



Influence of Light Scattering by Residual Alumina Nanoparticles on the Analysis of Surfactants Adsorption Using Spectroscopy

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Abstract. The adsorption of a surfactant mixture, based on an anionic surfactant, sodium dodecyl benzenesulfonate (SDBS) and a nonionic surfactant (Triton X-100, or TX100), on alumina nanoparticles was determined by solution depletion method combined with spectrometric measurement. It is shown that the light scattering, originated from the residual adsorbent alumina particles in the supernatant after centrifugation separation, interferes with the measurements of absorbance of the surfactant molecules, and therefore constitutes an error source for determination of the surfactant concentration in the supernatant by spectrometric means. The intensity of this light scattering, namely the influence of the residual alumina nanoparticles upon the surfactant adsorption, was related to the surfactant adsorption and its equilibrium concentration and varied among a batch. In this paper we report a Kalman filter method in order to eliminate the variational scattering background caused by non-separated residual alumina nanoparticles in each supernatant. This method is of interest as it is simple, easy to carry out and of high precision.

Keywords: adsorption, light scattering, surfactant mixture, Kalman filter

Introduction

Adsorption of surfactants at solid-liquid interfaces plays a crucial role in many industrial applications including detergents, enhanced oil recovery, surface wetting modification, emulsification, corrosion inhibition, foaming control, dispersion of solids, surfactant-based separation processes and flotation. In practical applications, a mixture of surface active homologues are used rather than isomerically pure surfactants, since the latter are more expensive to produce and generally have only a small potential advantage in performance over the surfactant mixture. In processes such as enhance

oil recovery, however, surfactant adsorption on reservoir minerals has to be avoided, since it contributes to undesirable reagent loss. Mixed surfactant systems offer several advantages over single component since the adsorption of surfactants on reservoir minerals can be controlled using appropriate composition and solution conditions. Hence, studies on adsorption behavior of surfactant mixture has increased significantly in the recent past (Somasundaran and Huang, 2000; Rao and Forssberg, 1997; Huang et al., 1996; Esumi et al., 2001; Somasundaran and Krishnakumar, 1997).

The adsorption isotherm is the very first and significant parameter of adsorption studies because the shape of the adsorption isotherm not only provides a quantitative relationship between the adsorbed amount

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and equilibrium concentration of adsorbate, but also reflects the manner in which the adsorbate molecules are adsorbed on the surface of the adsorbent. For the measurement of adsorption isotherm, solution depletion method is frequently employed. In the depletion method, the residual concentrations of adsorbate in the equilibrium suspension were determined based on its analytical characteristic. Various analytical techniques have been employed. If the adsorbate has absorbance in UV-Vis region, spectrometric method may be the simplest and convenient analytical technique. It is worthy note that the light scattering by absorbent particles interferes seriously the measurement of the absorbance of the adsorbate. Usually, the interfere of this kind of light scattering is assumed to eliminate by mean of separation of the adsorbent. In most of the works related to spectrometric measurements, centrifugation separation was employed and the influence of light scattering of adsorbent particles was ignored. But this assumption is challenged in the adsorption of surfactants on ultrafine particles especially for nanoparticles. It is well known that the dispersion of fine particle can be enhanced by the adsorption of surfactant molecules (Sharma, 1995; Bremmell et al., 1999). In the presence of surfactant, it may be difficult to separate all the well dispersed fine particles especially for nanoparticles by centrifugation method. In another word, a slight light scattering may exist in the clear supernatants even after centrifugation separation. To our knowledge, few literatures concerned the influence of residual light scattering of clear supernatant on the determination of adsorption amounts.

