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Role of conformation and orientation of surfactants and polymers in controlling flocculation and dispersion of aqueous and non-aqueous suspensions

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Abstract

Flocculation and dispersion of both aqueous and non-aqueous suspensions using surfactants and polymers have widespread applications. In this work, the role of adsorbed layer microstructural properties, namely their conformation and orientation at the solid–liquid interface, in controlling dispersion properties is examined. A multi-pronged approach, involving the use of fluorescence and ESR techniques along with measurements of surface charge and hydrophobicity, was used to explore the structure of the adsorbed layer.

The adsorption isotherm of sodium dodecylsulfate on alumina in aqueous solution interface showed different regions corresponding to different adsorption mechanisms. The suspension stability also displayed significant changes concomitant with changes in the structure of the adsorbed layer. When polymers are used their conformation can be manipulated by changing solution conditions such as pH and/or by the addition of a secondary polymer or surfactant. Such manipulation can be used to obtain desired levels of flocculation or stabilization.

In non-aqueous media, adsorption was found to depend on the solid–solvent–solute interactions as expressed by an effective interaction parameter δ_{eff}. The suspension stability was dependent on the amount adsorbed and the packing of molecules in the adsorbed layer. The presence of even trace polar impurities was found to have a critical effect on the suspension stability. For example, trace amounts of water were found to cause a significant enhancement of stabilization of alumina–cyclohexane suspension in the presence of adsorbed surfactant layers. However, at higher concentrations water induced rapid flocculation in these systems. Hydrophobic polymers were found to be effective stabilizers for alumina in both aqueous and non-aqueous media. In this case the polymer adsorbed at the interface in different orientations with the lyophilic side chains dangling into the solution to provide steric repulsion and thus stabilization. © 1998 Elsevier Science B.V.

Keywords: Aqueous; Dispersion; ESR; Fluorescence; Hydrophobic polymer; Non-aqueous

1. Introduction

Stabilization and flocculation of colloidal suspensions by the addition of surfactants and polymers are gaining increasing attention in both industrial and academic fields because of its vital role in a wide spectrum of areas such as water treatment, mineral processing, cosmetics and pharmaceutics, and microbial interactions and adhesions [1–3]. The stability of these suspensions is controlled by several forces besides the electrostatic

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force [4]. Stabilization can also result from steric repulsion or short-range solvation forces [5]. For flocculation of suspensions, bridging by adsorbed polymers is an accepted mechanism that complements charge neutralization.

The stability of dispersions in organic liquids has attracted increased attention due to its application in the processing of high performance ceramics, electronic printing and reprographics [6,7]. While the past literature reports good correlation between zeta potential and suspension stability [8], the theory behind the mechanism of charge development in organic solvents of low dielectric permittivity has been a subject of much controversy. The electrostatic effects are further complicated by the presence of trace amounts of water or other polar impurities that are almost unavoidable in these systems. The choice of stabilizer is quite important and usually an amphipathic molecule with a strong anchoring group and a tail that has a strong affinity for the solution phase is used [9].

Hydrophobically modified polymers have been developed recently to increase viscosity and elasticity of solutions because they undergo interesting intra- and inter-molecular associations [10]. Owing to their unique structure they can be used to modify dispersion properties in both polar and non-polar media.

The stabilization/flocculation provided by the adsorbed layers of surfactants and polymers depends to a large extent on the orientation of these molecules and the microstructure of the adsorbed layer, which contribute to the steric and bridging interactions between the particles [11]. The microstructural evolution of the adsorbed layers has been studied in detail by several workers and correlated with dispersion properties like wettability and hydrophobicity of the particles in aqueous suspensions [12]. Several spectroscopic techniques, like fluorescence, electron spin resonance (ESR), nuclear magnetic resonance and infrared spectroscopy have been used widely to study in situ the changes in the organization of the adsorbed layer [13,14]. In this article, we review some of our work on the correlation between dispersion stability and the orientation/conformation of the adsorbed molecules as evinced by spectroscopic techniques.

2. Experimental

2.1. *Adsorption*

The adsorption density in all cases was estimated by measuring the depletion in the surfactant/polymer concentration after contacting with solids for a fixed amount of time under controlled conditions.

