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The Colloidal Stability of Spectrally Sensitized 3-D AgClI Emulsions

Sridhar Sadasivan, Lloyd A. Lobo, Eric C. Wollman,† Seshadri Jagannathan, and Jerzy Budz▲

Eastman Kodak Company, Rochester, New York

The colloidal stability of silver halide emulsions precipitated in aqueous gelatin media is predominantly electro-steric in nature and is provided by gelatin adsorbed on the silver halide grains. It is believed that gelatin provides adequate colloidal stability for spectrally sensitized silver halide emulsions, where the sensitizing dyes compete with gelatin for the silver halide surface. We have examined the details of the interaction of gelatin with unsensitized and sensitized 3-D AgClI emulsions by evaluating the interfacial potential of the emulsions and their colloidal stability as a function of pH and ionic strength. The interfacial potential of the emulsions has been determined using electrokinetic sonic amplitude (ESA) measurements and the colloidal stability of the emulsions was studied using filterability measurements. The unsensitized and sensitized emulsions do not show any appreciable differences in their electrokinetic properties, while they do exhibit differences in their filterability properties upon pH cycling. It is surmised that gelatin is more easily desorbed from the surface of sensitized emulsions than unsensitized emulsions upon pH cycling, leading to aggregation. Hence, we conclude that the weaker adsorption of gelatin on silver halide emulsions is the root cause of the diminished colloidal stability of spectrally sensitized silver halide emulsions. The results suggest that sensitized silver halide emulsions are more prone to destabilization due to process variations than unsensitized silver halide emulsions.

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Introduction

Silver halide emulsions used in photographic applications derive their colloidal stability from gelatin. The colloidal stability provided by gelatin is electrosteric in nature; i.e., gelatin chemisorbed on the surface of silver halide grain provides steric barrier to aggregation. The magnitude of this steric barrier is affected by the pH and ionic strength of the emulsion. The pH and ionic strength dependence of the steric barrier has two root causes; (1) the pH and ionic strength dependence of the conformational properties of gelatin and (2) the pH dependence of the surface coverage of the silver halide emulsions by gelatin.

Examination of the literature on the colloidal properties of the unsensitized silver halide/gelatin system, provides the following information:[1]

- The surface coverage of silver halide emulsions by gelatin is at its maximum near the isoelectric point of gelatin (pH ≈ 4.8) and decrease on either side of the isoelectric point.
- The maximum adsorption near the isoelectric point is attributed to the more compact conformational structure of gelatin. The conformational structure of gelatin is believed to have a symmetric profile around the isoelectric point of gelatin; most compact near the isoelectric point and extended at pH values away (higher or lower) from the isoelectric point.
- The surface coverage is not symmetrical around the isoelectric point; i.e., the amount of gelatin adsorbed is much lower below the isoelectric point than above the isoelectric point.
- This observed asymmetry in surface coverage around the isoelectric point is attributed to a monotonic decrease in the adsorption strength of gelatin with increasing acidity.

From a colloidal stability (of silver halide emulsions) point of view, it is important to determine if the aggregation propensity has a symmetric or an asymmetric profile, with respect to the isoelectric point. A symmetric profile would indicate that gelatin conformation could be the primary factor responsible for stability towards aggregation, while an asymmetric profile would suggest that surface coverage of gelatin might be more important.

In this article, we summarize the results from our investigation of this subject, using unsensitized and sensitized 3-D silver chloro-iodide (AgClI) emulsions as test candidates, and electrophoresis and filterability as analytical tools.

Electrophoresis provides a measure of the interfacial potential of colloidal dispersions. Because the interfacial potential of silver halide emulsions in the presence of gelatin is primarily due to the adsorbed gelatin, electrophoresis provides a convenient way to examine the properties of adsorbed gelatin. The filterability of an emulsion through a well-characterized membrane provides information on the extent of aggregation in the emulsion, which, in turn, relates to the colloidal stabil-

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▲ IS&T Member

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ity of the emulsion. These two measurements carried out in tandem, as a function of appropriate experimental variables, provide valuable insight into the origin of colloidal stability/instability of silver halide emulsions.

Electrophoresis

Electrophoretic experiments are generally carried out by applying a static electric field between two electrodes introduced into a colloidal dispersion and measuring the rate of movement of the colloidal particles towards one of the electrodes.[2] The experimentally measured mobility μ, is related to a potential ζ, which is proportional to the interfacial potential ψ, on the particles. ζ potential is a measure of the potential difference between the plane of shear somewhere in the double layer and the bulk of the liquid.