The purpose of this work was to identify and deal with the influence of residual light scattering on spectrometric measurement in adsorption experiments. Anionic surfactant, sodium dodecyl benzenesulfonate (SDBS), and nonionic surfactant, Triton X-100 (TX100) were used as adsorbate because they have absorbance peaks in UV region. Alumina nanoparticles was chosen as it is one of the most common used model adsorbents (Colic et al., 1998; Sakagama et al., 2002; Nagashima and Blum, 2001; Wang and Kwak, 1999; Otsuka and Esumi, 1994; Esumi, 2000; Evanko, 1996; Bajpai, 2000). A Kalman filter method is employed to analyze the spectra of supernatants. The influence of residual light scattering by alumina nanoparticles on the adsorption amount were investigated. The influence of residual light scattering is corrected. And the residual concentrations of SDBS and TX100 in the supernatant were simultaneously determined.

Experimental

Alumina particle was purchased from Union Carbide. It was specified to be 90% α -Al₂O₃, and γ -Al₂O₃. The diameter of the particles is about 30 nm. The BET area (nitrogen adsorption) was $180 \pm 30 \text{ m}^2 \cdot \text{g}^{-1}$. Analytical-reagent grade chemicals and Mini-Q water were used. Nonionic surfactant Triton X100 (TX100), an octylbenzene ethoxylate mixture, average number of ethoxy segment 9.5 (Rohm and Haas), was used as received. In all calculations the molecular mass used for TX100 is 624. Anionic surfactant, sodium dodecyl benzenesulfonate (SDBS) was purchased from Sigma Chemical Co. and used without further purification. The concentration of SDBS in the stock solution was determined by the colloid titration using hexadecyl trimethyl ammonium bromide as the titrant and potassium tetrabromophenol-phtalein ethyl ester as the indicator.

A series of surfactants solutions, including SDBS, TX100 and their mixtures at varying ratios, were prepared using acetate buffer (0.1 mol/L NaAc + 0.05 mol/L HAc, pH5). 50 ml of each the solution was added to a capped glass vial, which contained 0.1 g of alumina. The vials were shaken for 24 h for equilibrium, and the vial samples were then subjected to centrifugation. The centrifugation was fixed to 1 h at 1×10^4 rpm, except otherwise stated. Absorption spectra of the sample solution were recorded every 1 nm in the range 202–320 nm on a spectrophotometer (Lambda 35, Perkin-Elmer Instrument). Acetate buffer was employed as the blank sample except where specified. The equilibrium concentrations of both TX100 and SDBS were simultaneously determined based on the absorbance data using the Kalman filter method. For the purpose of comparison and verification, the concentration of SDBS was also determined by the colloid titration method. All the experiments were performed at $25 \pm 1^\circ\text{C}$. For each experiment 3 parallel samples were prepared and subjected to the tests, only the averaged values are reported here.

Results and Discussion

Influence of Light Scattering on the Determination of Adsorption Amount

In the estimation of the adsorption amount in a solution depletion method, the residual concentration of the

adsorbate in the supernatant after adsorption is first determined, the adsorption amount of the adsorbate, Γ , is calculated by

$$\Gamma = \frac{(C_0 - C_{eq})V}{WS} \quad (1)$$

where C_0 and C_{eq} are the initial and residual concentration of the adsorbate; V the volume of adsorbate solution; and W and S the weight and specific area of the adsorbent, respectively.

In the adsorption experiments for surfactants on solid particles, various analytical techniques have been employed to determine the residual concentration of the surfactants according to their analytical characteristics. If a surfactant has absorbance in UV-V is region, spectrometric method may be the simplest and convenient analytical technique for its concentration determination. In the present work, the adsorption of SDBS and TX100 on alumina particles was investigated. The concentrations of SDBS and TX100 were analyzed by spectrometric measurement as they have UV absorbance in the wavelength region of 200–300 nm.

As a preliminary step for the measurements, the adsorption isotherms of SDBS on alumina particle from single SDBS solution were determined by UV spectrometric method and the colloid titration method, respectively. In the spectrometric method, the absorbance at a fixed wavelength of 223 nm was measured with acetated buffer used as the reference. As can be seen from Fig. 1, the two isotherms are slightly shifted. The residual concentrations of SDBS in the spectrometric method are a little higher than those in the colloid titration one in most of the studied area. As the same supernatants were used in the two analytical methods, the reason for the deviation was investigated.