2.2. *Suspension stability*

The stabilities of suspensions have been evaluated in terms of several parameters, such as the rate of descent of the upper interface (settling rate). The CAT-scan technique was used to characterize the structure of the flocs. In addition to the settling rate, the amount of particles settled in a given period was measured in terms of percent weight or volume of the sediment. In some cases, hydrophobicity of the particles was estimated by measuring their flotability.

2.3. *Surface charge*

Surface charge was estimated by measuring electrophoretic mobilities using a Penkem Laser Zee meter.

2.4. *In situ characterization of adsorbed layers*

Advanced spectroscopic techniques such as fluorescence and ESR spectroscopy were used to characterize the adsorbed layer microstructure.

Fluorescence spectroscopy makes use of the changes in the photophysical response of a molecule such as pyrene which is incorporated into the adsorbed layer [15,16]. Valuable information regarding the micropolarity and microviscosity of adsorbed layers can be obtained from these studies. The ratio of the intensity of the peak at 382 nm to that at 374 nm was found to be sensitive to the polarity of the probe environment and is termed the polarity parameter (I_3/I_1). In the case of polymers, the excimer fluorescence of pyrene attached to the polymer chains was used to study the conformation and association of polymers in solution and at the solid–liquid interface [17]. The ratio of I_e/I_m (excimer to monomer intensity) is related to the coiling/stretching of the labeled polymer. In the absence of intermolecular interactions a high value of I_e/I_m can be considered to be the result of a coiled conformation, while a low value is associated with a stretched conformation.

ESR spectroscopy monitors the changes in the spin characteristics of a paramagnetic probe that is incorporated into the system [18]. From the changes in the spectral line shape it is possible to obtain information on the micropolarity and microviscosity of the probe environment through measurements of the hyperfine splitting constant and rotational correlation time respectively [19]. In addition, ESR can also provide information on the orientation of molecules at the solid–liquid interface from their motional characteristics.

3. Results and discussion

3.1. *Alumina/surfactant/water system*

The dispersibility of bare alumina in water is controlled by the electrostatic forces between the particles and is hence dependent on the solution pH. The dispersion properties of alumina can be modified by adsorption of an ionic surfactant such as sodium dodecylsulfate (SDS) on the alumina surface. The adsorption of SDS on alumina has been studied widely, and the isotherm, which consists of four distinct regions, is a classical example of ionic surfactants adsorbing on charged surfaces. Fig. 1 [20] shows the adsorption of SDS on alumina at pH 6.5 under a constant salt concentration of 10^{-1} kmol m^{-3}. In region I, which has a slope of unity under constant ionic strength conditions, adsorption occurs predominantly by electrostatic interactions. In region II a conspicuous increase in adsorption is observed which is attributed to the onset of surfactant aggregation at the surface through lateral interactions between the hydrocarbon chains. This phenomenon is referred to as hemi-micelle or solloid formation [21,22]. Region III shows a decrease in the slope of the isotherm due to the increasing electrostatic hindrance to the surfactant adsorption following interfacial charge reversal, while region IV corresponds to micelle formation in the bulk beyond which no further adsorption occurs. Fig. 1 also shows the changes in hydrophobicity of the alumina particles as measured by the bubble pick-up technique; from these results one can conclude that the maximum in hydrophobicity corresponds to region II, where the molecular assemblies render the surface hydrophobic [23]. The presence of such hydrophobic aggregates on the surface have been confirmed by in situ studies using techniques such as fluorescence, Raman and ESR spectroscopy [12,13,24,25]. Fluorescence studies using pyrene have shown a sharp decrease in micropolarity (I_3/I_1) corresponding to the onset region II as shown in Fig. 2, which also shows the variation in zeta potential of the alumina particles in the various adsorption regions. The decrease in hydrophobicity at higher adsorption densities is speculated to be due to the formation of surfactant bilayers which make the surface hydrophilic.

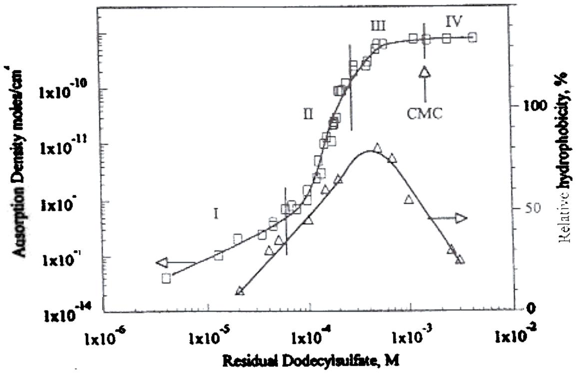

Fig. 1. Change in hydrophobicity of alumina particles as determined by the bubble pick-up technique as a function of dodecylsulfate adsorption.

