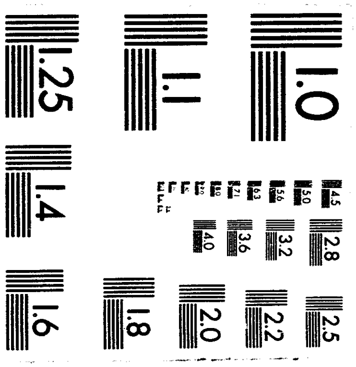
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A NOVEL, INTEGRATED TREATMENT SYSTEM FOR COAL WASTE WATERS:

QUARTERLY REPORT:

FOR THE PERIOD June 2, 1993 - September 1, 1993.

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ABSTRACT:

The aims of this study are to develop, characterize and optimize a novel treatment scheme that would be effective simultaneously against the toxic organics and the heavy metals present in coal conversion waste waters. In this report, the following findings have been reported and discussed. Acid-base titration of Duomeen-T (DT), a diamine surfactant, that has been used in this study to modify smectite surfaces to form smectite-DT complexes has been undertaken. In aqueous medium containing 5% by volume iso propyl alcohol (IPA), DT shows a broad distribution of pKa with a mean value of 7.55. This finding suggests that DT is a much weaker base than a typical diamine and helps explain the fact that Cu(II) adsorbs specifically onto DT with maximal affinity in the pH range 7.2 - 7.5. Electrokinetic sonic amplitude (ESA) measurements on DT-smectite complexes also reveal that the mean pKa of the adsorbed DT is around 7.0. This finding supports our earlier observations that Cu(II) and Cd(II) cations bind strongly through specific interaction to DT-smectite surface in the pH range 7.0 -8.0. Our results also show that DT is fully protonated at pH 4.5, and it is at this pH that Cr(VI) is maximally adsorbed as counterions to the DT-smectite surface. These and our earlier results provide a firm basis to conclude that a heterogeneous mixture of diamine surfactants can be used to adsorb and desorb cationic and anionic heavy metals from their respective aqueous solutions as a function of the solution pH.

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I. INTRODUCTION:

In our previous reports (1,2,3,4,5,6,7), we showed that a number of clay complexes can be prepared by a novel mixed bilayer approach, designated by us as the hydrophobic attachment method (HAM). In this method, the smectitic clay was first treated upto a monolayer (or the charge equivalence point) with a quaternary ammonium surfactant CBDA, a treatment that imparted hydrophobicity to the resultant clay. Subsequent attachment of an alkyl diamine (DT) or a long-chain carboxylic acid (palmitic acid, PA) by hydrophobic interaction between the alkyl chains of CBDA and those of DT or PA yielded a mixed bilayer on the clay surface and such clays were shown to be quite effective in reversibly adsorbing cationic heavy metals such as Cu(II) and Cd(II).

A second approach was to directly attach the protonated form of the diamine to the negative sites of the clay layer to form a bilayer. This approach, designated as the direct attachment method (DAM), was slightly less effective than the sequential treatment scheme mentioned above for the adsorption of cationic heavy metals such as Cu(II) and Cd(II). However, in our previous report (5) we have shown that both methods of attachment were effective in reversibly adsorbing anionic Cr (VI).

In an earlier report (4), we compared the relative effectiveness of two analogs of diamine surfactants: The water-soluble, Duomac-T (DuT), and the water-insoluble, Duomeen-T (DT). Duomac-T (DuT) is prepared by reacting DT with acetic acid to convert the amine group to ammonium, thus making DuT water-soluble (8). Our data revealed that DuT modification of hectorite-CBDA (Hec-CBDA) to form Hec-CBDA-DuT was ineffective with respect to Cu(II) adsorption. It was pointed out that the failure in this case might have arisen from the leaching of DuT coating on hectorite-CBDA-DuT by successive washings with deionized water. Alternatively, CBDA might have been displaced by DuT during the treatment of Hec-CBDA by DuT.