In a separated experiment, the SDBS concentration in a group of pure SDBS solutions was determined by the two methods. A good agreement was obtained between the two analytical methods. Hence, the deviations in adsorption isotherms were not acceptable within measurement errors. The disagreement indicates that an interfere was ignored in one of the methods. The most possible interfere factor is the light scattering by residual alumina particles in the supernatant for absorbance measurements.

To confirm this influence, a sample containing 0.1000 mmol/L SDBS and 1 mg/L alumina were analyzed again by the two methods. The concentration of SDBS in the sample was determined to be 0.0994 ± 0.0042 mmol/L in the colloid titration method, and 0.1076 ± 0.0092 mmol/L in the spectrometric method,

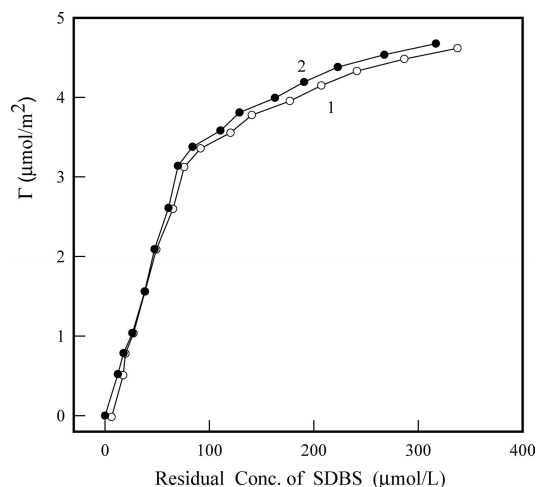


Figure 1. Comparison of the adsorption isotherms of single SDBS on alumina particles obtained by different methods. (1) direct spectrometric method at wavelength of 223 nm; (2) colloid titration method. pH = 5, 0.1 g alumina nanoparticle was shaken for 24 h in 50 ml SDBS solution for equilibrium then centrifugation at 1×10^4 rpm for 1 h.

respectively. As expected, the spectrometric method provides a slightly higher estimation for SDBS concentration in the presence of residual alumina particle. The reason is that a small part of the incident light is scattered by the alumina particles dispersed in solution phase. The scattering effect will decrease the intensity of the transmission light to the detector and thus results in an apparent increase in the absorbance, which gives a higher estimation for concentration of SDBS, especially in low concentration region.

As shown by curve 1 in Fig. 2, the influence of light scatter arising from residual particles on the adsorption amount of TX100 on alumina was very seriously. Because the adsorption of nonionic surfactants on alumina surface is weak (Lawrence, 1987), the decrease in the absorbance due to the adsorption of TX-100 is small. As mentioned above, the scattering of residual alumina particles in the supernatants results in an increase in absorbance. Obviously, the scattering effect offsets the absorbance decrease by adsorption. When the absorbance increase arising from residual particles scattering is greater than the absorbance decreases by adsorption, the absorbance of the supernatant is higher after the adsorption. According to absorbance data, the concentrations of TX100 in the supernatants are even greater than their initial values. Thus, a false “negative” adsorption amounts were given in such situation.

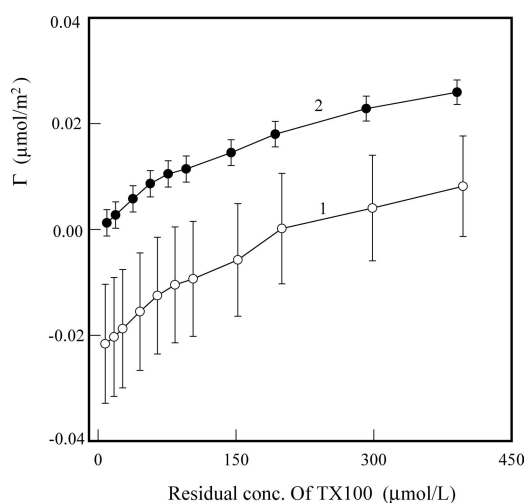


Figure 2. Influence of light scattering from residual alumina particles on the estimation of adsorption amount for TX100 on alumina. (1) direct spectrometric method at wavelength of 222 nm; (2) after correction for the light scattering by Kalman filter method. pH = 5, 0.1 g alumina nanoparticle was shaken for 24 h in 50 ml TX100 solution for equilibrium then centrifugation at 1×10^4 rpm for 1 h.

