SEMIQUINONE CATION ADSORPTION ON MONTMORILLONITE AS A FUNCTION OF SURFACE ACIDITY

by

Charles G. Dodd and Satyabrata Ray
School of Petroleum Engineering, University of Oklahoma, Norman, Oklahoma

ABSTRACT

Semiquinone cations derived from aromatic diamines by one-electron oxidation in aqueous solution possess characteristic colors that depend on hydrogen ion concentration. The colored free radicals are formed by oxidation on the surface of certain montmorillonite clay minerals, where they are stabilized by adsorption, apparently in cation exchange positions, but many clays react anomalously when the procedure is employed as a diagnostic test for montmorillonite. One of the problems involved is the chemical nature of the various semiquinones. Another is the effect of clay mineral crystal structure on the color that is produced.

The dihydrochlorides of benzidine, *p*-phenylenediamine, and N,N-dimethyl-*p*-phenylenediamine in aqueous solution have been used with a centrifuged Wyoming bentonite (montmorillonite) and a centrifuged hectorite clay, each suspended in various buffered solutions, to study the pH effect and the quantity and nature of the semiquinones formed. Hypothetical structures differing by one hydrogen (or hydronium) ion have been assumed for two semiquinone forms of each diamine, each formula representing a distinct hue, with the divalent cation formed at low pH and the monovalent cation at a higher pH. Mixtures of the two cations were assumed to exist at intermediate acidities corresponding to mixtures of the two hues. A simple set of equations was postulated to describe these reactions, and the theory was tested experimentally by determining the amount of nitrogen adsorbed on each clay sample at a series of fixed pH values ranging from 0.5 to 6.5.

The milligram atoms (mga) of nitrogen (or 2 × millimoles of diamine) adsorbed were found to increase with increasing pH in approximately the amount predicted in the range 1.0–4.2. In this pH range, however, the calculated base exchange capacity (BEC) for each clay was lower than the accepted value, presumably because an approximately constant fraction of the base exchange sites was occupied by nonexchangeable cations, probably aluminum and hydrogen ions. Amounts of base adsorbed were the same whether sodium or calcium ions were initially in exchange positions. At pH values of 5.5 and 6.5 the mga of nitrogen adsorbed showed a sharp increase, apparently because colloidally dispersed reagent diamine was formed as the free base and no aluminum or hydronium cations were adsorbed. When corrections were made for nonadsorbed free base (not adsorbed on exchange positions but physically adsorbed to the floccules) and, in the case of benzidine, for base lost in filtration, the calculated BEC's for each clay were in satisfactory agreement with accepted values.

INTRODUCTION

Various dye-staining procedures have been used sporadically by geologists as field tests and for identification of clay minerals in the laboratory. Faust (1940) has described staining procedures based upon artificially induced pleochroic effects and upon acid-base reaction mechanisms. Other dye adsorption tests dependent upon oxidation-reduction reaction mechanisms were introduced by Hendricks and Alexander (1940), Hauser and Leggett (1940), Weiss (1938), and Weil-Malherbe and Weiss (1948). The state of the art in 1952 was reviewed by Dodd (1955). The situation has been highly unsatisfactory, however, with respect to applications of any of these tests in the field. The most reliable laboratory procedures appear to be those described by Mielenz and King (1951).

The tests utilizing acid-base reaction mechanisms employ pH-sensitive dyes as indicators to measure clay mineral surface acidity, i.e. pH of the adsorbed surface aqueous layer after a prescribed pre-treatment. After acid treatment, for example, clay minerals possessing high BEC's would be characterized by a surface pH low enough to change the color of selected dyes. Walling (1950) has employed similar procedures for measuring surface acidities of silica and alumina gels.

The colors observed with oxidation-reduction dye tests also have been found to depend on clay mineral surface acidity. Mielenz and King (1951), for example, proposed the use of the lemon-yellow color that benzidine displays on a montmorillonite surface when pH is adjusted to approximately one. If more were known concerning the variables determining color development in oxidation-reduction color tests, this information might be applied to the solution of geological and physico-chemical problems involving clays.

A knowledge of the surface acidity of clay minerals should be of considerable help in the interpretation of geological environmental problems involving clays if it were possible to obtain significant experimental data. Surface acidities of clay minerals probably are reflections of the environmental conditions under which the minerals were formed originally or were altered by " diagenetic " processes.