In summary, we have amply demonstrated that the pH of the continuous phase could be used as a " switch" to adsorb/desorb cationic and anionic heavy metal ions from most, if not all, of the clay complexes prepared as a part of this study.

A list of the five modified-clay complexes that have been prepared as a part of this study is as follows:

(1)	Hectorite-CBDA-Duomeen T:	(Hec-CBDA-DT, HCDT, the diamine type)
(2)	Hectorite-CBDA-Palmitic Acid:	(Hec-CBDA-PA, HCPA, the carboxylic acid type)
(3)	Montmorillonite-Duomeen T:	(MONT-DT, the diamine type in which the functional moiety is directly attached to the clay surface)
(4)	Montmorillonite-CBDA-DT:	(Mont-CBDA-DT, similar to Hec-CBDA-DT).
(5)	Hectorite-CBDA-Duomac-T:	(Hec-CBDA-DuT, similar to Hec-CBDA-DT, but containing the water-soluble, ammonium form of the diamine surfactant).

Our studies so far indicate that the mechanism of Cu(II) adsorption is of specific nature onto HCDT. This was verified by the appearance of an intense absorption band at 626 nm in the spectrum of Cu(II)-DT complex in solution. Further, it was observed that adsorption of Cu(II) onto HCDT or MONT-DT imparted a blue color to the respective adsorbent. Similar colc hange was observed when Cu(II) adsorbed onto hec-CBDA-Palmitate, HCPA. However, increasing concentrations of 1:1 electrolytes in solution modified the adsorption of Cu(II) ions onto HCPA. A significant decrease in the affinity of adsorption with only a minor decrease in the limiting adsorption capacity were noted. Thus, it was concluded that adsorption of Cu(II) on HCPA was partly electrostatic and partly of specific nature.

We have also studied the adsorption of an ionogenic organic compound, β-naphthoic acid, (NA), as a probe of the surface charge density of the surfactant-modified clays as a function of pH. β-naphthoic acid has a pKa of 4.17, and its mode of adsorption was expected to be a combination of anion exchange, hydrophobic partitioning and H-bond interaction. It was shown that NA adsorbed to MONT-DT and HCDT strongly at pH 4.5 and 7.0, but weakly at pH 9.0 suggesting that the positive charge on the DT-modified clay surface is low at the latter pH (6, 7). Furthermore, Cr(VI) adsorption was also observed to be strong at pH 4.5, but very weak at pH 7.0 and 9.0 (7).

The above results show, by inference, that DT-modified clay surfaces are only weakly charged (with a positive sign) at pH above 7.0. This inference is supported by the specific adsorption of Cu(II) ions onto DT-modified clays at pH 7.2. However, It was felt that the determination of the basicity of the diamine, DT, and the surface charge characteristics of DT-modified smectites would add further support to the above conclusions. Thus, in the present quarterly report, we will discuss the results from:

- The potentiometric titration of DT in aqueous solution with and without added Cu(II) ions to determine the pKa of the diamine

- The electrokinetic sonic amplitude (ESA) measurements on hec-CBDA-DT (HCDT).

II. Potentiometric Titration of DT in aqueous solution:

2M HCl was used to titrate an aqueous solution of DT containing 1.05 mmoles of DT and 5% by volume of isopropyl alcohol (IPA). pH was monitored after each addition of the acid and it was observed that pH reading stabilized within 2 minutes. Blank titrations were also carried out and the acid consumption during blank titration was subtracted from the sample titration data to calculate the meq of acid that reacted with the secondary and the primary amino groups on DT. The solution was, in a few cases, back-titrated with 1M NaOH to determine whether there were any kinetic limitations (hysteresis) to acid-base reactions of DT in an aqueous medium. Since DT was observed to form a fine macro emulsion above pH 8.0, turbidity of the solution was monitored at 500 nm during the titration.