This result shows that the light scattering from residual alumina particle is a potential error resource in adsorption amount measurements, especially for the system of weak adsorption.

Decrease Light Scattering by Centrifugation Separation

As discussed above, spectrometric method suffers from the interference of light scattering by residual particles dispersed in solution phase. Hence, the residual particles in supernatants should be removed as completely as possible. A simple and efficient centrifugation method is extensively used in solution depletion method, especially for spectrometric measurements. The separation efficiency for alumina particle as function of the applied centrifugation time is tested. It is clearly shown in Fig. 4 that, as expected, the light scattering intensity reflected by the absorbance at 320 nm, decreased with increasing centrifugation time for all the tested systems regardless of the surfactant used in alumina adsorption. After centrifugation at 1×10^4 rpm for 30 min, clear supernatants were obtained. It is also interesting to note that the light scattering of the residual alumina particles is still measurable even after a centrifugation time of 2 h. It may be difficult or even impossible to achieve a complete separation of the

adsorbent particles from the supernatant by a simple centrifugation. That is to say, the influence of light scattering due to the remaining adsorbent particles on spectrometric measurements will indeed exist.

From Fig. 4, it is also seen that the longer the centrifugation time is, the less important the residual alumina nanoparticles in the supernatant. For all results reported in this study, the centrifugation was fixed to 1 h at 1×10^4 rpm, except otherwise stated. In addition, the light scattering intensity is related to the concentration of surfactants. It is easy to understand, because the interface properties of alumina particles varies significantly after surfactant adsorption.

On the other hand, the scattering intensity is stable in a supernatant but varies among the supernatants in the same batch. Figure 4 shows the error bars for the scattering intensity of alumina nanoparticles in acetate buffer. For the consideration of conciseness of the figure, the error bars for scattering intensity in surfactant systems were not plotted out, which are similar to those in curve 3. In general, the relative variations in scattering intensity were ranged of 30–50%. The variational light scattering intensity makes it difficult to correct the influence of residual particles by the common used blank reference in spectrometric method. In the present work, a chemometric method, Kalman filter was employed to eliminate the scattering effect and determinate simultaneously the concentration of SDBS and TX100 in the supernatants of mixed surfactants.

Kalman Filter Method Description

As shown in Fig. 3, the absorption spectra of SDBS and TX100 are markedly overlapped at certain wavelengths. In cases where the alumina nanoparticles are not completely separated, the scattering spectrum of residual alumina nanoparticles as a background overlaps their spectra. High errors would be expected if the conventional univariate regression method was used. The calibration and then prediction of multicomponent systems are of the most important research areas in chemometrics (Yu, 1992; Liang and Yu, 2000). One of the simplest methods investigated in this field was Kalman filter. The Kalman filter method was developed as a digital filter for processing complex data in electrical engineering applications (Kalman, 1960). In recent years the technique has increasingly been applied to the solution of a number of problems in analytical chemistry including multicomponent curve resolution,