Problems involving clay mineral crystal chemistry and surface chemistry also would be simplified if surface acidity measurements could be made on laboratory samples. It appears reasonable to assume, for example, that octahedrally substituted montmorillonites (in which the negative lattice charge is the result of divalent cation substitution for trivalent aluminum in the octahedral layer) would act as stronger acids per unit negative charge, i.e. hold hydrogen or hydronium ions relatively more weakly, than three-layer clay minerals in which the seat of negative charge is tetrahedral layer substitution. Surface acidity thus should be a function of both clay acid strength, an intensity factor, and total negative lattice charge, a related but not necessarily corresponding capacity factor. This line of reasoning may be extended to a comparison of the relative effects of aluminum and boron substitution for silicon in tetrahedral layers. The substitution of a cation of lower field strength, such as aluminum, for silicon in tetrahedral layers of three-layer clay minerals would lead to a higher surface acidity than would the incorporation of borate anions in the tetrahedral layer, or the substitution of boron for silicon. Both substitutions would increase the negative lattice charge the same amount, but the boron substitution would result in a higher surface pH. Hydrogen ions, or hydronium ions, would be held more tightly to the clay surface if boron were substituted for silicon, whereas the aluminum-substituted crystal surface would have a lower affinity for hydrogen ions.

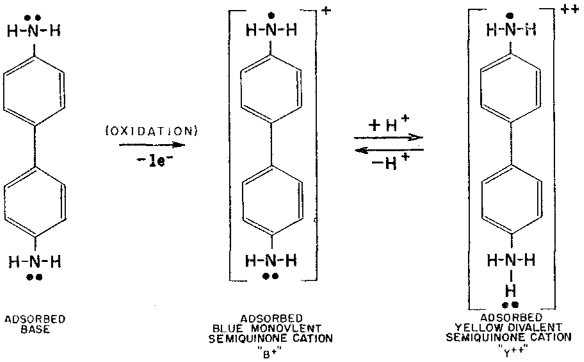
There is no direct means of measuring surface acidity of particulate solids dispersed in a bulk liquid phase. Glass and calomel electrodes used with a laboratory pH meter, for example, cannot be inserted into the surface layer of dispersed particles (Overbeek, 1953). The pH of the bulk liquid can be so measured, but it is not necessarily the same as that in the adsorbed surface layer, although it may be in equilibrium with the latter. The relationship between surface acidity and bulk liquid pH has been discussed by Bernstein (1960). When the bulk liquid contains a buffer system of sufficient capacity it can be shown that the surface pH is essentially equal to that of the bulk liquid.

During the present investigation it was noted that the amount of semiquinone-forming diamine required to flocculate a given mass of suspended montmorillonite varied with the pH of the aqueous slurry when this pH was held constant by a buffer system. The characteristic semiquinone color was developed on the surfaces of dispersed clay particles, and these particles flocculated and settled in the test vessel at the end point, leaving a colorless supernatant liquid. These observations suggested that the type of reaction occurring on clay mineral surfaces might be clarified by a quantitative study of semiquinone cation adsorption at saturation at various controlled pH values.

ADSORPTION OF SEMIQUINONES ON CLAY SURFACES

Hendricks and Alexander (1940) found that any diamines capable of producing colored semiquinone forms on oxidation exhibit the same colors after adsorption and oxidation on montmorillonite surfaces. When a compound such as *p*-phenylenediamine is oxidized to the corresponding quinone the process involves a loss of two electrons. It is possible, however, under certain conditions to observe the existence of an intermediate compound, a semiquinone, which is the result of a one-electron oxidation process. Semiquinones are " odd electron " compounds, free radicals which may be stable in aqueous solution. Semiquinones of the types discussed here are formed by the loss of one electron at the end of a molecular system of conjugated double bonds. Examples of compounds which may be oxidized to such semiquinones in aqueous solution are the aromatic diamines such as benzidine, *p*-phenylenediamine, *o*-phenylenediamine, and N,N-dimethyl-*p*-phenylenediamine, and substances such as *p*-aminophenol (Hambleton and Dodd, 1953). Semiquinones are stabilized by resonance energy and usually are colored, as are many other free radicals. The types of semiquinones used in clay mineral staining tests are cations stable only in restricted ranges of pH, and formed by one-electron oxidation processes. The chemistry of semiquinones has been reviewed by Michaelis (1935) and Branch and Calvin (1941, p. 329).

