

Correction Method for Ultraviolet Spectrophotometry of Turbid Systems: Determination of N-Polyethoxylated Alkyl Amide in Clay Supernatant

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Quantitative ultraviolet analysis of water-soluble compounds in clay supernatant has been difficult due to interferences by light scattering of colloidal materials and by specific absorption of impurities leached from clay particles. A combination of a turbidity extrapolation and a double-wavelength correction (DWC) is proposed to correct the interferences. In most cases, the correction method gives an accurate assay of polyethoxylated alkyl amides in a cation-exchanged montmorillonite suspension. The extrapolation method for turbidity correction alone eliminates only a small portion of the background interference in a Na⁺-montmorillonite system, but a large portion of the background interference in an Al³⁺-montmorillonite system. The situation for Mg²⁺-montmorillonite is in between. Sequentially, a DWC method is used, which assumes that the absorbance ratio at two wavelengths for the impurities (regarded as an integrated component) is independent of surfactant concentration. By this assumption, a surfactant-free system can be used to find the parameter required in solving simultaneous equations to give a correct surfactant absorbance. A combination of extrapolation and DWC is justified, since a small value of the error induced in the surfactant absorbance is found theoretically from an error propagation formula, as well as from the experimental results. This method is particularly useful in turbid systems having an absorption band in the very short wavelength region.

In studying the adsorption from solution of N-polyethoxylated alkyl amide (average ethylene oxide chain length = 20) surfactant onto various types of cation-exchanged montmorillonite particles, we have pursued quantitative UV-vis spectrophotometry on centrifuged seras of clay-surfactant suspensions. The UV-vis absorption band (due to the amide group) of the surfactant has a maximum absorption at 202 nm, which is very close to the low end of the operational wavelength range, 190 nm. The ultraviolet analysis of the surfactant in clay supernatant is complicated by the fact that traces of clay particles and soluble electrolytes that remain in the supernatant scatter and/or absorb light. Furthermore, the absorption base line cannot be easily determined, because only half of the absorption band is within the operational wavelength range.

The UV-vis spectrum of the clay mineral itself offers information on composition and structure (1) and surface properties (2). Light scattering as reflected in UV spectra has been used to study particulate dimensions in clay suspensions (3, 4). Light scattering usually does not cause a problem in long-wavelength spectrophotometry, such as vis or IR. As the background absorbance (due to light scattering) usually lies on a straight line (but not necessarily horizontal line), the concentration of the sample can be determined from the peak height above the base line. However, light scattering may cause a nonlinear background absorption, especially in the

very-short-wavelength UV region, according to light scattering theories (5-8). The use of surfactant-free clay supernatant for a blank is questionable since the clay-surfactant interactions can cause changes in the light scattering and/or absorbing properties of the suspension that cannot be compensated by use of either clay or surfactant alone.

Preliminary tests showed that the base line could not be straightened by either multicentrifugation or ultrafiltration. In fact, owing to the slight solubility of the clay, the equilibrium aqueous phase contains a small amount of Al³⁺ and Mg²⁺ dissociated from the octahedral sheet of the clay. Exchangeable ions, such as Na⁺ and its counterion in the Na⁺-montmorillonite system, also exist. Other possible impurities include monomeric, dimeric, etc., aluminosilicate compounds. Most of these impurities have UV absorption at a wavelength near 202 nm. The composition of the impurities was not determined; however, the existence of electrolytes was obvious, judging from the conductivity of the supernatant.

There appear to be very few UV analysis articles describing absorbance base line determination and interference corrections. A detailed theory should be very useful, particularly for a colloid system having an absorption band in the short-wavelength region, where turbidity and specific absorption of impurities are significant. In this article, a procedure combining light scattering correction and multicomponent absorbance analysis is described and the assumptions involved are discussed. The validity of the correction procedure was tested; spectral data of clay serums with a known surfactant concentration (postadded) were analyzed according to the correction method, and their corrected absorbances are compared to the expected value. The precision and limitation of the method are discussed.