In a separate experiment, 0.1 mmole of Cu(II) ions were added to the aqueous solution of DT containing 0.5 mmole DT and a Cu(II): DT molar ratio of 1:5. An intense blue color developed and its absorbance was measured at 626 nm. Following each addition of HCl, absorbance at 626 nm was re-measured and the titration continued to its end point.

The results are shown in Fig. 1, 2, and 3. The following points can be made with regard to the data presented in the above figures.

(1) The end point of the acid titration (2.1 mmoles HCl) establishes the dibasicity of the diamine, DT.

Fig. 1 Acid-Base Titration of DT
DT = 1.05 mmole

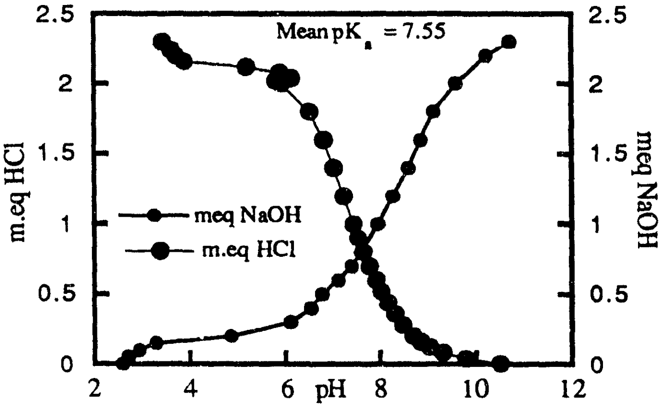


Fig. 2 Acid-Base Titration of DT;
Turbidity Measurements

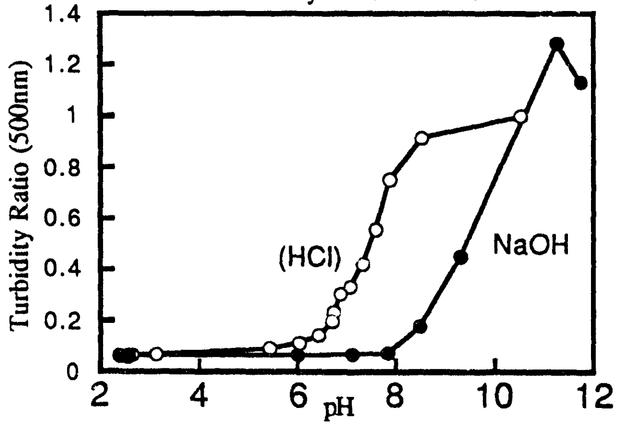
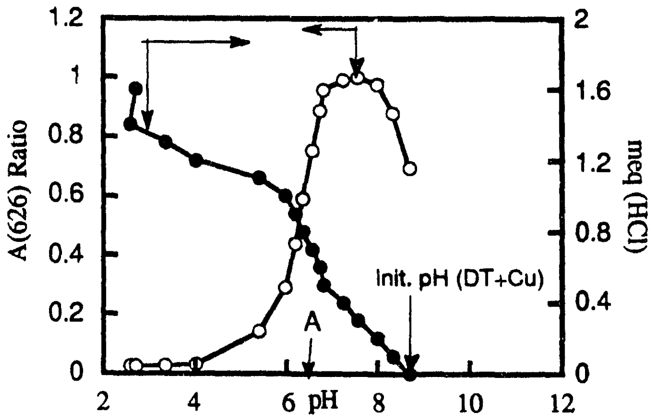


Fig. 3 Acid Titration of DT in Presence of Cu(II);
Cu(II): DT Molar Ratio = 1:5



(2) Both the acid and the base titration data (Fig. 1) show that DT has a broad distribution of basicities with a mean pKa of 7.55 (determined from acid titration data). The data were fitted to a fourth degree polynomial and solved for the value of pH at the inflection point of the resulting curve to determine the average pKa. The occurrence of a distribution of pKa (instead of a single or two values) suggest that DT, as expected, (being a commercial product) is a heterogeneous mixture. A second possibility is that DT may exist in aqueous solution as a microemulsion, especially in presence of iso propyl alcohol (IPA). This may happen at acidic pH when the amine groups on DT are fully protonated. Thus the distribution of pKa may represent the existence of DT in multiple environments, both in the aqueous phase and in the microemulsion pseudo phase.