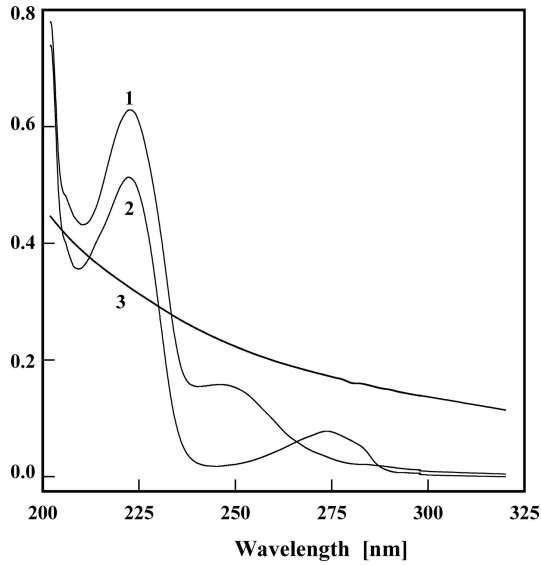


Figure 3. UV-absorbance spectrum of SDBS and TX-100 and scattering spectrum of alumina particle. (1) 60 $\mu\text{mol/L}$ SDBS; (2) 60 $\mu\text{mol/L}$ TX100; (3) 0.1 g alumina particle equilibrium with 50 ml buffer and stand for 3 h.

removal of variable background responses, calibration with drift correction and estimation of kinetic parameters (Andrew, 1999; Ye et al., 1998; Hassan et al., 1999; Navarro-Villoslada et al., 1995).

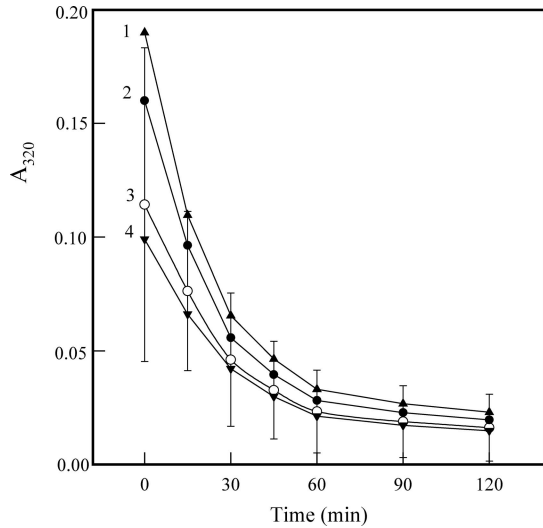


Figure 4. Dependence of light scattering intensity of residual alumina particles (stand for 3 h) on centrifugation time at 1×10^4 rpm. (1) 20 mg alumina equilibrium with 10 ml 1.5 mmol/L SDBS + 1.0 mmol/L TX100; (2) 20 mg alumina equilibrium with 10 ml 1.5 mmol/L SDBS; (3) 20 mg alumina equilibrium with 10 ml buffer. (4) 20 mg alumina equilibrium with 10 ml 1.0 mmol/L TX100.

The Kalman filter is a recursive technique in which one data point is processed at a time with the previous best estimate of the parameter of interest being used to calculate an updated estimate as each new data point is obtained. A Kalman filter relies on two models, one describing the dynamic system and the other expressing the measurement process. For multicomponent spectrophotometry, based on the Beer's Law, the system model can be formulated as:

$$\mathbf{A}(k) = \mathbf{S}(k)^T \mathbf{C}(k) + \mathbf{E}(k) \quad (2)$$

where $\mathbf{A}(k)$ is the vector of the absorbance of the supernatant; $\mathbf{S}(k)$ the vector consisting of the absorptivities of the components involved, $\mathbf{E}(k)$ the measurement noise, at wavelength λ_k , respectively. And $\mathbf{C}(k)$ is the vector of concentrations of the components in the supernatants.

In the present work, two surfactants are involved in the adsorption, and the light scattering was considered as the third component to be measured. In the Kalman filter treatment, the Mole absorption coefficients of SDBS and TX100 in the wavelengths used were first obtained from their absorbance spectra in a group standard solutions. The scattering spectrum of alumina nanoparticles in Fig. 3 was used the absorptivities. This treatment is acceptable as relative concentration of residual alumina, or relative scattering intensity is concerned here.