THEORY

The apparent absorbance, A , of a turbid surfactant-clay supernatant can be written as

$$A = A^s + A^i + \tau \quad (1)$$

where A^s and A^i represent the absorbances of surfactant and impurities, respectively, and τ is the turbidity.

The turbidity, τ , at the wavelengths where the surfactant was analyzed, must be estimated by some form of extrapolation employing measurements over a wavelength range where other species do not absorb. Turbidity is caused by light scattering from the clay particles and is wavelength dependent. For particles with diameters less than 5% of the wavelength, the turbidity is inversely proportional to the fourth power of wavelength according to Raleigh's law (5). For larger particles, Mie theory (6) predicts a more complicated relationship between turbidity and wavelength. Heller et al. (7) and La Mer (8) proposed that turbidity was an exponential function of wavelength as follows:

$$\tau = b\lambda^m \quad (2)$$

where b and m are related to particle size, its shape, and the refractive indexes of particle and medium. For monodisperse spherical particles, Heller et al. (9) have shown that the wavelength exponent, m , is a function of α , which is the ratio of particle circumference to wavelength. Depending on refractive index and the range of α , the wavelength exponent can be either a monotonic or an oscillatory function of α . They also showed that the oscillation was damped out for slightly heterodisperse systems. For montmorillonite, however, no theoretical formulation has been developed due to the complexity of the particle shape, size, size distribution, and the microaggregation (tactoid) structure of clay plates in suspension. Nevertheless, Banin et al. (3) had found empirically that m (a negative value) in eq 2 is independent of wavelength in the region of 700–300 nm for many montmorillonite suspensions. In the UV region, montmorillonite spectra show a band at 245 nm, which Banin et al. (3) attributed to specific absorption. As montmorillonite has a constant wavelength exponent over a wide range of wavelengths, 700–300 nm, it is assumed that the wavelength exponent is a monotonic function at shorter wavelengths. Linear $\ln \tau$ vs. $\ln \lambda$ extrapolation can be made if m is a constant. However, a higher order function of $\ln \tau$ vs. $\ln \lambda$ is more appropriate if m varies. Therefore, a turbidity-eliminated absorbance, A' , can be obtained as follows:

$$A' = A - \tau_{\text{extrapolated}} \quad (3)$$

A double-wavelength correction method (DWC) can be used to eliminate the impurity absorbance, A^i . When an overlapping of absorption bands occurs in a multicomponent system, it is necessary to express the apparent absorbance of the system as a function of specific absorptivity of each component at several wavelengths. A set of simultaneous equations are obtained. Multicomponent absorption analysis by solving simultaneous equations has been discussed in the literature (10). As the exact composition of impurities in centrifuged clay supernatant is unknown, all possible impurities are regarded as an integrated single component. Therefore, measurement at two wavelengths is sufficient. Our method correlated the absorbances of two components at two wavelengths, 202 and 190 nm, and then solved the simultaneous equations (eq 4–7), as the parameters K_s and K_i were known.

$$A'_{190} = A^s_{190} + A^i_{190} \quad (4)$$

$$A'_{202} = A^s_{202} + A^i_{202} \quad (5)$$

$$A^s_{190} = K_s A^s_{202} \quad (6)$$

$$A^i_{190} = K_i A^i_{202} \quad (7)$$

K_s was obtained from surfactant absorbance-concentration calibration curves at two wavelengths. To apply the DWC to an impurities-surfactant system, it was necessary to assume only that K_i was independent of surfactant concentration, regardless of the number of impurity species. Such an assumption allows us to calculate K_i from a blank clay supernatant (without surfactant), according to eq 8 where the su-

$$K_i = (A^b_{190} - \tau^b_{190}) / (A^b_{202} - \tau^b_{202}) \quad (8)$$

perscript b indicates the blank supernatant.