It has been suggested (Dodd, 1955), following the proposal of Weiss (1938), that the semiquinone forms of benzidine may be represented by the equations in Fig. 1, depending upon the acidity of the clay surface. A shorthand form of the right-hand equation (Fig. 1) showing the role of water in the adsorbed layer then might be written as:



(1)

Figure 1.—Semiquinone forms of benzidine (eq. (1)).

$$B^{+} + H_3O^{+} \rightleftharpoons Y^{++} + H_2O. \qquad (2)$$

The presence of a minimum amount of water on montmorillonite surfaces has been found to be necessary for development of a blue color, as indicated by eq. (2).

If eqs. (1) and (2) represent the formation of colored benzidine cations on clay mineral surfaces, the monovalent cation found at pH values higher than about 4 is responsible for the brilliant, royal-blue color first observed by Hendricks and Alexander (1940); the divalent cation may then be assumed to be the lemon-yellow color utilized by Mielenz and King (1951) in their modification of the benzidine test at a pH of approximately 1. It would be reasonable to expect that the formation of semiquinones from *p*-phenylenediamine, *o*-phenylenediamine, N,N-dimethyl-*p*-phenylenediamine, and *p*-aminophenol also could be expressed by similar sets of equations, but both the monovalent and divalent cation forms might not be observable with each reagent. Among other conditions, it appears that a surface, such as that of a montmorillonite clay, must be present to stabilize the colored free radicals by adsorption. The neutral or basic form of *p*-aminophenol apparently is not observable even in the presence of such a clay.

Benzidine, and possibly other diamines, also may exist at neutral and higher pH in the form of blue colloidal flocs if the amount of the diamine present is sufficient to exceed its solubility in water.

The reactions represented by eq. (1) and (2) have been reported to occur only in the presence of dispersed montmorillonite clay minerals, and the quantities of diamine required in our experiments to produce flocculation of the dispersed clay particles are dependent on the amount of clay present. It has seemed reasonable to us to assume that the semiquinone cations are adsorbed on basal plane surfaces of montmorillonite crystalline particles at base exchange sites, thereby neutralizing the residual negative charge in a montmorillonite crystal lattice. We have assumed, further, that the number of moles of a semiquinone divalent cation formed at a low pH and required to saturate base exchange sites and flocculate a given amount of clay should be approximately one-half the number of moles of monovalent cations required at a higher pH. At intermediate acidities both monovalent and divalent cations would be expected to be present on the clay surface and the number of moles of diamine required would be intermediate. There should thus be a gradual increase in the number of moles of diamine required to saturate the montmorillonite clay surface if the pH of the clay surface were raised. If each of the base exchange positions of the mineral were available and accessible to semiquinone cations, the meq of diamine adsorbed per 100 g of dry clay would approach the BEC of the mineral. The experiments described herein were designed to test this simple hypothesis.

In order to derive an equilibrium constant for the chemical reaction involving the equilibrium between acidic and basic forms of the semiquinone cation, eq. (2), it has been assumed that surface activities of adsorbed cations may be considered *proportional* to the easily measured quantity, number of millimoles adsorbed per 100 g of clay. As a consequence of the experimental conditions employed, i.e. adsorption on clay particles dispersed in bulk aqueous media, it seems reasonable to assume further that the effective hydrogen-ion concentration on clay mineral surfaces must be in equilibrium with, or effectively proportional to, that in the *buffered* bulk solution. Under these conditions, also, the effective concentration of water in eq. (2) is constant and large and can be neglected, as is conventional in calculating equilibrium constants. The following expression may be set up for calculation of the effective equilibrium constant for the reaction of eq. (2).

$$K = \frac{[\mathrm{Y}^{++}]_s\,[\mathrm{H_2O}]_s}{[\mathrm{B}^{+}]_s\,[\mathrm{H_3O}^{+}]_s} \tag{3}$$

or the simplified constant based on the assumptions discussed above may be written as:

$$K^* = \frac{\mathrm{Y}_s^{++}}{\mathrm{B}_s^{+}[\mathrm{H_3O}^{+}]_L} \tag{4}$$

or

$$\ln K^* = \ln\frac{\mathrm{Y}_s^{++}}{\mathrm{B}_s^{+}} + \mathrm{pH}_L. \tag{5}$$

In the above equations the brackets have their conventional significance as activities expressed in concentration units of moles per liter. The subscript s refers to the adsorbed aqueous layer on a clay mineral surface, and the subscript L to the bulk liquid. The absence of brackets in eqs. (4) and (5) implies concentration units expressed as millimoles adsorbed per 100 g of dry clay.