(3) In alkaline pH range, DT is de-protonated and is seen to form a separate macro emulsion phase (Fig. 2). The turbidity of DT in an aqueous medium containing 5% by volume IPA is plotted in Fig. 2. At pH above the mean pKa, turbidity ratio (defined as the ratio of turbidity at high pH to the turbidity at low pH) rises sharply. The absolute magnitude of turbidity @ 500 nm was low (between 0.2 - 0.3) indicating that the macro emulsion phase had very fine particles. Fig. 2 also shows hysteresis between acid and base ttrations. This is thought to occur in the following manner:

As the pH is raised, the pseudo microemulsion phase begins to separate as a macro emulsion phase. The time constant for the phase separation is perhaps lower than the duration between base additions (2 - 3 mins.), which would result in a **smaller** number of titratable surface groups due to transient mass transfer limitations at the interface, even though the solution is continuously mixed. This does not occur during acid titration because the DT/H_2O goes from a two-phase to a single and a pseudo phase system as the pH is lowered. Note that the turbidity goes to zero at pH below the mean pKa.

(4) In presence of Cu(II), an intense blue color develops in solution signaling the formation of Cu(II)-DT complex formation. The results are shown in Fig. 3. During acid titration, the absorbance of Cu-DT complex as a function of pH was measured at 626 nm and was ratioed against the highest value of absorbance. The following chemical reactions are thought to occur in solution during the acid titration of DT in presence of Cu(II) and will help explain the observed phenomena.

						Effect on pH
(a)	DT	+ 2 H_2O	=	$[DTH_2]^{2+}$	+ 2OH^-	Increase
(b)	OH^- + HCl		=	H_2O	+ Cl^-	Decrease
(c)	DT	+ Cu(II)	=	$[DT\text{-}Cu]^{2+}$		No change
(d)	Cu(II) + H_2O		=	$[Cu(OH)]^+$	+ H^+	Decrease

The initial pH of the DT solution prior to acid titration is lower (a value of 8.5 compared to 10.5 in the absence of Cu(II)) as a result of reaction (d). The point A (shown in Fig. 3) represents the pH of Cu(II) aqueous solution of identical concentration in the absence of DT.

The absorbance ratio goes through a maximum between pH 7.4 - 7.7. The loss of absorbance at lower pH is due to the fact that the Bronsted acidity of HCl is significantly greater than the Lewis acidity of Cu(II). Thus, HCl displaces Cu(II) from Cu-DT complex. The lower absorbance ratio at pH higher than the pKa is due to the formation of $[Cu(OH)]^+$ (reaction (d)) which lowers the stability of Cu-DT complex. Note that the absorbance maximum occur around pH 7.5 which is the mean pKa of DT and our earlier results have shown that Cu(II) adsorption onto the surfaces of MONT-DT or HCDT occurs around the same pH.

The data shown in above figures thus reinforce our earlier findings that MONT-DT and HCDT are strong anion exchangers at pH 4.5 and form high affinity complexes with cationic metals such as Cu(II) at mildly alkaline conditions.

III. ESA Studies on HCDT:

Electro kinetic sonic amplitude (ESA) measurement is a recent technique that has been used to quantify surface charge characteristics of mineral oxides and clay complexes (9,10). ESA measurement was undertaken to correlate potentiometric studies on DT in solution (described above) to the surface properties of clay-DT complexes .

