number of polymers per droplet. The deviation between a power law asymptote for I(q) at high q and Gaussian coils suggested chain swelling due to excluded volume effects of polymer layer [81].

1.4 Universal Models for Phase Transitions and Rheology

Several authors have attempted to derive universal models to connect inter particle interactions to phase behavior and rheology in colloidal systems. In any colloidal dispersion system, the forces between components, usually expressed in terms of inter particle potential, play a significant role in the structure, phase stability and rheology of the system. Typical inter particle potentials have a repulsive component and an attractive component of depth min/kT, as despicted in Figure 1-2.

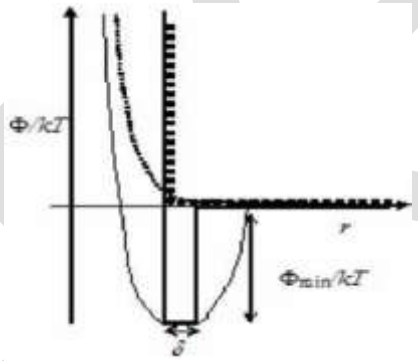


Figure 1-2. Typical pair potentials for colloids, showing hard sphere, soft sphere , attractive hard sphere, and attractive soft sphere.

The dependence of solution rheology on the inter particle potential for dilute to moderately concentrated dispersions has been revealed by experiments, non-equilibrium theories, and simulations [89, 91, 93, 97-86]. Equilibrium phase transitions also are determined by the nature of the potentials. The transition of a crystalline solid from a disordered liquid at high concentrations is a typical example [90-91].The liquid-gel transition between a liquid and a disordered viscoelastic solid, which is actively debated and studied, is suggested to occur through one of two mechanisms, attractive aggregation or formation of a glass. These two mechanisms also can be unified into "jamming transitions", a more general description [54]. Attractive aggregation in systems with inter particle attractions creates a fractal network of colloids in which the mass M within a radius r is given by M ~ rd. Here d, a fractal dimension, can be measured using scattering techniques [73, 76]. The rheology of such systems can be described using percolation theory [65] and characterized by the particle volume fraction p, with critical value of gelation, pc. The equilibrium modulus G0 and the low shear viscosity rj0 are given by:

$$G_0 \sim \left(\frac{|\phi-\phi_c|}{\phi_c}\right)^t \text{ for } \phi>\phi_c \text{ and } \eta_0 \sim \left(\frac{|\phi-\phi_c|}{\phi}\right)^s \text{ for } \phi<\phi_c$$

Near the critical gel point, G' and G", the storage and loss modulus, have a power-law dependence on frequency [109, 110], with G' ~ G" ~ rnA [94, 92]. G_0 Can be scaled by considering energy stored in interparticle bonds [85]:

$$\frac{G_o}{kT} \sim \frac{\phi^2}{a^2}\left(-\frac{\Phi_{\min}}{kT}\right)^{3/2}$$

A disordered viscoelastic glass can be formed in both attractive and purely repulsive colloidal systems as first observed by Pusey and van Megen [103, 113]. For monodisperse hard sphere systems the liquid-glass transition occurs at G=0.56-0.60 [113, 114]. Above the glass transition, G' starts to dominate over G" and becomes independent of frequency [80]. Colloidal glasses can also be formed in hard particles with short range attractions, such as colloids subject to depletion forces [88] and some polymeric micelles [97]. Jamming transitions are found to occur in a wide variety of attractive colloid systems and be able to unify the phenomena of gelation, aggregation, and the glass transition [70]. In these systems, the viscosity diverges as a critical volume fraction c is approached, and G' develops a low frequency plateau [76].

COUNTERION EFFECTS IN AOT SYSTEMS

The simplest micro emulsion systems are composed of a surfactant, water and oil. Aerosol OT, which is sodium bis(2 ethylhexyl) sulfosuccinate and simply called AOT, is a model surfactant that can form nanometer size reverse micelles and micro emulsion water droplets in many oils (Fig. 2-1). for clarity we will use NaAOT to refer to the surfactant with a sodium counterion. NaAOT has been extensively studied and has important applications in drug delivery, enhanced oil recovery, cosmetics, detergency, and so on. It has been found that the type of counterion, solvent, solvent content, droplet volume fraction and temperature all have important effects on the droplet size, shape, structure and properties of AOT-based micro emulsion systems.