3.2. *Alumina/polymer/water system*

3.2.1. *Manipulation of polymer conformation through pH shifting*

Flocculation of alumina with polyacrylic acid exhibits marked dependence on the conformation of the adsorbed polymer rather than the electrostatic force. The polyacrylic acid molecules stretch out (I_e/I_m decreases) with increase in pH because of the ionization of carboxyl groups and the resul-

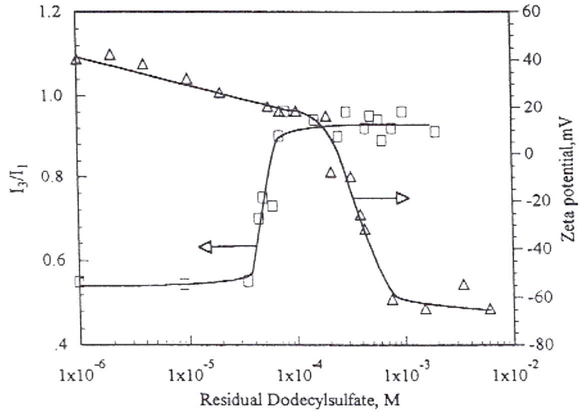

Fig. 2. Diagram illustrating the variation in zeta potential and polarity parameter (I_3/I_1) of the alumina particle surface as a function of dodecylsulfate.

tant electrostatic repulsion between charged groups (Fig. 3). It can be seen that the stretched polymer results in better flocculation in terms of the settling rate, while the effect is opposite in terms of the supernatant clarity. Simultaneous CAT scan studies showed the size of the flocs obtained to be smaller at low pH than at high pH [26].

In order to investigate the effect of on-site conformational changes of adsorbed polymer on flocculation, polyacrylic acid was adsorbed on alumina at pH 4 and pH 10 and the pH was then shifted up and down respectively. As can be seen from Fig. 4 [27], when pH was shifted up, enhanced flocculation was observed in terms of both the settling rate and the supernatant clarity. When pH was shifted down, the flocculation was similar to that observed under fixed pH conditions in terms of settling rate, and a maximum in supernatant clarity occurred at pH 7 which corresponds to the isoelectric point of the polymer-adsorbed alumina. From simultaneous fluorescence studies, it was clear that the coiled polymer, adsorbed on the alumina surface at low pH, stretched out when the pH was raised and caused superior flocculation, while the initially stretched polymer adsorbed at high pH remained in the stretched form even when the pH was lowered.

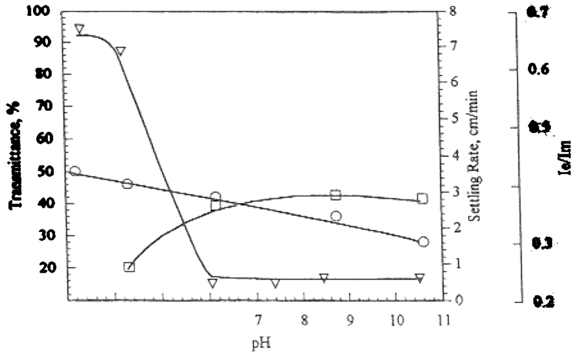

Fig. 3. Flocculation of alumina with 20 ppm polyacrylic acid (▽ I_e/I_m, ○ transmittance, □ settling rate).

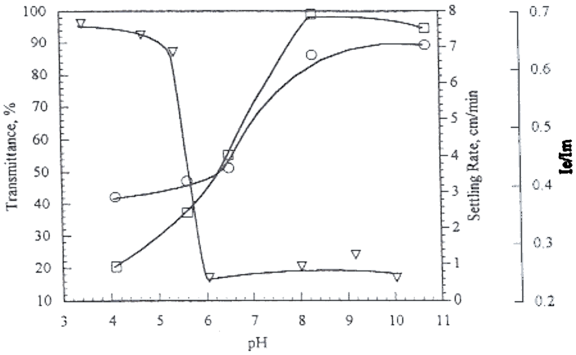

Fig. 4. Flocculation of alumina with polyacrylic acid under changing pH conditions; Initial pH = 4 (▽ I_e/I_m, ○ transmittance, □ settling rate).