Electrokinetic sonic amplitude (ESA) is a complex quantity that represents the magnitude and the phase of the macroscopic pressure wave induced in a suspension of charged colloidal particles when subjected to an oscillatory electric field. The differential acceleration of the particle dipoles relative to solvent molecules produces a net momentum flux on a pair of electrodes placed in the suspension. The theory and the measurement of ESA have been reviewed extensively (9). The observed ESA signal is given by:

$$\mathrm{ESA}(\omega) = P/E = (c)(\Delta\rho)(\phi)(G_f)(\mu_d) \qquad [1]$$

P: pressure amplitude of sound wave (mPa)
E: amplitude of applied field gradient (V/m)
c: velocity of sound in the medium (m/s)
$\Delta\rho$: density difference between the particle and the continuous phase (kg/m3)
ϕ: volume fraction of the solids (dimensionless)
G_f: electrode geometrical factor (dimensionless)
μ_d: frequency dependent electrophoretic mobility (m2/sec/V)
ω: frequency of the applied ac field.

Eq. 1 is valid in the " linear " regime of particle volume fraction (0.05 or less) and is applicable to the experiments reported here that have been carried out at a volume fraction of 0.013. Quantitative theories for converting the dynamic electrophoretic mobility, μ_d, in Eq. 1 to zeta potential from the ESA signal have been developed (10), but a knowledge of particle size and density is required to make this conversion. The ESA as given by the left hand side of Eq. 1 is a measurable quantity and can be separated into magnitude (modulus) and phase angle components. The latter refers to the "lag" in the

Fig. 4 ESA Measurements on HCDT

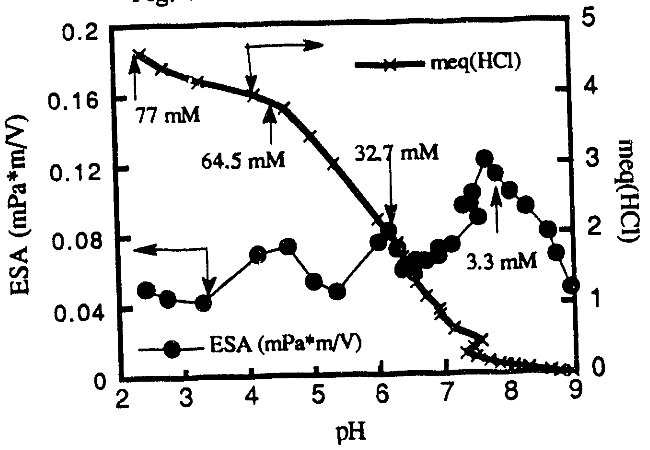


Fig. 5 ESA Signal: Ionic Strength Effect

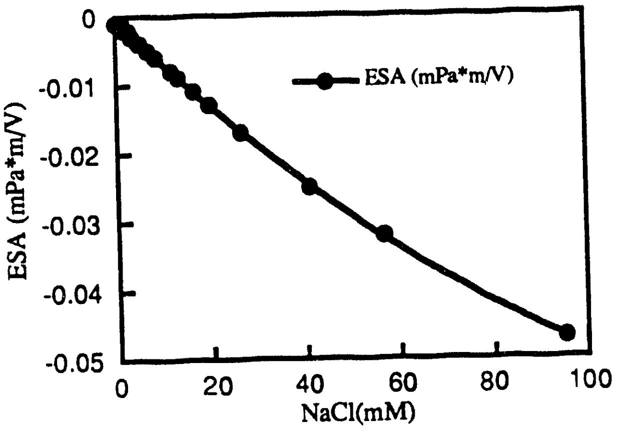
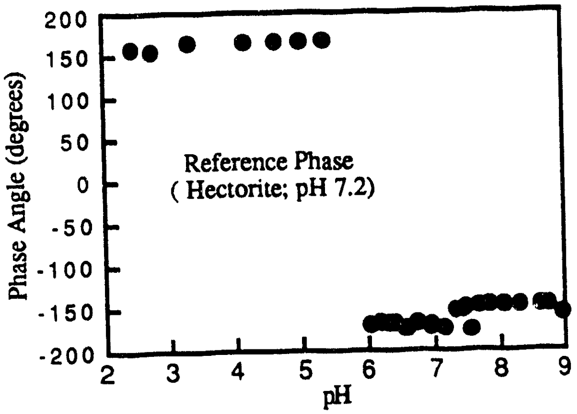