The quantities Y_s^{++} and B_s^{+} may be determined by the additional relations:

$$Y_s^{++}+B_s^{+} = \text{number of millimoles of base (diamine) adsorbed per 100 g of dry clay} \tag{6}$$

$$2Y_s^{++}+B_s^{+} = \text{BEC of clay.} \tag{7}$$

Equations (6) and (7) are based on the assumption that semiquinone cations are exchangeable on all clay surface base exchange sites.

If the K^* values at different pH conditions should be found to agree within limits, the simple theory developed above might be considered a feasible first approximation to the complex clay surface chemistry involved.

EXPERIMENTAL

Materials Used

Centrifuged samples, $< 2\mu$ particle size, of Wyoming bentonite (montmorillonite) and hectorite[1] were selected for the present study, because these clays have been studied extensively. The organic bases used were Eastman grade dihydrochlorides of benzidine, *p*-phenylenediamine, and N,N-dimethyl-*p*-phenylenediamine. Buffer solutions and analytical reagents used were A.C.S. reagent grade.

Experimental Procedure

Approximately 0.1 g of clay mineral, dried at 110°C for 24 hr, was dispersed in 200 ml of distilled water in Erlenmeyer flasks. The slurries were buffered at selected pH values ranging from 0.5 to 6.5 and an excess of base in aqueous solution was added. The sample flasks were shaken and allowed to stand overnight before filtering the flocculated clay–diamine complex. Excess base was washed from the residue, by repeated washing with the respective buffer solutions until the washings gave negative tests for base with an ammonium phosphomolybdate reagent (which turns blue with each of the three diamines). The solid residues were analyzed for their nitrogen content by means of standard Kjeldahl methods. From the nitrogen content the number of millimoles of base per 100 g of dry clay was calculated.

Mixtures of citric acid and NaOH solutions were used for buffer solutions in the high pH range from 3.2 to 6.5. In the low pH range the buffer solutions listed in Table 1 were used.

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[1] Supplied by the Baroid Sales Division of National Lead.

The dissolution of hectorite in HCl at pH values around 1, the dispersing effect on a clay mineral slurry of phosphate ions in the buffer solution made of citric acid and Na_2HPO_4 at a pH above 2.2, and the insolubility of benzidine in the buffer solution of pH 1.5 prepared with solutions A and B; all were taken into consideration in selecting suitable buffer solutions.

TABLE 1.—BUFFER SYSTEMS

Mineral	Organic Base	pH	Buffer
Wyoming bentonite (montmorillonite)	Benzidine *p*-phenylenediamine N,N-dimethyl *p*-phenylenediamine	0.5 to 1	HCl
Wyoming bentonite (montmorillonite)	Same	2.0	Mixture of solutions A and B[1]
Hectorite	*p*-phenylenediamine N,N-dimethyl-*p*-phenylenediamine	1.5	Same
Hectorite	Benzidine	2.2	Citric acid plus Na_2HPO_4

[1] Solution A: Oxalic and boric acids.
Solution B: Boric and succinic acids and Na_2SO_4.

RESULTS AND DISCUSSION

The results are summarized in Tables 2 and 3. Plots of mga of nitrogen/2 or millimoles of organic base adsorbed by 100 g of dry clay vs. surface acidity are shown in Figs. 2 and 3 on which curves are drawn through the data points considered most reliable. Experimental reproducibility was particularly unsatisfactory in the higher pH ranges where it was impossible to free the clay-semiquinone complexes from excess base because the water-soluble diamine dihydrochlorides hydrolyzed to form the corresponding relatively insoluble free bases. Slightly oxidized floccules of free *p*-phenylenediamine and N,N-dimethyl-*p*-phenylenediamine were co-flocculated with clay particles at pH values of 5.5 and 6.5. To obtain reliable data it was necessary to make blank runs without clay and subtract the nitrogen found.