Unless all species that cause interference in a surfactant-clay system are known, one has to use a surfactant-free clay system in order to evaluate K_i according to eq 8 and assume it is the right value for eq 7. In some cases, error can be involved. The reason is described in the following paragraph.

The extrapolation discussed previously gave a precise turbidity correction only when the wavelength exponent at the low-wavelength region did not change significantly from that in the 700–300-nm region; otherwise, under- or over-

estimation of turbidity resulted. Because the DWC method follows the extrapolation correction sequentially, the excess turbidity not covered by extrapolation is carried over mathematically as a part of A^i and must be corrected by the DWC method. In this case, K_i becomes surfactant-concentration-dependent. To illustrate the dependency, let us assume that A^i contribution comes predominately from the excess turbidity. Therefore, A^i in eq 7 can be approximated by τ , which then can be expressed as a function of wavelength exponent according to eq 2. Hence

$$K_i = \frac{A^i_{190}}{A^i_{202}} \approx \frac{\tau_{190}}{\tau_{202}} = 0.94^m \quad (9)$$

The aggregation structure of particles is known to be affected by surfactant, hence, the light scattering of the aggregate is affected by surfactant. Therefore, m and K_i are dependent on surfactant concentration.

In the case described, the K_i value obtained from a blank clay system will result in an error of A^s when it is used in solving the simultaneous eq 4–7. Nevertheless, the error propagation can be estimated according to the following equation derived from the partial derivative of A^s_{202} with respect to K_i :

$$\frac{\delta A^s_{202}}{A^s_{202}} = \frac{A^i_{202}}{A^s_{202}} \frac{K_i}{K_i - K_s} \frac{\delta K_i}{K_i} \quad (10)$$

where the ratio of δA^s_{202} to A^s_{202} represents the relative error of the final estimated surfactant absorbance and $(\delta K_i/K_i)$ is the relative error of K_i due to the effect of surfactant on the particle turbidity. The factor $K_i/(K_i - K_s)$ can be minimized by the proper choice of the two wavelengths in the DWC method. In cases where $(\delta K_i/K_i)$ is small, or $A^s_{202} \gg A^i_{202}$, the error of A^s_{202} becomes negligible.

EXPERIMENTAL SECTION

Bentolite L, a montmorillonite, was from the Georgia Kaolin Co. (NJ). The clay was saturated with 1 M NaCl solution. To obtain cation-exchanged clay, a process using electrolyte solution replacement was used according to the literature (11). To verify the feasibility of the proposed correction method, specific samples were prepared as follows. The ion-exchanged, well-rinsed (to conductivity minimum) Na^{+} , Mg^{2+} , and Al^{3+} -montmorillonite suspensions were centrifuged with a Sorvall RC-5B refrigerated superspeed centrifuge at 19 690 relative centrifugal force for 1 h to give blank clay serums. A known amount of N-polyethoxylated octyl octamide was added to the blanks. The UV-vis spectrophotometry was run with a Perkin-Elmer Model 559. Absolute zero absorbance base line was obtained from DI-water vs. DI-water. No parallel shift of base line (electronic zeroing) is allowed because the turbidity correction is made. Spectra, i.e., apparent absorbance, A , vs. wavelength, λ , were run in the wavelength range of 600–190 nm. They were analyzed according to the following procedure.

(1) Fit A vs. λ data, in the wavelength range of 600–300 nm, to solve the unknown coefficients in the following equation:

$$\ln A = a(\ln \lambda)^2 + b(\ln \lambda) + C \quad (11)$$

(2) Calculate τ_{202} and τ_{190} from

$$\ln \tau = a(\ln \lambda)^2 + b(\ln \lambda) + C \quad (12)$$

by using λ as 202 and 190, respectively.

(3) Calculate A'_{202} and A'_{190} , which are $(A_{202} - \tau_{202})$ and $(A_{190} - \tau_{190})$, respectively.