The equations relating ζ or ψ and μ are derived in the limit of thick or thin double layers, which may be calculated from the inverse Debye length, κ^{-1}, expressed in meters, which is defined by the following equation:

$$\kappa = \left(\left(\frac{1000\, e^2\, N_A}{\varepsilon K_B T} \right) \sum_i z_i^2 M_i \right)^{1/2} \tag{1}$$

where e is the charge of an electron in Coulomb, N_A is the Avagadro's number in mol^{-1}, ε is the dielectric constant of the medium in F/m, K_B is the Boltzmann constant in J/K, T is the temperature in K, z is the valence of the electrolyte and M is the molar concentration of the ions in mol/m^3. For a 1:1 electrolyte, the summation becomes 2I, where I is the ionic strength.

For systems with a thick double layer ($\kappa R << 1$), where R is the hydrodynamic radius of the colloidal particle in m, the electrophoretic mobility and the ζ potential expressed in V, are related by the following equation:

$$\mu = \frac{2\varepsilon\zeta}{3\eta} \tag{2}$$

where η is the medium viscosity in Pa-s, μ is the electrophoretic mobility in m^2/V–s and ε is the dielectric constant of the medium in F/m.

For systems with thin double layers ($\kappa R >> 1$), the electrophoretic mobility and ζ potential are related by the following equation:

$$\mu = \frac{\varepsilon\zeta}{\eta} \tag{3}$$

These two scenarios represent the limiting cases. Most experimental systems fall in between the two and can be represented in an approximate form:

$$\zeta = \frac{3\eta\mu}{2\varepsilon f(\kappa R)} \tag{4}$$

where $f(\kappa R)$ is the dimensionless Henry's function. For systems with $\kappa R << 1$, the function becomes unity and for systems with $\kappa R >> 1$, it becomes 3/2. For examining relative trends in ζ potential, the assumptions used to calculate ζ potential may be avoided by comparing the experimentally determined mobility (μ) of the particle, recognizing that it is proportional to the ζ potential, as shown in Eq. 4.

An alternative approach to measure interfacial potential is to apply a high frequency alternating electric field between two electrodes and monitor the oscillation of the colloidal particles in the AC field. The magnitude and the phase shift (from the oscillating frequency) of the particle oscillation can be related to the particle size and surface charge. The particle oscillation may be conveniently measured by the pressure (sound) wave generated because of the density difference between the particles and the medium. This is the basis of the electrokinetic sonic amplitude (ESA) measurement.[3]

The electrophoretic mobility of particles obtained from ESA measurements is related to the frequency of the applied electric field and is known as the dynamic mobility. For a colloidal dispersion of known solids volume fraction ϕ, the dynamic mobility $\mu_\delta(\omega)$ expressed in m^2/V–s is related to the ESA signal S in Pa–m/V by the following equation:

$$\mu_d(\omega) = \frac{S\gamma}{c\,\phi\,\Delta\rho} \tag{5}$$

where γ is the instrument constant, which is dimensionless, c is the speed of the sound in the continuous phase in m/s, $\Delta\rho$ is the difference in density between the particle and the surrounding medium in kg/m^3. The instrument constant can be obtained by calibrating the instrument with a colloidal dispersion of known mobility, concentration, and density. Typically, colloidal silica (Ludox-TM in 0.01 M KNO_3) is used.[4] This equation assumes a linear relationship between the ESA signal and the volume fraction of the particles in the dispersion. This is true in the limit of low volume fractions. The onset of non-linearity varies from system to system, but can be measured. The signal is linear for colloidal silica up to 5% (v/v).

When a high-frequency electric field is applied to a charged colloidal dispersion, the particles oscillate with respect to the field. Depending upon the size and charge of a given particle and the frequency of the field, either the particle may oscillate in resonance with the field or may lag behind, due to inertial effects. For small particles and low frequencies, inertial effects are insignificant. However, the inertial effects have to be accounted for in the case of large particles or larger frequencies when converting dynamic mobility ($\mu_d(\omega)$) to the static mobility μ.[5] Typically, for systems with thin double layers, such as the system in this work, this inertial correction is expressed as a ratio of dynamic mobility to static electrophoretic mobility according to the following equation[6]:

$$\frac{\mu_d(\omega)}{\mu(0)} = \frac{1 - i\alpha\left(3 + 2\left[\frac{\Delta\rho}{\rho}\right]\right)}{9\left(1 + (1-i)\left[\frac{\alpha}{2}\right]^{1/2}\right)} \tag{6}$$

where $\alpha = \omega R^2/\nu$, R is the particle radius, and ν is the kinematic viscosity (η/ρ, where η and ρ are the viscosity and density, respectively, of the continuous phase).

In any case, it is clear from the discussion above that the dynamic mobility measured by ESA is proportional to the static mobility measured by conventional electrophoretic techniques, which, in turn, is proportional to the ζ potential of the particles in a colloidal dispersion. Because we are interested in understanding the relative trends in the ζ potential as a function of experimental variables such as pH and ionic strength, the dynamic mobility $\mu_\delta(\omega)$ will be used as the experimental measure of interfacial potential.