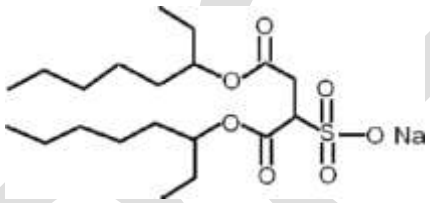


Figure 2-1. Chemical structure of NaAOT

Materials and Methods:

KAOT, Mg (AOT) 2 and Ca(AOT)2 are prepared from NaAOT purum(Sigma-Aldrich), using previously described methods [10, 11, 19]. Micro emulsions were formulated by mixing dried and recrystallized surfactant with water and decane at fixed volume fraction p, calculated from the specific volumes, and then diluting with decane and filtering through 0.22 ^m Millipore membrane syringe filters into the Ubbelohde capillary viscometers. The values of X cited are the stoichiometric ones, neglecting the small amount of water of hydration (AX < 0.5 for KAOT and Ca(AOT)2, AX < 1 for Mg(AOT)2) that normally cannot be removed from the surfactant easily. Measurements of the viscosity were performed in capillary viscometers at a fixed temperature T=30°C maintained within ±0.1°C with a Neslab R211 constant temperature water bath. Three repeat runs of each sample were performed, with the standard deviation between runs in the range of 0.02-0.08% for all samples. Capillary viscometers of size 0C, 1C, and 1 were used, corresponding to capillary radii ~ 1.0 mm. This is much larger than the size of the AOT micro emulsion droplets, which have radii in the range 2.0-5.0 nm [5], and thus we do not expect any edge effects from the capillary walls. The phase stability was studied in oven at different temperatures. Some of the solution samples are filtered into tubes for droplet size measurement using Argon laser (wavelength A=514.5nm) for dynamic light scattering at 30°C.

Results and Discussion: Ca (AOT)2/water/n-decane system. The relative viscosity of Ca(AOT)2/water/n-decane systems initially increases with increasing X, reaches a maximum at X = 15, and then decreases with further increases of water amount or X (Figure 1-4). Similar to NaAOT, the position of the maximum does not depend on p, but the magnitude increases with p.

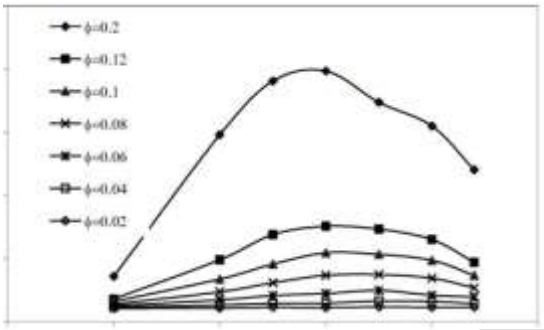


Figure 2-2. Relative viscosity r versus X, the molar ratio of water to $Ca(AOT)_2$, at fixed *p* for the $Ca(AOT)_2$/water/n-decane system. Lines are guides for the eye.

The Ca (AOT)2/water/n-decane system at fixed X (Figure 2-3) allows the intrinsic viscosity [r] to be determined from the intercept.

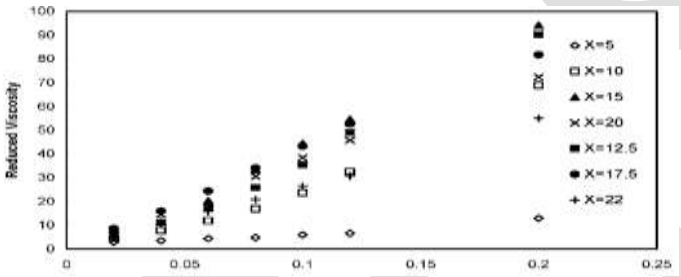


Figure 2-3. Reduced viscosity r_{sp} versus *p* for the $Ca(AOT)_2$ system

	X								
Surfactant	0	2.5	5	10	12.5	15	17.5	20	22
KAOT	3	--	2.6	2.5	--	2.4	--	2.3	--
$Ca(AOT)_2$	--	--	2.3	2.4	2.5	2.6	2.7	2.5	2.6
$Mg(AOT)_2$	2.8	3.0	3.9	--	--	--	--	--	--

Table 2-1. Intrinsic viscosity of Ca(AOT)2/water/n-decane, KAOT/water/n-decane, andMg(AOT)2/water/n-decane microemulsions as a function of *X*, the molar ratio of water to surfactant.