When the absorbance of the supernatant at k th wavelength λ_k , $\mathbf{A}(k)$, was measured, the concentration of the three components were updated by:

$$\mathbf{K}(k) = \mathbf{P}(k)\mathbf{S}(k)[\mathbf{S}^T(k-1)\mathbf{P}(k-1)\mathbf{S}(k-1) + \mathbf{E}(k)]^{-1} \quad (3)$$

$$\mathbf{C}(k) = \mathbf{C}(k-1) + \mathbf{K}(k)[\mathbf{A}(k) - \mathbf{S}^T(k)\mathbf{C}(k-1)] \quad (4)$$

$$\mathbf{P}(k) = [\mathbf{I} - \mathbf{K}(k)\mathbf{S}^T(k)]\mathbf{P}(k-1)[\mathbf{I} - \mathbf{K}(k)\mathbf{S}^T(k)]^T + \mathbf{K}(k)\mathbf{E}(k)\mathbf{K}^T(k) \quad (5)$$

here \mathbf{K} is the Kalman gain, \mathbf{P} the error covariance, respectively.

The filter is initiated with $\mathbf{C}(0) = 0$, $\mathbf{E} = 10^{-6}$, and $\mathbf{P}(0) = \mathbf{I}$, where \mathbf{I} is the identity matrix. When new data were added, a group of new concentrations are obtained. After sufficient wavelength used, the concentrations of the components involved converges to their true values. The calculation was done with a software named Matlab 6.0. The validity of the Kalman filter method was repeatedly tested in a set of

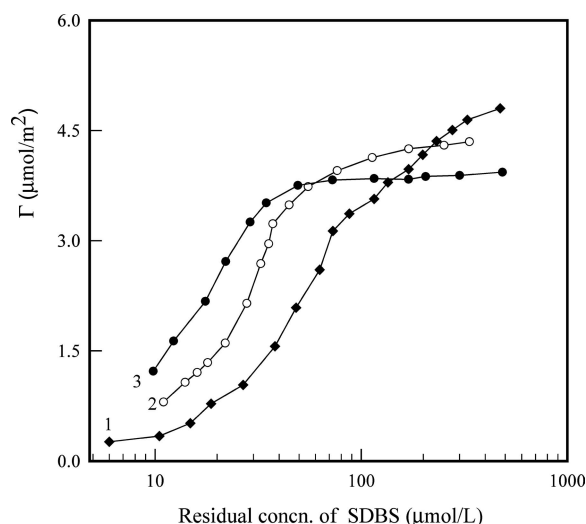


Figure 5. Adsorption amount of SDBS on alumina particles. (1) adsorption of SDBS from single solution; (2) adsorption of SDBS from mixed solution of SDBS and TX100 at feed molar ratio of 8:2; (3) adsorption of SDBS from mixed solution of SDBS and TX100 at feed molar ratio of 6:4. The adsorption conditions were the same as that in Fig. 1.

known mixtures of SDBS and TX100 without alumina nanoparticles. Very good agreement was obtained between the experimental and calculated concentrations from Kalman filter method. For the adsorption isotherm in Fig. 1, the residual concentrations of SDBS determined by the Kalman filter method agree well with those obtained by the colloid titration method. The data was presented in Fig. 5 rather than Fig. 1 because they were very close to curve 2 in Fig. 1. As presented in Fig. 2, the previous “negative” adsorption amounts in curve 1 are corrected by the Kalman filter treatment. As the scattering influence was efficiently eliminated, the small adsorption amount can be measurable. And the measurement precision are significantly improved.

It is to note that in order for us being able to use Kalman filter to determine SDBS and TX100 concentrations in a supernatant with precision, the content of residual alumina nanoparticles has to be low enough, so that the measurement can be processed. This is easy to understand that a too high concentration of alumina would suppress the absorbance signals of the surfactants, or even no transmittance is detectable in a turbid liquid with high alumina content. For example, a turbid liquid was obtained for alumina dispersed in pure water. Therefore a centrifugation is necessary in order to obtain a clear supernatant prior to the subsequent spectrometric analysis. That is to

say that the spectrometric measurement is always done to the supernatant after the centrifugation rather than the starting mixture of the surfactants and the alumina nanoparticles.