Filterability

The extent of aggregation in an emulsion can be determined from the filtration characteristics of the emulsion by using a filter medium with a pore diameter that is much larger than the particle size distribution of the emulsion grains. The rate of change in filtration rate through such a medium is a measure of the extent of plugging of the filter medium. Because the pore diameter of the filter medium is much larger than the particle size distribution of the emulsion, a colloidally stable emulsion will not exhibit a measurable change in the filtration rate. However, a colloidally unstable emulsion containing aggregates will plug the filter medium to varying extent during the filtration process and will exhibit a measurable decrease in filtration rate.

The standard blocking (SB) model provides a formal description of how the change in the filtration rate of material passing through a filter may be used to understand the mechanism of plugging of the filter medium.[7] In this model, the inverse flux of material passing through the filter (time/weight or t/W) is plotted against the time (t) as material passes through the filter medium. In such a plot, decrease in the filtration rate with time would manifest as an increase in slope.

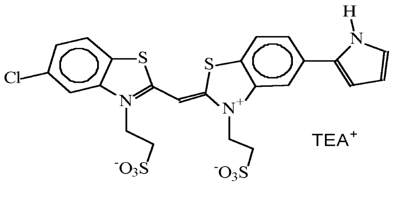
$$\frac{t}{W}=\frac{t}{K}+\frac{1}{q_0} \tag{7}$$

where q_0 is the initial rate of filtration and K is defined as Standard Blocking Index (S. B. Index), which is the reciprocal of the slope. This index, which has dimensions of mass is a qualitative measure of the extent of plugging of the filter medium; i.e., the smaller the value of the index, greater the extent of plugging. Hence, the relative trends in the S. B. index of an emulsion as a function of experimental variables, such as pH and ionic strength, is an experimental measure of extent of aggregation of the emulsion; i.e., a measure of the colloidal stability of the emulsion.

Experimental

Materials

3-D cubic silver chloro-iodide (AgClI) emulsions, with a cubic edge length of 0.64 μm, with 4.02% (v/v) silver as AgClI and 7.7% (w/w) lime processed ossein gelatin were used in this study.[8] The emulsions were deionized with MB-150 "Amberlite" mixed-bed ion-exchange resin. The ion exchange process reduced the conductivity of the emulsion below 100 μS/cm. The pH of the ion-exchanged emulsion was ~4.9. No morphological changes were observed in the SEM pictures of the emulsion samples before and after the deionization process. The pH of the deionized emulsion was adjusted using 1 N HNO_3 and 1 N NaOH. The ionic strength was varied by the addition KNO_3, and the pCl of the emulsion was varied using KCl. Spectral sensitization was simulated by adding 0.6×10^{-3} moles of blue sensitizing dye as shown below, to 1 mole of the AgClI emulsion.[9]



Conductivity

The conductivity of the emulsions was measured with an Orion model 125 conductivity probe. The probe was calibrated with a 1040 μS/cm KCl standard.

pH and pCl

The pH and pCl of the emulsions were measured by potentiometry, using an apparatus similar to the one described by Shiao and co-workers.[10] pCl and pH were measured after the ESA experiments were performed on the samples.

ESA

The ESA measurements were performed on the emulsion samples using an MBS-8000 MATEC ESA System controlled by MATEC STESA software in single-point mode. The experiment was performed with a SP-80 probe with a gold cap. The experimental apparatus and procedure are described in detail elsewhere.[11] All the experiments were performed at 40°C. The instrument was calibrated with a 5% (v/v) Ludox-TM in 0.01 M KNO_3.

Filterability

The filtration test unit consists of a temperature controlled, pressurizable 3L reservoir with a 47 mm diameter filter holder connected to the bottom outlet. The filter holder is loaded with a 47 mm diameter disk of the chosen filter medium. A fiberglass medium of average pore diameter 3 to 5 μm was used. The reservoir was filled with 300 grams of the emulsion maintained at 40°C. The top was capped and the unit was pressurized to 1.5 psig by a pressure regulator. The filtrate was collected in a beaker on an electronic balance. The output from the balance was fed into a computer with a software program that collects cumulative filtrate weight as a function of time. The collected data has been analyzed using the Standard Blocking Model.[6]

Results and Discussion

Effect of pH

ESA experiments were performed on AgClI emulsions containing 4.85% (w/v) gelatin. Figure 1 shows the change in electrokinetic sonic amplitude (ESA) of emulsions as a function of volume fraction (ϕ) of the particles. The ESA value varies linearly with volume fraction. The region of linear behavior extends to $\phi \sim 0.04$. The ESA values of gelatin solution are within the range of experimental noise. Because the density difference between the gelatin and water is negligible, we do not see any appreciable signal due to free gelatin in the solution.

Figure 2 shows the variation in the dynamic mobility of these emulsions with pH. The dynamic mobility of the emulsions becomes zero around the isoelectric point of the gelatin (pH ~ 4.9). Above the isoelectric point, the negative dynamic mobility indicates the particles have a net negative interfacial potential. The higher the negative value, the higher is the net potential on the particle and vice versa. Below the isoelectric point, the positive mobility indicates that the particles have a net positive interfacial potential.