The corresponding k_H values at each *X* are very high and reach a maximum of nearly 80 at $X = 15$ (Figure 2-4). Figure 2-5 shows q_r versus *p* for the Ca $(AOT)_2$/water/«- decane system at fixed *X* along with quadratic fits to the data. Figure 2-5 includes data at very low *p* (0.005-0.1) that are not shown in Figure 2-2 and 2-3; these data allow us to obtain more accurate values of fit parameters. In all cases, the data fit a quadratic form very well.

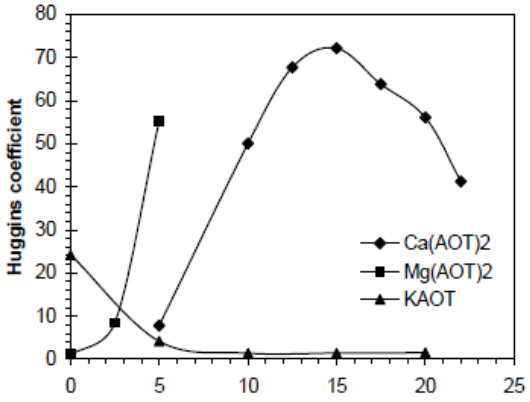


Figure 2-4. Huggins coefficient *kH* versus *X*, the molar ratio of water to surfactant. Lines are guides for the eye.

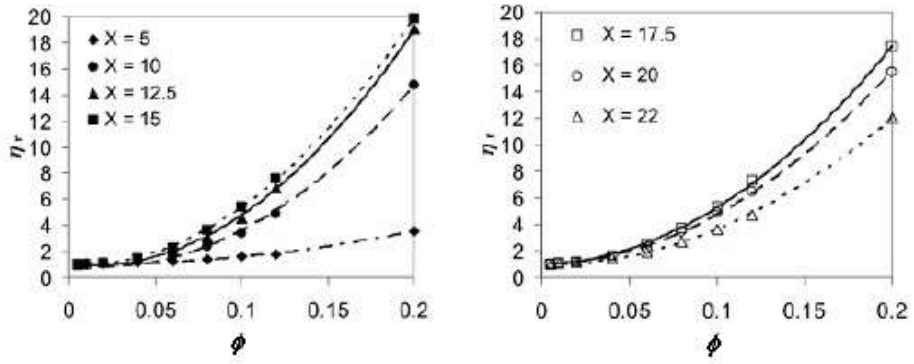


Figure 2-5. Relative viscosity ηr versus □ for the Ca(AOT)2 system. For clarity, data at different X are shown on separate graphs for values below (left) and above (right) the viscosity maximum. Lines are fits to $\eta r = 1 + 2.5$□ + (6.0 + 1.9/τ)□ □2. Symbols and lines are as follows: X = 5, filled diamond and dot-dashed line; X = 10, filled circle and dashed line; X = 12.5, filled triangle and solid line; X = 15, filled square and dotted line; X = 17.5, open square and solid line; X = 20, open circle and dashed line; and X = 22, open triangle and dotted line.

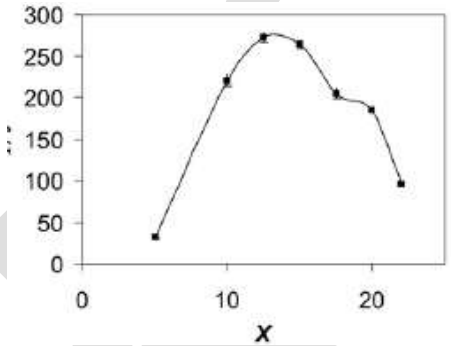


Figure 2-6. Stickiness parameter for Ca(AOT)2/water/*n*-decane microemulsions versus X, the molar ratio of water to surfactant. The line is a guide for the eye.