The benzidine semi quinone–clay complex also was found to be dispersed during washing, coloring the filtrate. It was necessary to reflocculate the suspended material and add it to the clay sample to obtain consistent data at pH values of 5.5 and 6.5.

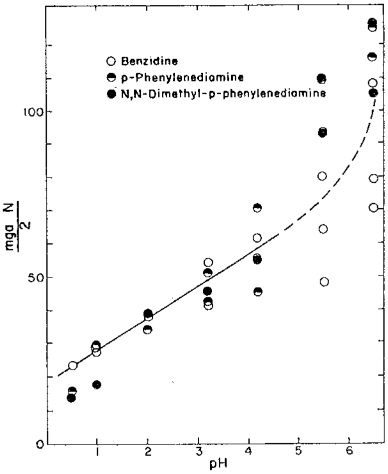

Figure 2.—Adsorption of semiquinone cations on Wyoming bentonite (montmorillonite).

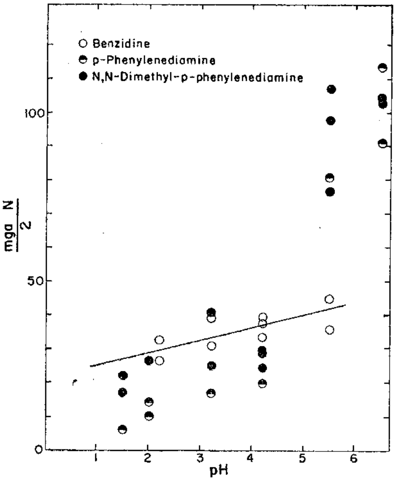

Figure 3.—Adsorption of semiquinone cations on hectorite.

In spite of these serious experimental difficulties, several significant conclusions can be drawn from the data presented in Tables 2 and 3 and Figs. 2 and 3:

(*a*) The amount of semiquinone adsorbed by both montmorillonite and hectorite increased uniformly with decrease of surface acidity in the pH range from 0.5 to 4.2.

(*b*) The ratios between the adsorption (in millimoles per 100 g dry clay) of the two semiquinones formed by one diamine, presumably representing one-electron and two-electron oxidation products of the same diamine, are approximately 2 : 1. The pH at which the semiquinone was judged to be entirely one form or the other was determined by the purity of hue. Essentially pure divalent semiquinones appeared to be formed at a pH of 0.5 to 1.5; the pure monovalent form apparently was formed at 4.2. Semiquinone colors at pH values of 5.5 and 6.5 were often masked by excess floccules of

TABLE 2.—EXPERIMENTAL DATA: ADSORPTION OF SEMIQUINONE CATIONS ON WYOMING BENTONITE

Surface Acidity in Terms of pH of Buffer Solution	Benzidine Dihydrochloride		*p*-Phenylenediamine Dihydrochloride		N,N-Dimethyl *p*-Phenylenediamine Dihydrochloride	
	milli-moles*	Color	milli-moles*	Color	milli-moles*	Color
0.5	23	Pale yellow	15	Pale green changing to pale blue	13	Pale violet to pink
1.0	29 27	Yellow	29	Pale green	17	Violet to pink
2.0	38	Bluish yellow	34	Yellowish green	39	Pale bluish green
3.2	54 41	Pale blue	51 43	Green	45	Bluish green
4.2	57 61	Blue	45 71	Deep green	55	Deep bluish green
5.5	94[1] 64[3] 30[3] 48[3]	Royal blue	109[2] 137[3] 134[3]	Dark violet	93[2] 110[3]	Dark green
6.5	108[1] 70[3] 79[3]	Royal blue	116[2] 140[3] 125[3]	Black with violet tinge	107[2] 136[3] 145[3] 126[3]	Greenish black

[1] These data were corrected by reflocculating dispersed benzidine–clay complex in filtrate and adding to sample before Kjeldahl analysis.

[2] These data were corrected for the presence of free excess diamine by making a blank run and subtracting the nitrogen found.

[3] These data were uncorrected.

* Millimoles adsorbed per 100 g dry clay.

free base when *p*-phenylenediamine and N,N-dimethyl-*p*-phenylenediamine were used.

(*c*) There was a sharp increase in measured semiquinone adsorption at pH values of 5.5 and 6.5, compared to the lower pH range.