The parameter that is relevant to the discussion in this report is the magnitude of the mobility, as a function of pH. The magnitude of the mobility in Fig. 2 clearly shows the asymmetry in interfacial potential around the isoelectric point of the gelatin; i.e., the mobility values are higher above the isoelectric point of the gelatin than below the isoelectric point of gelatin. As pointed out earlier, the acid/base titration behavior

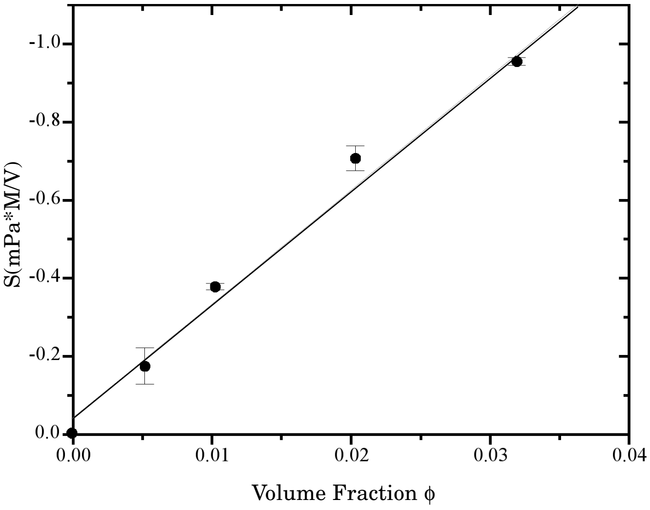


Figure 1. Dynamic mobility versus volume fraction of gelatin stabilized AgClI emulsion with 4.85% (w/v) gelatin at pH 5.6.

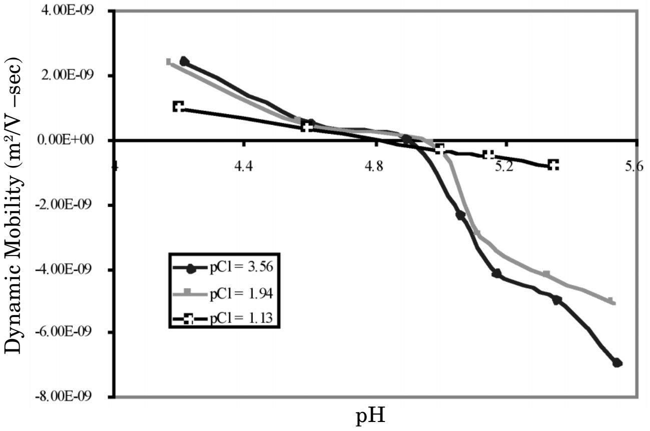


Figure 2. Variation of dynamic mobility of gelatin stabilized AgClI emulsions with pH for 2.09 % (v/v) AgClI emulsion stabilized with 4.85% (w/v) gelatin.

of gelatin reported in the literature,[12] indicate that there is no inherent anisotropy in the charge of gelatin around the isoelectric point. This is shown in Fig. 3, where the variation of net charge on the gelatin molecule (~ MW 10^5) is plotted as a function of pH. The net charge is symmetric around the isoelectric point between pH values 4 to 6. Hence, it is verified that there exists an anisotropy in the adsorption of gelatin on AgClI emulsions around the isolectric point of gelatin, as indicated in the literature.[13]

Effect of [KCl] and [KNO_3]

Addition of KCl to the silver chloride changes the surface [Cl^-] (on the AgClI emulsion) and the ionic strength, while addition of KNO_3 changes only the ionic strength of the medium. Literature data suggests that the interfacial potential of gelatin stabilized emulsions is not very sensitive to pCl and its insensitivity to pCl is attributed to adsorbed gelatin being the dominant contributor to the interfacial potential of such (gelatin stabilized) emulsions.[14]

However, we find that the magnitude of the mobility of 3-D AgClI emulsions decreases with decreasing pCl, across the entire range of pH. This trend is shown in Fig. 4, which is a plot of the data obtained from ESA measurements. We believe that the interfacial potential of gelatin stabilized 3-D AgClI emulsions are not perturbed significantly by change in pCl. However, the change in ionic strength that occur concurrently with the change in pCl is significant and will alter the interfacial potential, which is manifested as a change in the mobility of the emulsion.