Figure 2-6 shows the values of $1/\tau$ that can be derived from the data, along with uncertainties based on the goodness of fit. The relative uncertainty in the $1/\tau$ values are 2–5%. The values of $1/\tau$ are very high and reach a maximum at X = 12.5 (Figure 2-6). Again, similar to the NaAOT system, the droplet interactions appear to mirror the viscosity maximum, with a maximum attraction at a value of X near the viscosity maximum.

One interesting feature is the high value of kH or 1/□ for Ca(AOT)2 microemulsions, suggesting strong attractive interactions between droplets. Corresponding values for the NaAOT system are in the range 1.0-10.0 [5]. Values of kH for the NaAOT system are in the range 1.0–10.0, which would roughly correspond to $1/\tau$ values in the range 0.1–30.0 assuming that the droplets can be described as adhesive hard spheres [5]. The high values may be a consequence of approximating the interdroplet potential by a simple adhesive hard sphere model; if this is not an adequate description of the potential, the data must be interpreted in terms of qualitative trends only. Bergenholtz et al. [4] found that a square well model could not provide quantitative agreement between values for the interdroplet attraction derived from SANS and viscometry. However, these high values may also suggest strong interactions in the Ca(AOT)2 system than in the NaAOT system. This may be related to the divalent counterion. When the Ca2+ counterion is released and surfactant exchange occurs between droplets, the resulting pair of oppositely charged droplets will each have a higher net charge than in the Na+ case, resulting in a stronger electrostatic attraction.

Mg (AOT)2/water/n-decane system. From Figure 2-11 and 2-12, the relative viscosity and reduced viscosity of the Mg(AOT)2 system change quickly with water content. Its relative viscosity increases sharply with water content below X ^ 5. The intrinsic viscosity of Mg (AOT)2 system increases slightly from below 3 to above 3 with water content increasing. Here only the monophasic systems at X = 0, 2.5 and 5 were diluted for the investigation of Huggins coefficient and stickiness parameter (Figure 2-13).

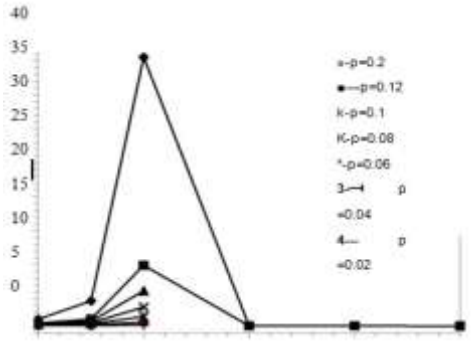


Figure 2-11. Relative viscosity r changes with X, molar ratio of water to Mg $(AOT)_2$. Lines are guides for the eye.

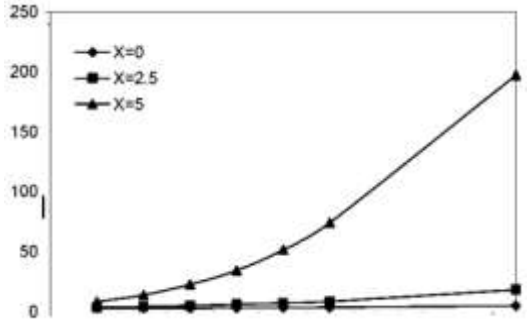


Figure 2-12. Reduced viscosity changes with *p*, the volume fraction of droplet to total solution of Mg(AOT)2. Lines are guides for the eye

2.4.4 Effects of Water Content

Water content plays an important role in the phase stability and microstructure. For divalent counterions, there is a trend to form cylindrical aggregates when water content increases [12]. We observe similar behavior (Table 2-1 and Figure 2-4) in Ca (AOT)2 and Mg(AOT)2 systems, the intrinsic viscosities of increase with water content (Table 2-1). Spherical droplets are present if the hydration radius *Rh* of counterion < 3.0 Å, and cylinder shape droplets are present if *Rh* >3.0 Å because the *Rh* will affect the interaction