From surfactant-free supernatant, K_i is found as the ratio of A'_{190} to A'_{202} . In a separate experiment, K_s can be obtained from absorbances of the surfactant at the two wavelengths. As K_i and K_s are known, the spectrum of the surfactant-clay supernatant is analyzed according to the above procedure to obtain A'_{190} and A'_{202} , which are then plugged into the simultaneous eq 4–7 to find the corrected surfactant absorbance, A^s_{202} .

Table I. Results of Extrapolation and Double-Wavelength Correction in Na⁺-, Mg²⁺-, and Al³⁺-Montmorillonite Systems

	test sample		
	Na-S	Mg-S	Al-S
apparent A_{202} (% error) ^a	0.4590 (21)	0.460 (21)	0.4615 (21)
extrapolated range, nm	600-325	800-300	700-250
extrapolated τ_{202}	0.0215	0.0550	0.0677
A'_{202} (% error) ^a	0.4375 (15)	0.4060 (7)	0.3938 (3.4)
K_i	1.5032	2.300	2.592, 1.630
A^s_{202} (% error) ^a	0.3700 (-2.9)	0.3836 (0.7)	0.3852 (1.1), 0.3767 (-1.1)

^a % Error refers to the error from expected true surfactant absorbance: expected surfactant absorbance = 0.3809.

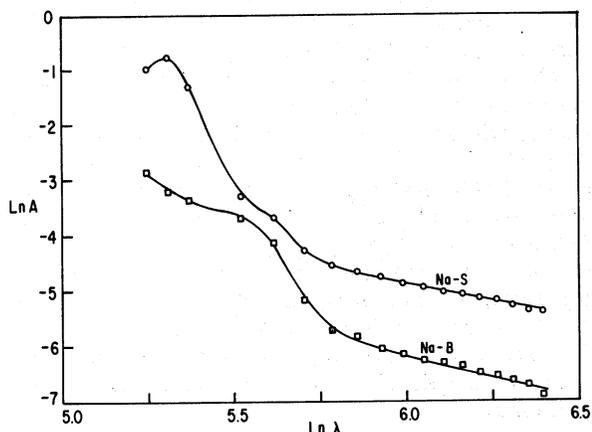


Figure 1. $\ln A$ vs. $\ln \lambda$ spectra of Na⁺-montmorillonite supernatants: Na-S, containing surfactant; Na-B, no surfactant.

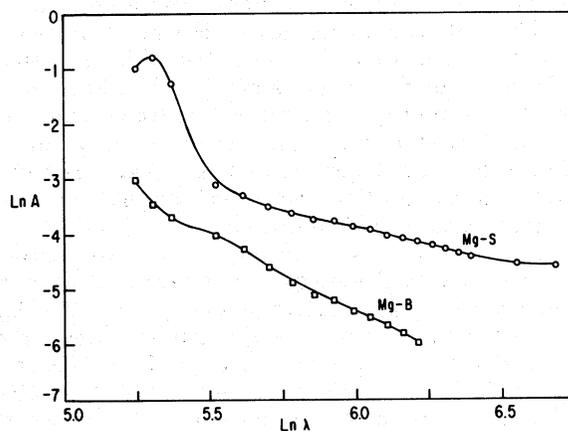


Figure 2. $\ln A$ vs. $\ln \lambda$ spectra of Mg²⁺-montmorillonite supernatants: Mg-S, containing surfactant; Mg-B, no surfactant.

RESULTS AND DISCUSSIONS

Pure surfactant solution had a concentration-independent ratio of apparent absorbance at 190 nm to that at 202 nm, i.e., $K_s = 0.6673$. However, a surfactant-clay supernatant gave a different ratio, indicating the absorption band was interfered with.

For extrapolation purpose, the spectra of Na⁺-, Mg²⁺-, and Al³⁺-montmorillonites blank (no surfactant) and test (containing surfactant) samples are presented in a $\ln A - \ln \lambda$ scale, as shown in Figures 1, 2, and 3, respectively.