Fig. 6 pH Titration of HCDT:
Phase Angle vs pH



ESA signal relative to the signal of a reference material of the same polarity (i.e., having the same sign of surface charge). Since the phase angle changes sharply at the onset of charge reversal, any change in the sign of surface charge during acid-base the titration can be located more precisely using the phase angle component than the modulus of ESA. Thus, the observed ESA signal was used as an indicator of the magnitude of the surface charge.

2 gms of HCDT were conditioned in DI water for 36 hours with initial sonication for 15 minutes and continuous mixing thereafter. The suspension was titrated with 2M HCl (as was done with DT in solution) and the ESA signal, the pH and the temperature of the suspension were measured after each acid addition. ESA measurements were obtained using the MATEC ESA-8000 instrument (Matec Applied Sciences, Hopkinton, MA). Blank ESA titrations with increasing concentrations of NaCl were also carried out to correct for the contribution of the indifferent electrolyte to the ESA signal. The results are shown in Figs 4 - 6. The following points can be made from Figs 4 -6.

(1) The addition of H^+ ions to HCDT suspension produces a titration curve similar to the one observed in the solution of DT. However, the apparent mean pKa of the adsorbed DT (Fig. 4) is lower because, the more basic of the DT molecules may have reacted with the negative sites on hectorite.

(2) The ESA signal (Fig. 4) is of very low magnitude, but positive over the entire pH range of the titration. This suggests superequivalent adsorption of the surfactant leading to positive surface charge on the modified-smectite surface.

(3) The above assertion is verified by the phase angle data (Fig. 6) which show that the phase of the observed ESA signal is shifted by 180 degrees with reference to the ESA signal of unmodified smectite (hectorite) which is negatively charged over the pH range studied.

(4) The equivalence point of acid titration (Fig. 4) yields a value of 1.25 mmoles DT/g HCDT which is close to the value of 1.4 mmoles/g HCDT measured by organic carbon and Ninhydrin assay methods.

(5) The ESA signal increases as HCl is added to the suspension indicating protonation of surface diamine groups. However, the ESA signal decreases at even lower pH and shows oscillations. The following is the explanation for the observed behavior of the ESA signal.

Titration of HCl into HCDT suspension adds Cl^- ions to the suspension and, as shown in Fig. 5, the ESA signal of the background electrolyte such as NaCl can be 30 - 50 % of the ESA signal of HCDT, but **opposite** in polarity. The various concentrations of the chloride ion during titration (ranging from 0 - 77 mM) are shown in Fig. 4. Thus, the decrease in ESA signal can be partly accounted for. It appears that the phase angle of the background signal does affect the observed phase angle. Instead of being close to ± 180 degree, it is closer to ± 150 degrees.

The oscillation in the ESA signal is perhaps due to the low magnitude of signal itself.

Thirdly, a large number of the surface diamine groups may be in the interlayer space of a smectite such as hectorite. These interlayer diamine groups will be " accessible " to protons, but the observed ESA signal arises from the protonated surface groups on the external surface of the modified-smectite. Further work is in progress to build upon the initial results discussed in this report.

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V. Presentations:

(1) Removal and Recovery of Cationic and Anionic
Heavy Metals Using Surfactant-smectite Complexes:

Keeran R. Srinivasan and Henry Y. Wang
The Annual Clay Minerals Society Meeting
San Diego, CA
Sept. 27, 1993.

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