between counterion and hydrated SO3 - group as some authors stated [12]. The *Rh*s of Na+, K+, Mg2+ and Ca2+ are 1.6Å, 1.1Å, 3.1Å and 2.7Å respectively [11]. As Table 2-1 shows, Mg(AOT)2, Ca(AOT)2 and KAOT systems all have a structure transition when they switch from the waterless binary systems to ternary systems with water since all the hydration radius of counterion increases with addition of water. As Figure 2-3 shows, the Mg (AOT) 2 system containing water has a stronger interaction than waterless system. However the KAOT system has reverse behavior and its intrinsic viscosity also decreases with addition of water. The shape fluctuation may also make contribution to interaction. The results of DLS experiments provide some explanations. At constant volume fraction, the surfactant content decreases slowly and water content increase sharply, and the droplet size increases with water content except KAOT systems, shown in Figure 2-14 – Figure 2-16. The swelling of the droplets increases the possibility of penetration of solvent or overlapping of surfactant tails, leading to a stronger interaction and higher viscosity. But when the swelling grows to some degree, the droplets merge into larger droplets. This merging will decrease the amount of droplets and their interaction surface area, leading to the decrease of the viscosity. In low volume fraction KAOT systems, the droplet size does not change too much with water content. It shows K+ has very low hydration capacity. The large droplet can be stabilized only in high volume fraction KAOT systems. It suggests that the bicontinuous structures exit in high water content systems, especially in KAOT and Mg(AOT)2 systems.

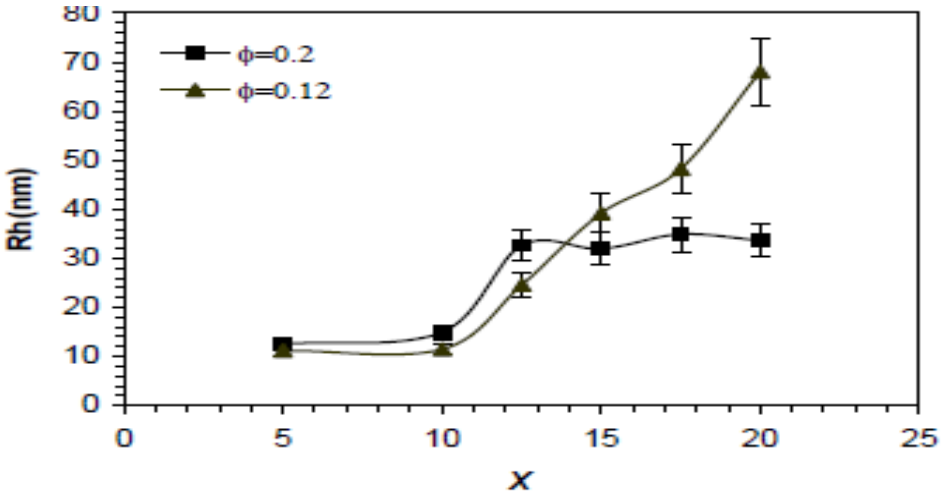


Figure 2-14. Average hydrodynamic radius of Ca(AOT)2/water/decane microemulsion droplets. Lines are guides for the eye

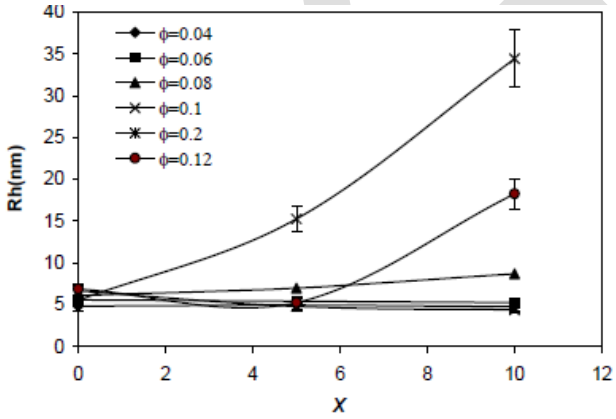


Figure 2-15. Average hydrodynamic radius of KAOT/water/decane microemulsion droplets. Lines are guides for the eye.