In Figure 1, the slope (absolute value) of Na-S (containing surfactant) is smaller than that of Na-B (no surfactant) in the wavelength range of 600-250 nm. The Mg-blank and Mg-S in Figure 2 also show that surfactant lowers the absolute value of the slope. In Figure 3, Al-blank and Al-S have slopes about the same. Generally, surfactant affects the interaction between colloidal particles and therefore results in a change of aggregation or tactoidal structure of clay suspensions; therefore it changes the light scattering properties. For this reason, an external surfactant-free reference cannot be used to correct the turbidity background of the surfactant-clay supernatant. Instead, an internal background extrapolation method should be used. We have found that the surfactant enhances the sedimentation volume of clay suspensions, which suggests that adding surfactant increases the particulate dimension. Such an occurrence would explain a lowering of $\ln A$ vs. $\ln \lambda$ slope, as observed experimentally.

Banin and Lahav (3) reported that montmorillonite had a linear $\ln - \ln$ curve within the wavelengths 300-700 nm and a specific absorption band from 300 to 220 nm with an absorption maximum at 245 nm. The peak height was cation-dependent. Figures 1, 2, and 3 show that the relative peak height is greater for Na⁺- than Mg²⁺-montmorillonite. But the band was hardly seen in Al³⁺-montmorillonite. The beginning of the specific absorption band set a lower limit for the range from which the turbidity can be extrapolated. The

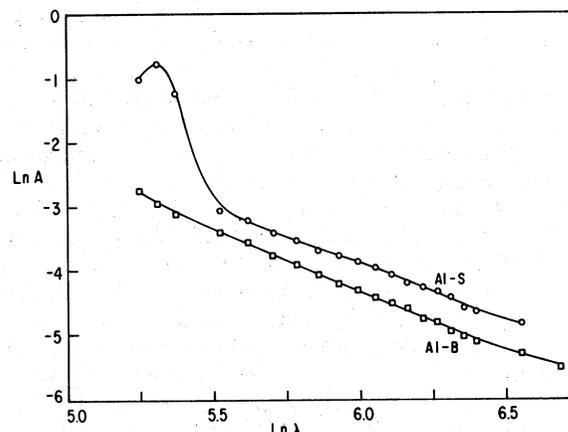


Figure 3. $\ln A$ vs. $\ln \lambda$ spectra of Al³⁺-montmorillonite supernatants: Al-S, containing surfactant; Al-B, no surfactant.

lower limits are 325, 300, and 250 nm for Na⁺-, Mg²⁺-, and Al³⁺-montmorillonite systems, respectively.

The apparent absorbances and the corrected values are gathered in Table I. Every test sample shown in the table contains amide surfactant, 5.078×10^{-5} g/mL, and is expected to have a true surfactant absorbance of 0.3809. However, test samples actually had about the same apparent absorbances, 0.45-0.46 at 202 nm, which represented 21% relative error from the expected value. The magnitude of error remaining at each stage of correction is dependent on the type of clay. For example, Na-S, containing surfactant in Na-montmorillonite supernatant, had a turbid background, $\tau = 0.0215$; therefore, the turbidity-eliminated absorbance, A'_{202} , was 0.4375, a relative error of 15%. The corresponding error is less for Mg-S and even less for Al-S. The double-wavelength correction for Na-S gives a final corrected surfactant absorbance, A^s_{202} , equivalent to 0.3700, which represents only a 2.9% error. The corresponding errors for Mg-S and Al-S are less.