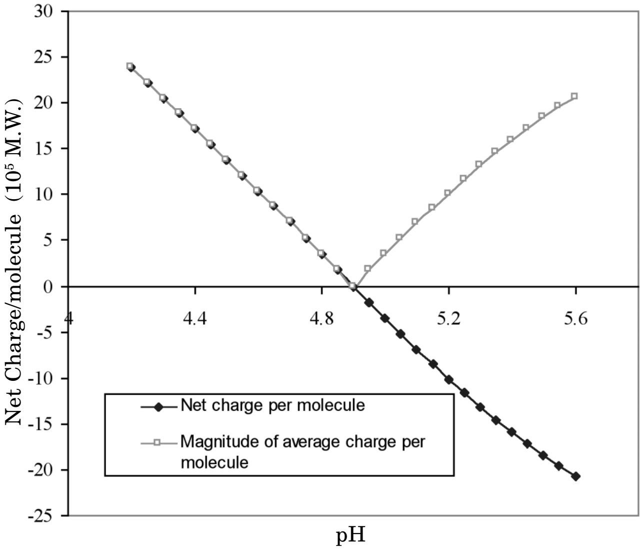


Figure 3. Net molecular charge for alkali pretreated bone gelatin. The closed diamonds indicate the net molecular charge, while the open squares indicate the absolute net charge for a gelatin molecule with ~ 10^5 molecular weight.[12]

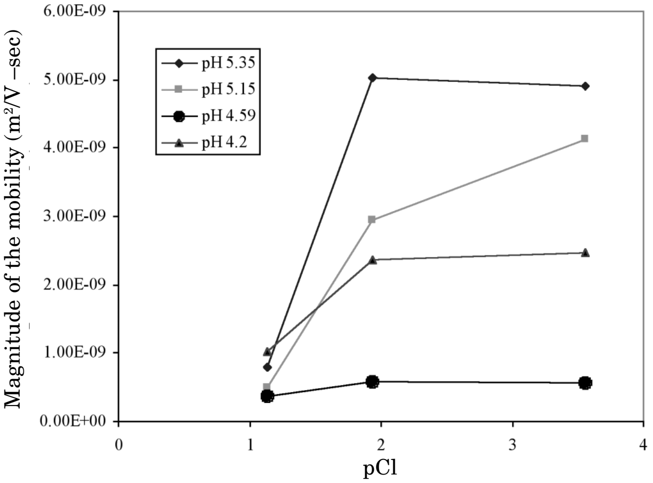


Figure 4. Magnitude of the mobility versus pCl at different pH values for 2.9% (v/v) AgClI emulsion with 4.85% (w/v) gelatin.

To verify that the effect of pCl is due to variations in ionic strength, the mobility of emulsions were also measured as a function of [KNO_3], which is shown in Fig. 5. The trend in Fig. 5 is the same as the trend in Fig. 4 and this is illustrated in Fig. 6, which combines the data shown in Figs. 4 and 5, at pH 5.5. The effect of [KCl] in reducing the dynamic mobility magnitude of the particle is very similar to that of [KNO_3]. Addition of either salt affects the mobility in a similar manner; i.e., by

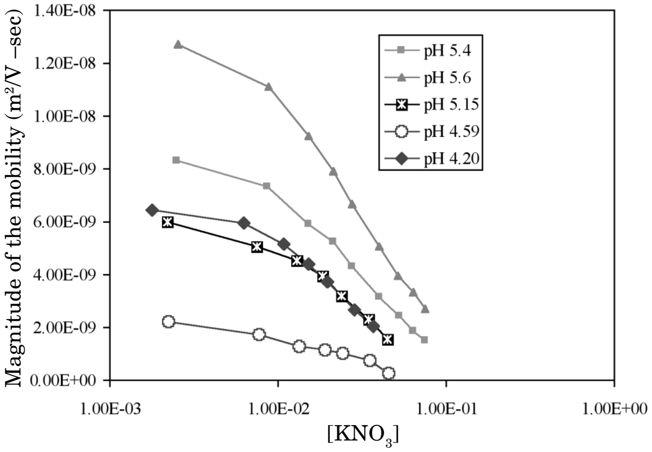


Figure 5. Magnitude of the mobility versus [KNO_3] at different pH values for 4.2%(v/v) AgClI emulsion with 5.58% (w/v) gelatin.

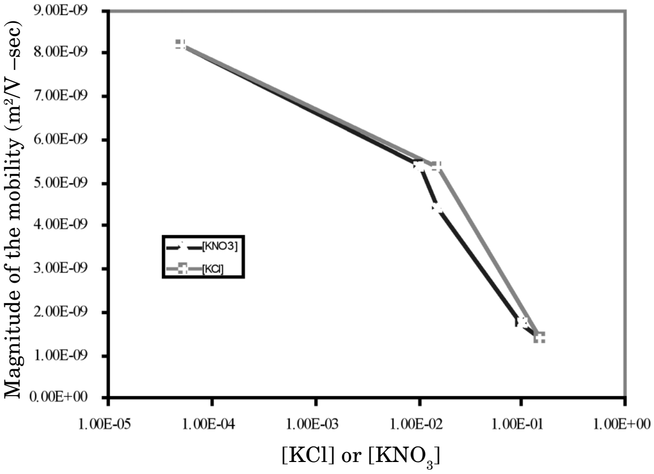


Figure 6. Magnitude of the mobility versus [KCl] or [KNO_3] at pH 5.5 for 2. 9% (v/v) AgClI emulsion with 4.85% (w/v) gelatin.

increasing the ionic strength of the emulsion and screening the interactions between the charged emulsion grains and leading to a reduction in the interfacial potential. This is true far away from isoelectric point of gelatin. Near the isoelectric point of gelatin, where the measured ESA signal is low, we do not observe significant changes in mobility with ionic strength.