A two-stage flocculation mechanism was proposed to explain the superior flocculation obtained with pH up-shift. At low pH, the oppositely charged polymer chains capture all ultrafine particles to form small flocs. When pH was shifted up, the stretched polymer chains bridge the small flocs to form large flocs. With all the fines captured due to charge neutralization, the supernatant obtained is also clearer than that obtained otherwise.

3.2.2. Flocculation with multipolymers

As shown in Fig. 5, a marked difference in flocculation was obtained between the use of individual and dual polymers. It was found that cationic polyacrylamide used in combination with polystyrene sulfonate provided excellent flocculation, though it did not produce any flocculation by itself [28]. Zeta potential results suggested the flocculation not to be controlled by electrostatic forces. Another feature worthy of note in Fig. 5 is

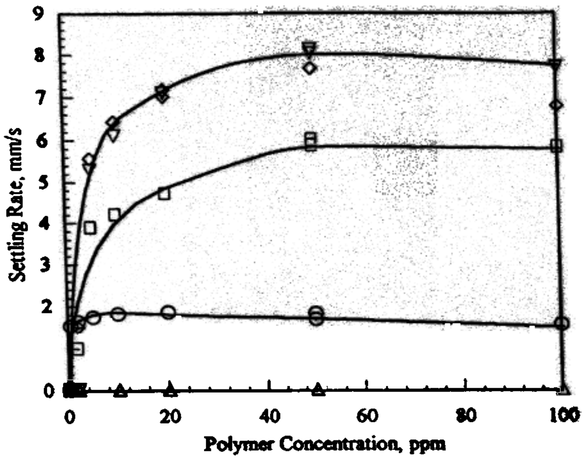

Fig. 5. Flocculation response of alumina suspension with dual polymer systems (□ C-PAM alone, ◇ PSS alone, △ C-PAM after PSS, ▽ PSS after C-PAM).

the marked effect of the mode of polymer addition (sequential or mixture). Adsorption results showed that the presence of polystyrene sulfonate (either in solution or adsorbed at the interface) caused complete adsorption of cationic polyacrylamide which alone did not adsorb on the positively charged alumina particles. Polymer solution viscosity studies suggested that the coadsorption was caused by complexation of the two oppositely charged polymer at the interface and in the solution. The coadsorption of long chain cationic polymer provided better interparticle bridging and thus significant enhancement in flocculation with the use of dual polymer. However, the reason for the drastic effect of the mode of addition remains to be explored.

3.3. *Alumina/surfactant/organic media*

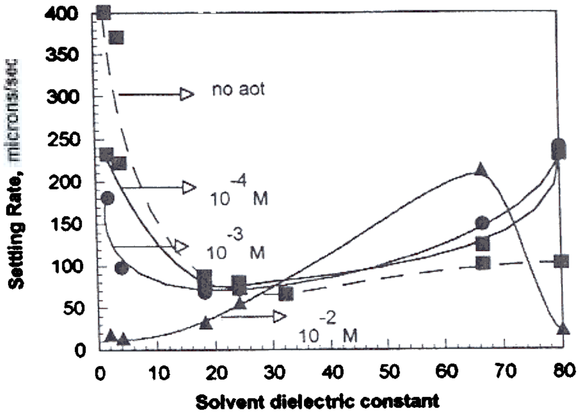

Fig. 6. Settling behavior of alumina as a function of solvent dielectric constant at different levels of AOT.