Figures 1, 2, and 3 show all blank samples have nonlinear $\ln\text{-}\ln$ curves in the 215–190-nm region. For the blank samples, the turbidity at 202 or 190 nm estimated by extrapolation from 300–600 nm is always less than the apparent absorbance, even though a second-order $\ln A\text{-}\ln \lambda$ fitting was used. It is not known if this discrepancy is due to specific absorption or excess turbidity. The discrepancy between the extrapolated turbidity and apparent absorption at 202 nm for blank samples decreases in the order of



This is undoubtedly the explanation for the error remaining after employing the extrapolation method on the test samples, where as shown in Table I, the same order is observed.

No matter whether A^i is due to specific absorption or excess light scattering or both, it can be corrected by the double-wavelength method. Table I shows that the DWC reduces the relative error to a small number. The Na-S system gave the highest absolute value of the relative error, about 3%.

We can estimate the error in our analytical method by evaluating each of the three factors on the right-hand side of eq 10. K_i depends on the surfactant concentration if A^i results from excess turbidity. We have found that m varies between -1.2 and -2.7 for the clay systems (see Figure 2). Assume, for example, that the light scatterer has $m = -2.7$ in the blank clay supernatant, but $m = -1.2$ in the surfactant-clay system. From eq 9 the K_i 's are 1.18 and 1.08, respectively. Therefore, the value of $(\delta K_i/K_i)$ is 0.09. The factor $K_i/(K_i - K_s)$ is about 2. Also, if the light scattering contributes 15% error to the surfactant absorbance, $(A^i_{202}/A^s_{202}) = 0.15$. Then, the error of true surfactant absorbance from the DWC method is only 3%, according to eq 10.

If A^i is due exclusively to light scattering, the maximum possible value of K_i is 1.28, corresponding to $m = -4$ for Rayleigh scatterers, according to eq 9. In fact, the K_i values obtained for Na^+ , Mg^{2+} , and Al^{3+} -montmorillonite blank samples experimentally are 1.50, 2.30, and 2.59, respectively. A K_i value greater than 1.28 suggests that the supernatant also had specific UV absorption at 190 and 202 nm and the absorbance ratio is greater than 1.28. For example, it was found that the 0.1% solutions of NaCl , MgCl_2 , AlCl_3 , and sodium silicate (all are possible impurities in the clay supernatant) gave UV absorption ratios (A_{190}/A_{202}) of 12.4, 29.0, 21.9, and 6.6, respectively. When such electrolytes exist in clay supernatants along with any light scatterer, the K_i value can be greater than 1.28. If A^i is due exclusively to true absorption, the K_i is assumed independent of surfactant unless the surfactant causes leaching of UV-absorbing material from clay particles.

The value of K_i is evaluated from A^b and τ^b according to eq 8. As the value of τ^b is closer to A^b (as in the case of

Al-blank sample, see Figure 3), the inaccuracy of K_i is greater. On the other hand, A^i approaches zero as τ approaches A^i . In that case, the corrected absorbance, A^s , obtained by solving the simultaneous equations is insensitive to the value of K_i over a reasonable range. In the third column of Table I, two K_i values found independently at two runs are used for the double-wavelength correction of Al-S sample. The results show that the final corrected surfactant absorbance is very close to the expected value with 1% error.

It must be pointed out that this method did not work well for high-electrolyte clay systems. Due to the strong absorbance of most electrolytes at 190 nm, the absorbance of surfactants at the same wavelength becomes relatively small, and the accuracy of the double-wavelength correction is poor. Also, it has been found that aging a clay suspension serum gives increasing apparent absorbances, more at 190 nm than at 202 nm. This is probably due to the electrolyte leaching of clay particles or glassware. Therefore, only fresh samples (rinsed to conductivity minimum) stocked in plastic bottles and held no longer than 1 week should be used. The blank clay serum from which K_i is evaluated should be subjected to the same experimental conditions as those for unknown samples.

As a conclusion, the method described above can be used for a precise UV determination of surface-active material in a turbid sample. Relevant systems are soil solution and surface waters that can contain dissolved humic materials having surface-active properties, which can affect turbidity. Proper choice of blank material will ensure that errors from this source are minimized.

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