Adsorption from Mixture of SDBS and TX100

In the Kalman filter method, the scattering background of the remaining alumina nanoparticles was corrected. The concentrations of SDBS and TX100 were simultaneously determined in the presence of residual adsorbent particles. Figure 5 shows the amounts of SDBS adsorbed from SDBS solutions or the mixtures of SDBS and TX100. It can be seen that the adsorption isotherms of SDBS from single surfactant system has an S-type shape, which is close to the results in references under similar experimental conditions (Somasundaran and Fuerstenau, 1966; Somasundaran et al., 1992). For the adsorption of SDBS with presence of TX100, a synergistic effect was observed at low concentration region, where the adsorption was enhanced. As the feed ratio of TX100 increases, the adsorption isotherms shift toward lower concentration region. The presence of non-ionic surfactant between the sulfonate ion in the adsorbed layer enhances sulfonate adsorption by reducing the lateral electrostatic repulsion between the ionic sulfonate head groups. At higher solutions concentrations, the adsorption amount of SDBS decreases with the increases in the percentage of TX100. This is due to the partition of TX100 in the mixed adsorption.

Figure 6 presents the adsorption amount of TX100 as the function of surfactants. When single surfactant is used, the adsorption of TX100 on the alumina surface is very weak and the adsorption amount is small. In the presence of SDBS, the amounts of TX100 adsorbed increase about two magnitudes. The reason is that the adsorbed anionic sulfonate provides nucleation sites for the adsorption of TX100 through hydrophobic chain-chain interaction interactions at the interface. The high activity of the non-ionic surfactant at the solid/liquid interface is manifested by its higher surface activity in solution as compared to that of the anionic sulfonate (Somasundaran, 2000). As constant feed ratio of two surfactant was used, the adsorption amounts of TX100 in low concentration region were not given in curve 3 due to the limitation of the sensitivity of the spectrometric measurement, where the concentration of SDBS can not be analyzed accurately.

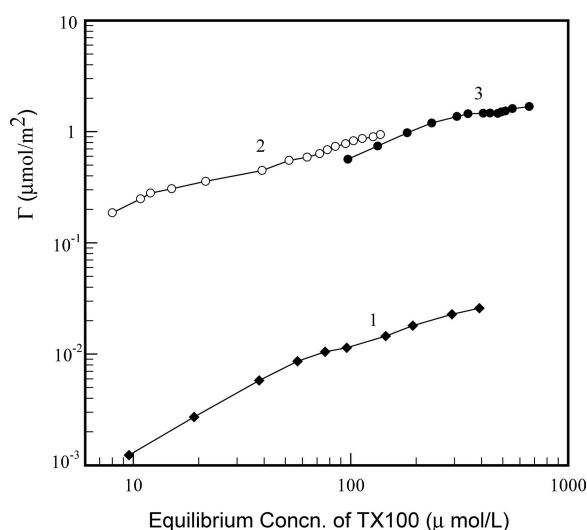


Figure 6. Adsorption amount of TX100 on alumina particles. (1) adsorption of TX100 from single solution; (2) adsorption of TX100 from mixed solution of SDBS and TX100 at feed molar ratio of 8:2; (3) adsorption of TX100 from mixed solution of SDBS and TX100 at feed molar ratio of 6:4. The adsorption conditions were the same as that in Fig. 1.

Residual Light Scattering by Alumina Nanoparticles on Surfactant Solutions

In the Kalman filter method, the light scattering background was distinguished from the total absorbance spectra of the supernatants. Under our experimental conditions, the light scattering intensity of the residual particles (mainly alumina) in surfactants solution is depicted in Fig. 7. The ordinate R is the ratio of the relative concentration of particles in a surfactant supernatant to the blank one. The averaged value of the relative concentration for ten blank supernatants without surfactant was used for R calculation. The value of R is an indicator for the light scattering intensity of residual particles. A larger R value means stronger light scattering by more or bigger particles existed in supernatant.