Fig. 6 shows the settling rates of alumina particles in different liquids at three different levels of surfactant (Aerosol-OT, AOT) addition [29]. It can be seen that the dispersions in the non-polar solvents are stabilized significantly by the presence of the surfactant. The dispersions in the highly polar solvents were also seen to undergo changes in their dispersion behavior. However, dispersions in the moderately polar liquids do not show any change in their dispersion behavior as measured by the settling rate. The adsorption of the surfactant on alumina from different solvents is shown in Fig. 7. It is clear that the adsorption itself is influenced by the solvent polarity with less adsorption from solvents of intermediate polarity. We have found in our earlier work that the adsorption of AOT is less favorable from solvents ($20 < \epsilon < 65$) in which it does not aggregate significantly [30]. This leads to the inference that the changes in dispersion behavior are caused only when a substantial amount of surfactant is adsorbed at the solid–liquid interface. Using interaction parameters δ to characterize the solid–solute–solvent

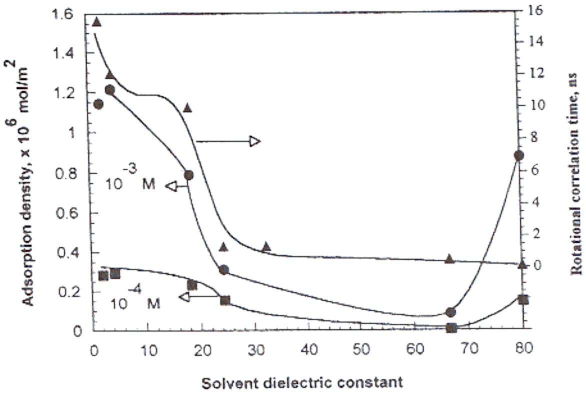

Fig. 7. Adsorption of AOT on alumina as a function of solvent dielectric constant at different initial levels of AOT. Also shown is the variation in rotational correlation time of 7-doxyl stearic acid bound to the alumina surface when treated with a 30 mmol l^{-1} solution of AOT in different solvents.

interactions, we have calculated an effective interaction parameter δ_{eff} as follows [31]:

$$\delta_{\text{eff}} = \text{abs}\left\{ A|\delta_{\text{solid}} - \delta_{\text{solvent}}| + B|\delta_{\text{solute}} - \delta_{\text{solvent}}| - C|\delta_{\text{solid}} \quad \delta_{\text{solute}}| \right\}$$

where A, B and C are numerical constants. δ_{eff} was found to correlate well with the adsorption/desorption of various surfactants on different solids in non-polar media.

In the low dielectric constant solvents AOT adsorbs on alumina with its polar head group interacting with the polar alumina surface and the hydrocarbon tail extending out into the bulk. This makes the surface rather hydrophobic with a concomitant reduction in the Hamaker constant A_{SLS} value for the particles, thereby imparting stability. Fig. 7 also shows the changes in mobility of an ESR probe (7-doxyl stearic acid) bound to the surface when the surface is treated with a concentrated solution of AOT (30 mM) [29]. It can be seen that the probe becomes less mobile due to its incorporation in the adsorbed surfactant layer in the non-polar solvents, suggesting that the adsorbed layer in these cases is more-or-less well packed.

3.3.1. Effect of water on suspension stability

Fig. 8 shows the effect of water on the stability of alumina suspensions which have been dispersed in cyclohexane by the adsorption of a monolayer of AOT [14]. In an extremely dry state the dispersions flocculated rapidly and the addition of trace amounts of water stabilized the suspensions quite significantly. Thereafter the suspensions remained stable over a range of water concentration and then flocculated very rapidly at higher water concentrations. The concentration of water at which the suspension reflocculates correlated well with the solubility of water in the bulk solution. Surface charge measurements made using the electrokinetic sonic amplitude (ESA) system have shown clearly that addition of trace amounts of water can induce a significant amount of charge at the surface. At higher water concentrations there was a slight decrease in the surface charge as measured by the ESA. However, this decrease in surface charge cannot explain fully the massive flocculation observed in this case. From the water adsorption isotherm also shown in Fig. 8 it can be seen that the water adsorption increases sharply close to the onset of flocculation.

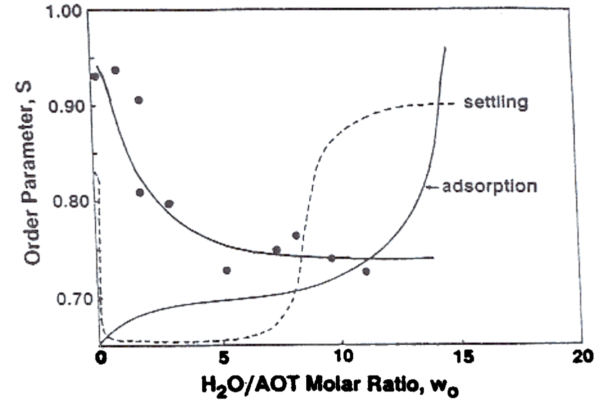

Fig. 8. Diagram illustrating the settling behavior (– – –) of alumina suspensions in cyclohexane as a function of water concentration in the presence of adsorbed AOT. Also shown are the water adsorption density (———) and the order parameter (●) as determined by ESR.