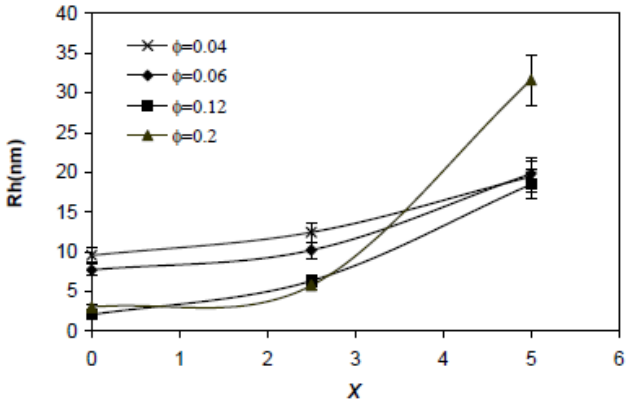


Figure 2-16. Average hydrodynamic radius of Mg(AOT)2/water/decane microemulsion droplets. Lines are guides for the eye.

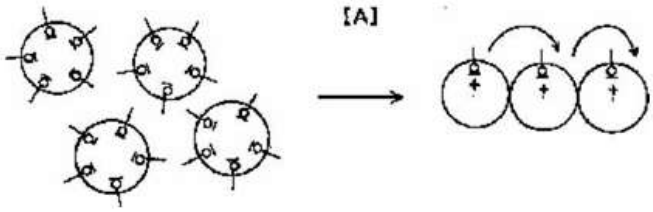
These results suggest that the hydration capability of the counterion plays an important role in the droplet size and the viscosity behavior. In the series we have examined, Mg2+ has the strongest hydration capability and K+ has the weakest hydration capability. So water content has more obvious effects on the droplet sizes of Ca(AOT)2 and Mg(AOT)2 systems.

Effects of Temperature

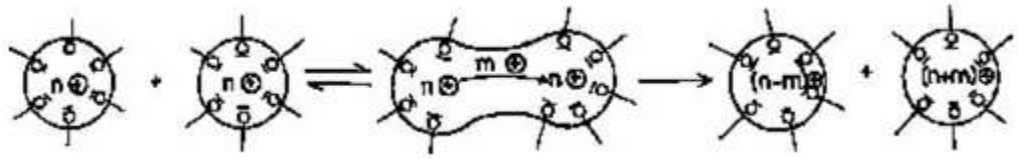
The three kinds of systems in this work have different sensitivities to temperature. KAOT and Ca(AOT)2 systems are more sensitive than Mg(AOT)2. Compared with the insensitivity of M(AOT)2/water/cyclohexane to temperature and the less sensitivity of NaAOT/water/cyclohexane to temperature [10], this shows that the sensitivity may partially arise from the long chain of n-decane that can penetrate into the tails of AOT

Effects of Ion Hydration and Mobility

We have compared the viscosity behavior of NaAOT, KAOT, Ca(AOT)2, and MgAOT)2 with each other, and discussed the effects of ion charge, hydrodynamic ion radius, water and volume fraction on the viscosity, and tried to use charge fluctuation model to explain the viscosity anomalies. The charge fluctuation model suggested a possible origin of viscosity anomaly. At present, there are two existing mechanisms to describe charge fluctuations in micro emulsion [2] (Figure 1-7). One mechanism is hopping, indicating surfactant ions hop from one droplet to another one. The other one is that ions transport by fusion and fission. The asymmetric shape of droplets or deviation from spherical shape may also affect the viscosity, which is indicated by the intrinsic viscosity.



Random dispersion cfiarg* transfer restricted bv tne distant of separation **Association augmenting charge transfer by hopping**



Fusion Fission

Transfer of Ions Nat transfer of

Figure 2-17. [A]. Hopping mechanism. Ions hop in the direction indicated by the curl heads. [B]. Ion transport by fusion and fission. *n* cations in the droplets. *m* cations are involved in the transfer process. (Source: Ref [2])

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CONCLUSION

The bio-oil could be considered as an emulsion system since it contains water and organic compounds, so there are a lot of hydrous micro domains and anhydrous micro domains. Most of the chemicals listed in Table 1 are unstable. The functional groups are very reactive and can cause various polymerization reactions in two kinds of micro domains. So in the future work, while investigate the removal of acids and chars, we propose to investigate the reaction mechanisms existing in the bio-oil with concerns of cationic, anionic, radical polymerization and cross-link reaction, and then find cost- effective polymerization inhibitors.

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