TABLE 3.—ADSORPTION OF SEMIQUINONE CATIONS ON HECTORITE

Surface Acidity in Terms of pH of Buffer Solution	Benzidine Dihydrochloride		*p*-Phenylenediamine Dihydrochloride		N,N Dimethyl *p*-Phenylenediamine Dihydrochloride	
	milli-moles*	Color	milli-moles*	Color	milli-moles*	Color
1.5			6	Pale green	22 17	Pale pink
2.0			14 10	Yellowish green	27	Pink
2.2	32.5 26.3	Light yellow				
3.2	39 32	Bluish white	17	Green	25 41	Bluish green
4.2	38 34 40	Pale blue	30 20	Deep green	29 25	Deep bluish green
5.5	45[3] 36[3]	Blue	81[2] 144[3]	Dark violet	77[2] 97[3] 108[3]	Dark green
6.5		Royal blue	114[2] 91[2] 187[3]	Black with violet tinge	113[2] 114[3] 200[3]	Greenish black

[1, 2, 3] See Table 2.

* Millimoles adsorbed per 100 g dry clay.

(*d*) The previously reported base exchange capacities of the minerals agree more closely with the amount of semiquinone cations adsorbed at a pH of from 5.5 to 6.5.

(*e*) Wyoming bentonite shows a sharper increase of adsorption with increase of pH than does hectorite.

(*f*) Rather limited experimental results indicate that the amount of semiquinone cation adsorbed does not depend on whether the clay minerals are in the calcium or sodium form initially.

The results suggest further that, within the pH range from 0.5 to 4.2 the amount of semiquinone adsorbed cannot account fully for the reported BEC of the minerals (106 for Wyoming bentonite and 75 for hectorite). This has been interpreted to indicate that certain of the exchange sites are not occupied by semiquinone cations at low pH values. One would expect to find hydrogen or hydronium ions on exchange sites at the lower pH values. Of more importance, however, is the occurrence of " nonexchangeable " sites at all pH values below approximately 5. These nonexchangeable sites probably are occupied by cations of high field strengths—probably hydrated trivalent aluminum cations, although hydrated ferric ions, and possibly hydronium ions, may be present also. At pH values above approximately 5 the amphoteric metals, such as aluminum, occur only as anions and the concentration of hydronium ions is essentially nil; hence all exchange sites are occupied by semiquinone cations.

The cation exchange sites on montmorillonite thus may be divided roughly into a group of high energy sites, always occupied by " nonexchangeable " cations at pH values below about 5, and a group of lower energy sites occupied by semiquinone cations in this pH range. Further, at the lowest pH values some hydronium ions displace semiquinone cations. Titration curves of acid clays also indicate such a duality of levels of exchange site energy.

Distribution of Cations on Base Exchange Sites

The data discussed above exhibit a sharp increase in the amounts of semiquinone cation adsorption between pH values of 4.2 and 5.5. If one assumes that the meq of semiquinone adsorbed at a pH of 4.2 suffices to saturate all the lower energy exchange sites, the difference between this and the accepted base exchange capacity of the clay minerals represents higher energy sites occupied by "nonexchangeable" cations such as hydrated trivalent aluminum. This concept may be expressed analytically by modifying eq. (7) to read:

$$2Y_s^{++}+B_s^{+} = \text{meq of semiquinone adsorbed at pH 4.2 per 100 g dry clay.} \tag{8}$$

Hydronium ions are assumed not to be held on exchange sites at pH = 4.2. The quantity of nonexchangeable sites may then be calculated as:

$$\text{BEC} - (2Y_s^{++}+B_s^{+}) = \text{meq of nonexchangeable cations per 100 g dry clay.} \tag{9}$$

The results also indicate that adsorption of semiquinone cations at pH values of the order of 0.5 to 1.5 amounts to less than half that at pH 4.2. If one assumes that the number of nonexchangeable sites remains constant, it then is necessary to account for this discrepancy by assigning hydronium ions to the remaining vacant sites at the lowest pH values.

If the simpler theory as represented by eqs. (5), (6) and (7) is modified as indicated by eqs. (8) and (9), and if experimental values within the range of experimental error are selected to produce consistent calculated values, it is found that the calculated equilibrium constants, K^*, remain surprisingly constant, to a degree seldom exceeded in chemical kinetic studies. The calculated results based on this modified theory are presented in Tables 4 and 5. An arbitrary distribution of the measured amount of nitrogen adsorbed at a pH of 1.0 was made in each case by allocating 2 mga of nitrogen to the monovalent semiquinone cation form. The meq of nonexchangeable cations was calculated on the basis of eqs. (8) and (9) and was assumed constant throughout the range of pH under study. The calculated results in Tables 4 and 5 do not prove the theory presented herein to be valid, but they do demonstrate that the development is reasonable.