It can be seen that the scattering intensity depends significantly on the components of the supernatant. In the systems of single SDBS and the mixtures of SDBS and TX100, with increasing SDBS concentration, the light scattering intensity decreased to a minimum at first, followed by an increase at higher concentration. These characteristics may be explained by the surface charge variation on the alumina nanoparticles.

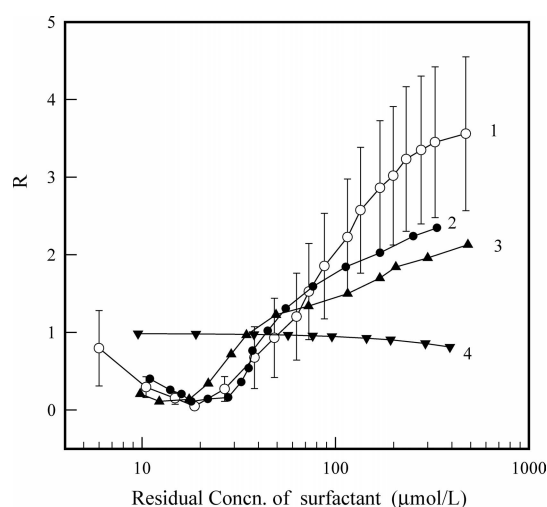


Figure 7. Dependence of the residual particles scattering intensity on the residual concentration of surfactants. The ordinate R is the ratio of the relative concentration of residual particles in surfactant supernatant to that in the blank supernatant. (1) single SDBS solutions; (2) mixed solution of SDBS and TX100 at feed molar ratio of 8:2; (3) mixed solution of SDBS and TX100 at feed molar ratio of 6:4; (4) single TX100 solutions. The adsorption conditions were the same as that in Fig. 1.

As the isoelectric point of alumina in aqueous solution is about pH 9 (Somasundaran, 1966), the alumina nanoparticles are positively charged under the condition of pH 5. Because of the electrostatic repulsive force between the same charged particles, alumina nanoparticles can be well dispersed in acetate buffer. At low concentration of SDBS, the adsorption of SDBS^- on the positively charged alumina surface lowers its charge density, the electrostatic repulsive force between the alumina nanoparticles would thus decrease, which means a decline in dispersed particles' stability. The flocculation of the particles increases and reaches a maximum at the point nearby the zero charge reflected by a minimum in the concentration of residual particles. After this point the adsorption of SDBS^- would lead to particles with more and more negative charges. By consequence, the particles are getting better dispersed and the more alumina nanoparticles will remain in the supernatant under similar experimental conditions, the scattering effect is seen as increased. TX100 is a kind of nonionic surfactant, the adsorption of TX100 on alumina does not change significantly the charge distributing for alumina nanoparticles. Hence, the dispersion stability of alumina nanoparticles decreases only slightly with increasing TX100 concentration.

On the other hand, the variation for scattering intensity in the supernatants in batch is also obviously. For the consideration of conciseness of figure, only a group of error bar data was added in cure 1. The error bars for other systems were similar to that case. The variational scattering intensity is one of error sources for a direct spectrometric method. The Kalman filter method offers the advantages of being simple, convenient and of precision.

Conclusions

In the determination of adsorption amount in solution depletion method combined with spectrometric measurements, the residual light scattering by adsorbent is a potential error. In the adsorption related to surfactants, the scattering intensity varies significantly with the component of the supernatant. The variational scattering intensity increases the measurement error for residual concentration of surfactants, especially for low concentration region. False "negative" adsorption amounts for alumina from single TX100 solutions were given without correcting the influence of light scattering from residual alumina nanoparticles. This influence of the scattering effect in each supernatant was independently corrected by the Kalman filter method. The concentrations of SDBS and TX100 in the supernatants were simultaneously estimated in the presence of residual alumina nanoparticles. The adsorption isotherms of SDBS and TX100 on alumina nanoparticles were determined in single or mixed surfactants solutions. The Kalman filter method offers the advantages of being simple, convenient and of precision.

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