The water-induced flocculation was further investigated by monitoring the spectral response of 7-doxyl stearic acid which is co-adsorbed along with the surfactant. 7-Doxyl stearic acid adsorbed on the alumina surface gave a characteristic anisotropic spectrum which was quantified using the order parameter which can be calculated from the spectral characteristics. The order parameter varies between $S=1$ (highly ordered, restricted) and $S=0$ (highly random and mobile) and reflects the state of the environment in which the probe resides. The order parameter calculated in this case decreases with increase in water concentration and levels off at approximately the water concentration corresponding to that of the onset of flocculation (Fig. 8). These results indicate that there is a significant change in the structure of the adsorbed layer, with the surfactant layer becoming more fluid and mobile as water adsorbs at the interface. This opens up the possibility for the water layers on different particles to penetrate across the surfactant layers and bridge the particles together during collision, thereby causing the massive flocculation observed.

3.4. *Alumina/hydrophobic polymer/aqueous or non-aqueous system [32]*

In addition to the wide use as rheological modifiers, hydrophobically modified polymers find increased application in controlling the stability of suspensions. Fig. 9 shows the effect of DAPRAL addition on the stability of alumina water suspensions along with the zeta potential and the adsorption isotherm (the structure of DAPRAL is shown in the inset). A comparison of the zeta potential data with stability data shows the suspension stability to remain unchanged up to a polymer concentration of 150 ppm, even though the zeta potential of alumina particles did undergo a marked change (from +11 to −50 mV) in this concentration range. Furthermore, the stability of the suspension increased markedly above the DAPRAL concentration of 150 ppm even though there was only a minor change in the zeta potential. It is clear that stabilization cannot be attributed in this case to the electrostatic forces.

Using pyrene fluorescence spectroscopy, hydrophobicity of alumina particles was studied; the results are shown in Fig. 10 as a function of DAPRAL concentration. At a DAPRAL concentration of 5 ppm the I_3/I_1 value begins to increase, from 0.6 (typical value of water solution), approaching a typical value >1 of the hydrocarbon solvents at a DAPRAL concentration of 500 ppm and then remained unchanged. Relative hydrophobicity obtained with two-phase partition showed agreement with the fluorescence results at low DAPRAL concentration, but a decrease in hydrophobicity was found at high concentrations. Continued adsorption even after charge reversal without any change in zeta potential was attributed to such aggregation of DAPRAL on the alumina particles.

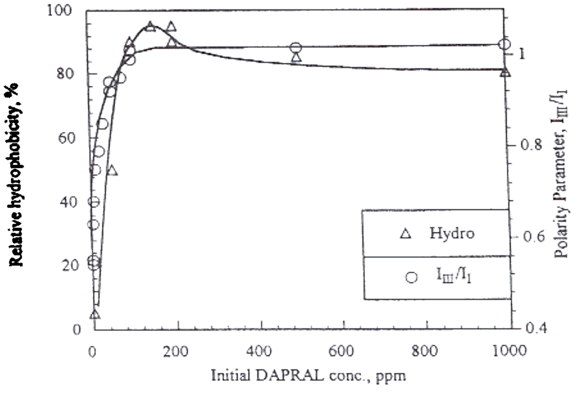

Fig. 9. Changes in surface hydrophobicity and polarity parameter of alumina particles as a function of DAPRAL adsorption.

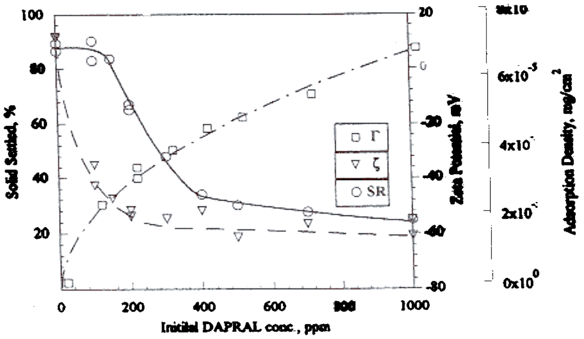

Fig. 10. Adsorption of DAPRAL on alumina and its effect on the stability and zeta potential (pH=8, S/L=2.5%, ▽ zeta potential, □ adsorption, ○ settling rate).