The *p*-phenylenediamine data were not considered reliable enough to justify similar calculations; furthermore, the colors observed with this diamine were less stable with time and no pure hues were formed at pH values corresponding to the behavior of the other two reagents.

Nature of the Oxidizing Agent and Conclusions

Throughout this paper it has been assumed that some property related to the clay mineral surface is responsible for its power to oxidize the organic compounds to their semiquinone forms. Although an effort has been made to determine the nature of the oxidant associated with montmorillonoid clay surfaces, no satisfactory progress has been made in this direction to date. The work reported herein is concerned solely with a study of the surface acidity variable.

The interpretation developed above concerning distributions of cations on clay mineral exchange sites appears to be consistent with our knowledge concerning the behavior of acid clays or hydrogen clays that normally is experienced during electrodialysis. The concept that hydrated aluminum cations migrate to cation exchange positions at low pH values is widely accepted. The modified theory outlined above apparently makes it possible for the first time to calculate the number of high-energy base exchange sites which should be satisfied by hydrated aluminum cations. The relative numbers of high- and low-energy sites is of the same order of magnitude as determined by acid-base titration curves in the authors' laboratory. The concept of high-energy and low-energy sites on montmorillonite is in agreement with results obtained by McAtee (1958).

ACKNOWLEDGMENTS

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TABLE 4.—CALCULATED RESULTS: ADSORPTION OF BENZIDINE ON WYOMING BENTONITE

Bulk Solution pH	Measured Amount of Nitrogen Adsorbed	Y_s^{++}	B_s^{+}	Calculated Equilibrium Constant[1]	$2Y_s^{++}+B_s^{+}$	Exchangeable Hydrogen Ions	Non-exchangeable Sites
	Milligram atoms of nitrogen (mga)/100 g dry clay			K*	Milliequivalents (meq)/100 g dry clay		
		2					
0.5	23[3]	22.75	0.25	288	46	14	46
1.0	28	27[2]	1[2]	270	55	5	46
2.0	35[3]	25	10	250	60	0	46
3.2	51[3]	8	43	294	59	1	46
4.2	59[3]	1.06	57.94	290	60	0	46[2]

[1] See equations (4) and (5).

[2] At a pH of 1 it is assumed that essentially all adsorbed semiquinone cations are in the divalent, lemon-yellow form. The choices of $Y_s^{++} = 37$ and $B_s^{+} = 1$ are arbitrary, based on the observation of an essentially pure lemon-yellow hue at this pH, and subject to equation (6). When this assumption is made, however, the approximate value of K^* is fixed. If no exchangeable hydrogen ions are adsorbed at a pH of 4.2, then the clay BEC minus $(2Y_s^{++}+B_s^{+})$ gives the fixed value for nonexchangeable cations, according to equations (8) and (9).

[3] These values of nitrogen found were within the range of experimental reproducibility and selected to satisfy requirements of constant K^* and consistent variations of other calculated quantities. They are not presumed, necessarily, to represent the only correct values, but rather to illustrate the reasonableness of the theoretical development.

TABLE 5.—CALCULATED RESULTS: ADSORPTION OF N,N-DIMETHYL-*p*-PHENYLENEDIAMINE ON WYOMING BENTONITE

Solution pH	Measured Amount of Nitrogen Adsorbed	P_s^{++}	G_s^{+}	Calculated Equilibrium Constant[1]	$2P_s^{++}+G_s^{+}$	Exchangeable Hydrogen Ions	Non-exchangeable Sites
	Milligram atoms of nitrogen/100 g dry clay			K*	Milliequivalents/100 g dry clay		
	2						
0.5	13[3]	12.75	0.25	161	26	31	49
1.0	18	17[2]	1[2]	170	35	22	49
2.0	31[3]	18	13	138	49	8	49
3.2	47[3]	5	42	188	52	5	49
4.2	56	0.6	55.4	171	57	0	49[2]

[2, 3] See Table 4.

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