By normalizing the mobility value of an emulsion at any pH with the magnitude of the mobility value obtained for the deionized and unsensitized emulsion at that particular pH, it is possible to plot the normalized mobility of all the emulsions as a function of measured conductivity of the emulsions in a single plot as shown in Fig. 7. The conductivity is a measure of the ionic strength of the medium. A good exponential fit verifies that the mobility and hence the interfacial potential decreases exponentially with increasing ionic strength, as would be expected from the theory,[15] even though the theory represents the interfacial potential of a planar charged surface. From a practical point of view, this empirical relationship could be used to estimate the relative mobility of an emulsion just by measuring its pH and conductivity values.

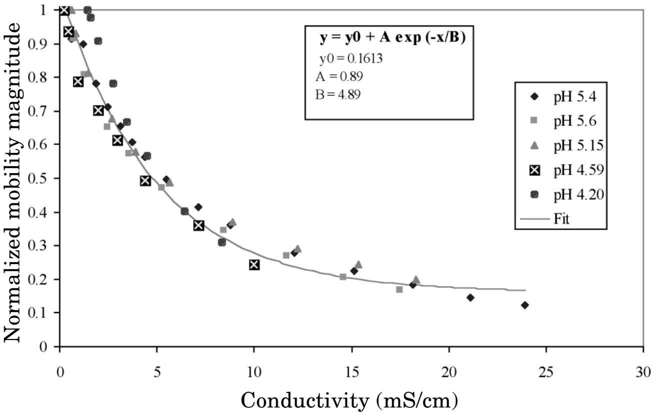


Figure 7. Experimental and estimated normalized mobility values as a function of conductivity at different pH values. The magnitude of the mobility has been normalized with the magnitude of the mobility of the deionized emulsion at different pH values.

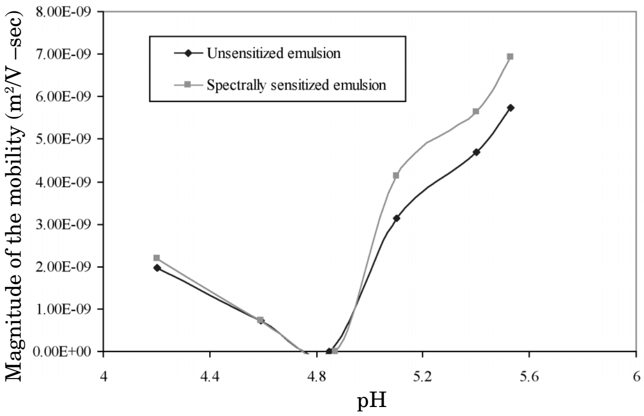


Figure 8. Magnitude of the mobility versus pH for 4.2% (v/v) AgClI emulsion with 5.58% (w/v) gelatin, with spectral sensitizer.

Effect of Spectral Sensitization

We examined the dynamic mobility of spectrally sensitized emulsions, in order to understand the role of the spectral sensitizer on the colloidal stability of the emulsions. The magnitude of the mobility of the spectrally sensitized emulsions as a function of pH is shown in Fig. 8. It was found that the addition of spectral sensitizer induces a measurable increase in the mobility of emulsions in the region above the isoelectric point of gelatin.

The spectral sensitizer is expected to be intimately adsorbed on the surface of the emulsion (a requirement for photographic performance). If the spectral sensitizer displaces gelatin from the surface of the emulsion to a significant extent, mobility of the emulsion would be expected to decrease. However, the data indicates an increase in mobility suggesting that little or no gelatin is displaced from the emulsion surface.

The important point to be noted is that the dynamic mobility measurements by ESA indicate that the mobility values of the sensitized emulsions are **not** less than the mobility values of the unsensitized emulsions. This suggests that the concentration of adsorbed gelatin on the spectrally sensitized emulsion is probably similar to the concentration of adsorbed gelatin on the

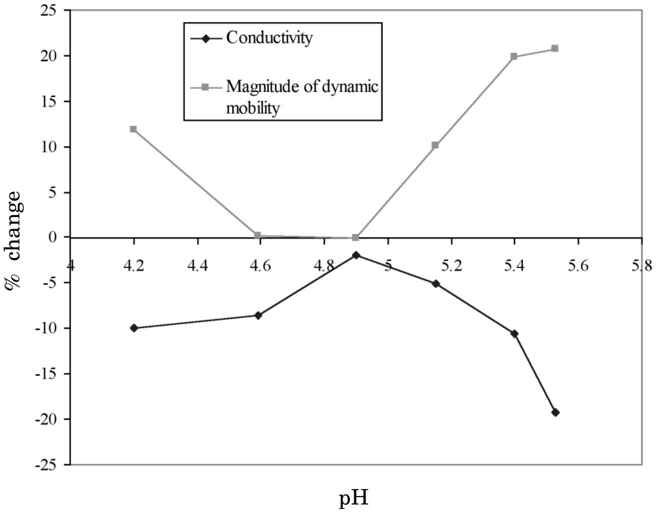


Figure 9. Change in conductivity observed upon addition of spectral sensitizer to the unsensitized emulsion as a function of pH.