Results obtained for the settling rate of alumina in toluene are shown in Fig. 11 as a function of DAPRAL concentration. In the absence of DAPRAL settling occurs rapidly, since alumina particles tend to form aggregates in apolar solvents and the suspension stability increases markedly with its addition. Adsorption tests showed the polymer to adsorb completely on alumina in the concentration range studied (up to 500 ppm). The wavelength of the emission maximum of 7-dimethyl amino 4-methylcoumarin (coumarin 311) was correlated with the hydrophobicity of its environment, changing from 391 to 471 nm when the solvent is changed from hexane to water. It is seen that, with the increase in polymer concentration, the maximum emission wavelength shifts towards the shorter wavelength range, reaching the value for hydrocarbon solvents (390 nm) at 500 ppm of DAPRAL. This observation supports the mechanism proposed earlier for polymer adsorption in toluene. The shift of the emission maximum correlated well with the suspension stability, both undergoing significant

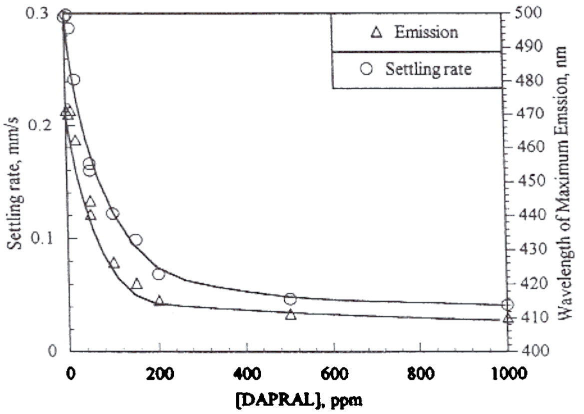

Fig. 11. Effect of DAPRAL on the stability and hydrophobicity of alumina in toluene.

changes when the polymer concentration is below 200 ppm and leveling off at higher concentrations.

The dispersion behavior of alumina suspensions in the presence of DAPRAL can be explained as follows. In aqueous media, at low polymer concentrations such interactions can permit formation of aggregates of polymer-"coated" alumina particles in spite of the electrostatic repulsion. At higher polymer concentrations, the possibility for interactions between adsorbed polymer molecules with those in the bulk solution increases. Such interactions can cause formation of bilayers with hydrophilic side chains dangling into the solution, as suggested by the observed decrease in the hydrophobicity. In non-aqueous media, DAPRAL adsorbs on the alumina surface with the hydrocarbon side chains stretched out into solution to provide steric repulsion.

4. Concluding remarks

The role of adsorbed layer microstructure on the dispersion properties of suspensions in aqueous and non-aqueous media is seen to be prominent. Using advanced spectroscopic techniques we have correlated the nature of the adsorbed layer to the stabilization/flocculation behavior. In aqueous systems the surfactant adsorption generates hydrophobic patches at relatively low surface coverages and imparts sufficient hydophobicity to the particles. However, in organic liquids, where such surface aggregation is not observed, higher surface coverages are required to obtain sufficient hydrophobicity. In non-polar media, stability can also be affected by the presence of trace polar impurities, such as water, that can induce ionization in the adsorbed layer.

The flocculation efficiency of polyelectrolytes is dependent critically on their conformational state at the interface, as this governs their ability to capture other particles in the "bridging" process. The conformation itself can be controlled by adjusting solution conditions during the adsorption and flocculation processes. Sequential addition of polymers improved the flocculation efficiency considerably, possibly due to formation of complexes at the interface that provide better bridging conditions.

Hydrophobically modified polymers such as DAPRAL, due to their unique structure, can adsorb at interfaces with different orientations, depending upon the properties of both the substrates and the media. In water the hydrocarbon side chains of DAPRAL molecules on an alumina surface cause either hydrophobic or steric interactions, depending on the polymer concentration. In the alumina–toluene system the stabilization of the suspensions is achieved by the steric hindrance provided by lyophilic side chains.

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