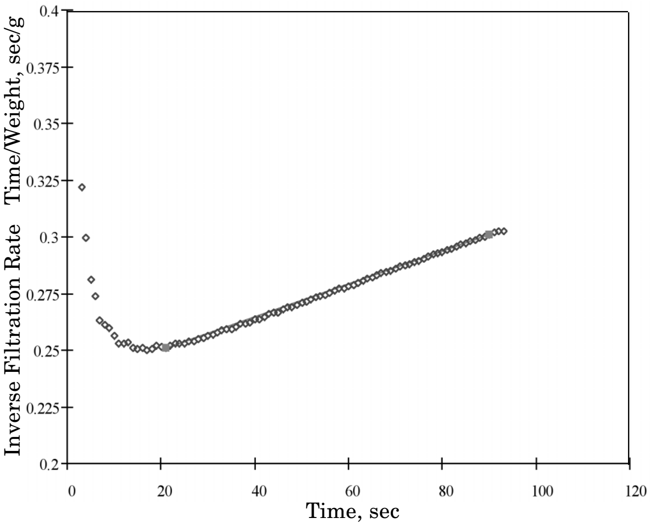


Figure 10. Raw data converted to inverse filtration flux as material flows through the filter.

unsensitized emulsion. This result has two important consequences.

The first consequence is that, differences in colloidal stability of unsensitized and spectrally sensitized emulsions are **not** attributable to differences in the concentration of adsorbed gelatin on the emulsion. The second consequence is that the interaction of gelatin with the surface of spectrally sensitized emulsions is likely to be different from (and possibly weaker than) the interaction of gelatin with the surface of unsensitized emulsions.

In all the experiments reported here, the concentration of gelatin in the emulsion is ca., 5%, which is sufficient to induce saturation coverage of the emulsion surface. The quantity of spectral sensitizer added to the emulsion during the sensitization process is also sufficient to induce near saturation coverage. Because the spectral sensitizer and gelatin cannot simultaneously occupy the same location on the AgClI surface, it is suggested that only one of the species (spectral sensitizer or gelatin) is in intimate contact with the AgClI surface; i.e., one of the species may be adsorbed on the on the top of the other—a layered structure.

Because the spectral sensitization by the spectral sensitizer is an indication that it is in intimate contact with the AgClI surface,[9] it is surmised that gelatin may be adsorbed on the top of the adsorbed spectral sensitizer; i.e., gelatin interacts with the spectral sensitizer adsorbed on the surface of the emulsion (and not directly with the silver halide surface of the emulsion). As a result, the interaction of gelatin with the surface of the spectrally sensitized 3-D AgClI emulsion is expected to be different from (and weaker than) the interaction of gelatin with the unsensitized 3-D AgClI emulsion. Hence, gelatin may be expected to be displaced from the surface of spectrally sensitized emulsion more easily than from the surface of unsensitized emulsions, leading to a decrease in colloidal stability.

An interesting behavior is seen in the conductivity data as well, which is shown in Fig. 9. The conductivity of the emulsion decreases in the region where an increase in the mobility of the emulsion is observed. It is interesting the relative difference in conductivity between the sensitized and unsensitized emulsion and the relative difference in the mobility between the sensitized and unsensitized emulsions are similar in magnitudes. We postulate that the adsorbed spectral sensitizer that is associated with gelatin also limits the mobility of Cl^- ions that contribute to the ionic strength of the emulsion, thus decreasing the conductivity of the emulsion, which, in turn, manifests as increase in mobility of the spectrally sensitized emulsions.

Colloidal Stability of Sensitized and Unsensitized Emulsions

The aggregation propensity of AgClI emulsions has been observed to be influenced by the sequential addition of acid and base solutions to the emulsions. The aggregation propensity of silver halide emulsions is easily measured by monitoring the filtration performance of the emulsions.[16] Increase in aggregation propensity manifests as a decrease in filtration performance.

We carried out a series of experiments where sensitized and unsensitized emulsions were subjected to such an acid and base addition process and evaluated for the filtration performance. The first two sets of experiments were base line experiments where filtration performance of the emulsions was evaluated without being subjected to the acid and base addition process. In the next two sets of experiments the unsensitized and spectrally sensitized emulsions were subjected to the sequential acid and base addition process. The raw data collected from the filtration experiments was analyzed using the Standard Blocking Model (Fig. 10).

In the first set of experiments, the conductivity of the unsensitized emulsion was adjusted to 10 mS/cm at 40°C by adding KNO_3, the pH to the desired value, the emulsion held at 40°C for 30 min and evaluated for its filtration performance. The second set of experiments consisted of adding 50 g of 0.3% spectral sensitizer solution to 250 g of unsensitized emulsion maintained at a conductivity of 10 mS/cm at 40°C, adjustment of emulsion pH to the desired value, held at 40°C for 30 min and evaluated for its filtration performance.

In the third set of experiments, the conductivity of an unsensitized emulsion was adjusted to 10 mS/cm at 40°C, the pH of which was then lowered to 4.2, increased to 5.6, then lowered to 5.0, where it was held at 40°C for 30 min, and evaluated for its filtration performance. In the

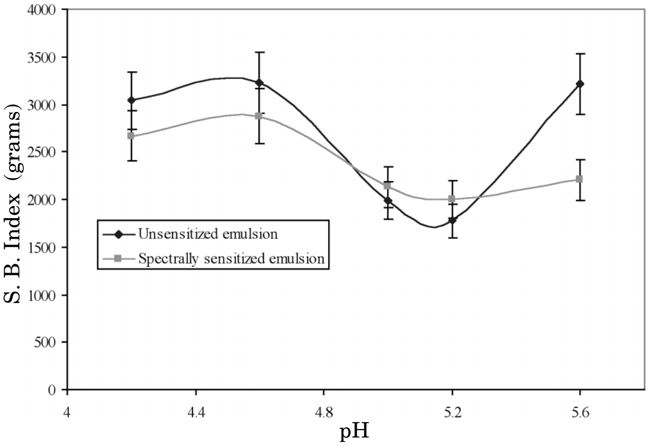


Figure 11. S.B. Index values for spectrally sensitized and unsensitized emulsions as a function of pH.

fourth set of experiments, 50 g of 0.3% spectral sensitizer solution was added to 250 g of an unsensitized emulsion maintained at a conductivity of 10 mS/cm at 40°C. The pH of the emulsion was then cycled similar as in the third set of experiments, the emulsion held at 40°C for 30 min, and evaluated for its filtration performance.

The unsensitized emulsions and the spectrally sensitized emulsions from experiments 1 and 2 (not subjected to the acid and base addition process) have index values ranging between 2000 to 3000 grams over the entire range of pH, as shown in Fig. 11, indicating that these emulsions have low aggregation propensity.

The unsensitized emulsion after it was subjected to the acid and base addition process (third set of experiments) shows a high S. B. index value of 1000 grams, indicating good colloidal stability. However, the spectrally sensitized emulsion that was subjected to the same pH cycling, showed remarkably lower S. B. index value of 200 grams; indicating a greater propensity for aggregation than the rest of the unsensitized and sensitized emulsions; indicating significantly reduced colloidal stability. We suggest that the acid and base addition process displaces gelatin more easily from the spectrally sensitized emulsions than from the unsensitized emulsions, leading to a greater propensity for aggregation. This supports our earlier stated hypothesis that the interaction of gelatin with spectrally sensitized emulsion is weaker than the interaction of gelatin with unsensitized emulsions and hence can be displaced more easily.

Conclusions

We have examined the colloidal stability of 3-D AgClI emulsions as a function of pH, ionic strength, and a spectral sensitizer. The unsensitized emulsions show no appreciable change in colloidal stability over the range of pH and ionic strength or the process of pH cycling. However, the spectrally sensitized emulsions show a dramatic change in colloidal stability when subjected to the process of pH cycling. This decrease in colloidal instability of the spectrally sensitized emulsions upon pH cycling is attributed to weaker interactions of gelatin with the surface of the sensitized emulsion; thus allowing for easier displacement of gelatin from the emulsion surface and promoting aggregation.

The surface concentration of gelatin in both the unsensitized and the spectrally sensitized emulsions is similar and is not the root cause for the observed colloidal instability upon pH cycling. The results suggest that sensitized silver halide emulsions are more prone to destabilization because of process variations than unsensitized silver halide emulsions. A similar scenario may also be observed with any sensitizing chemical that strongly interacts with the silver halide emulsion surfaces and changes the nature of gelatin adsorption.

We have established an empirical relationship between the normalized mobility of these emulsions (and hence their interfacial potential) and their conductivity at various pH values. As a result, measurement of pH and conductivity will allow for the estimation of the normalized interfacial potential of gelatin stabilized silver halide emulsions in general and hence, colloidal stability.

This work also indicates that ESA technique can be used to probe the charge behavior of polyampholytes. The polyampholytes have very low density and their charge behavior cannot be studied directly using ESA measurements. By adsorbing them on to a surface of colloidal particle, their charge behavior can be studied.

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