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A theoretical explanation of the aggregation of humic substances as a function of pH and electrolyte concentration

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Abstract—The surface ionization and aggregation properties of humic acid samples obtained from a brown coal were examined by means of potentiometric and conductometric acid–base titrations, molar mass determination and coagulation experiments with NaCl. The surface ionization model was applied to the humic acid–Na-humate system to explain the dependence of the surface electric properties and the aggregation state on pH and electrolyte concentration. The considerable dependences of molar masses and coagulation values on pH were interpreted on the basis of model calculations.

Key words—humic acid, humate, aggregation, coagulation, ionization model

INTRODUCTION

The state of aggregation of humic substances is known to depend on their nature and the solvation conditions under which they exist. In an aqueous medium, humic acids can be dissolved or precipitated depending on the pH and electrolyte present. Such dissolution and precipitation take place continuously in nature, e.g. the formation of a brown color in solutions of alkaline soils, or in the formation of marine sediments. A theoretical explanation of these phenomena has not been published.

In their review, James and Parks (1982) suggested a new model for the description of the surface electric properties of different aqueous colloidal systems. This model gives a more realistic approach to the dissociation and ion-pair formation processes taking place on the surface, and to the electric properties determined by these equilibria. The solution of a system of equations describing both dissociation and electrical double-layer equilibria results in a quantitative description of the dependence of surface potential or charge and the associated properties on pH and neutral electrolyte concentration. Model calculations have been performed mainly for oxide hydrosols (James and Parks, 1982) and clays (James and Parks, 1982; Tombácz *et al.*, 1986; Tombácz *et al.*, 1990), but also for proteins (Steinhardt and Reynolds, 1969). A quantitative description of the surface electrical characteristics of humic acid and humate is problematic and was unknown until recently (Tombácz *et al.*, 1988b). It is well known that the macromolecular structure of humic colloids varies not only with pH, but also with ionic strength and sample concentration (Gosh and Schnitzer, 1980).

Marinsky (1985) published a model (two-phase model) to interpret the extreme sensitivity of weakly acidic (basic) polyelectrolytes equilibria to excess neutral salts. The characteristic differences between the protonation properties of weakly acidic (basic) salt-permeable and salt-impermeable gels were derived from the analysis of potentiometric titrations in the presence of excess neutral electrolytes when the data were evaluated on the basis of a two-phase model. This was extended to linear polyelectrolytes, too. Their rigidity or lack of rigidity and their permeability or impermeability to simple salt could be deduced with certainty from the plots of apparent pK vs (pH + pX) or pH alone. The plots of pK^{app} vs α as a function of ionic strength could be used to help correct the electrostatic disturbance of the Henderson–Hasselbalch equation. Evaluating the potentiometric titration curves of humic and fulvic acids the authors (Marinsky and Ephraim, 1986; Ephraim *et al.*, 1986) stated that in aqueous medium certain fulvic acids exist as essentially rigid, impermeable polymeric molecules, but others as flexible chains. These authors analyzed the dependences on fulvic acid and salt concentration but did not evaluate intrinsic dissociation constants.

Previously attempts were made to model proton binding by humic substances, considering their polymeric nature and their heterogenity, but most of these models took into consideration only one of these two factors. For example, intrinsic pK values were evaluated from potentiometric titrations in the site-binding model (Sposito, 1977; Paxéus and Wedborg, 1985) which neglected the electrolyte concentration effects, or the great variety of functional groups were overestimated in the continuum models (Gamble, 1972; Perdue and Lytle, 1983).

The coagulating effect of electrolytes on humic substances in aqueous solution is also known. Ling Ong and Bisque (1968) stated that the Schulze–Hardy rule, the theory of Derjaguin and Landau (1941), Verwey and Overbeek (1948) (DVLO-theory) and the ion radius effect are valid for the coagulation of humic substances, but no data have been published on the effect of pH, or more precisely on the joint effect of pH and neutral salts. Dental (1988) published a quantitative model of coagulation with aluminium salts, which described the suspension stability as a function of pH on the basis of electrokinetic characteristics of colloidal material. This model was used to describe coagulation in water containing humic substances which were considered merely as small colloids which contributed to the surface area in the system. Dental (1988) used the expression of Dempsey and O'Melia (1983) to characterize the surface charge and zeta potential of the fulvic acid as a function of pH and ionic strength.

The present study demonstrates the application of an ionization model to humic colloids, the determination of the material constants, and the results of calculations on a brown coal humic acid as an example. The results of the model calculations, i.e. the change to be expected in the aggregation state, are compared with molar masses determined at different pH values and electrolyte concentrations, and with coagulation values of humic acid and Na–humate solutions.

MATERIALS AND METHODS

We had to prepare a relatively well-defined, purified and fractionated humic acid sample to overcome the inherent heterogenity problem of humic substances considering both the particle or macromolecule size and the functional groups. Therefore, we chose a frequently used extraction and purification methods, and a special fractionation with neutral salts which provides a relatively homogeneous fraction from the respect of sensitivity against the electrolytes which depends on both the quality and the quantity of functional groups on the unit surface.

Humic acid was obtained from brown coal (Tatabánya, Hungary) and 0.1 mol/dm^3 NaOH. It was purified in the usual way (Schnitzer and Khan, 1972), then fractionated with NaCl. The raw humic acid was dissolved in 0.1 mol/dm^3 NaOH, then precipitated with 0.1 mol/dm^3 HCl at $\mathrm{pH} < 2$. After standing for 2 h the suspension was centrifuged (5000 rpm, 30 min). The precipitate was collected and dissolved again in alkaline solution. This procedure was repeated three times. The ash content of humic acid was reduced by HF/HCl treatment (Schnitzer and Khan, 1972). The dried, ground humic acid was extracted with benzene/ethanol in a Soxhlet apparatus for 72 h to remove the tar component. The dried sample (vacuum oven, 60°C) was dissolved in 0.1 mol/dm^3 NaOH solution, calculated to be equivalent to the total acidity of the humic acid measured by conductometric titration. A weakly alkaline humate solution (0.5 g humic acid and 15 g NaCl/100 cm^3) was prepared by the diluting a concentrated humate solution with salt solution. Some humic acid precipitated (about 2.5%) and was removed by centrifugation (5000 rpm, 30 min). The NaCl concentration in the supernatant liquid was increased to 20 g/100 cm^3 by the addition of solid NaCl. After stirring for 2 h the humic precipitate ($\sim 15\%$) was separated (centrifuge) and washed twice with dilute HCl ($\mathrm{pH} = 2$), then with distilled water ($\times 3$). In each washing cycle the solid was separated by centrifugation (5000 rpm, 15 min) and redispersed by stirring. The dried humic acid sample (vacuum oven at 60°C) had an ash content of 0.8%.

We examined the different properties of humic acid and Na–humate solutions. Each humic acid solution was made by passing an alkaline humate solution through a column of cation-exchange resin (hydrogen form). Na–humate solutions were made by neutralizing this humic acid with an amount of NaOH equivalent to the total acidity of the sample measured by conductometric titration (Schnitzer and Khan, 1972).

Conductometric and potentiometric titrations on 0.5 g/100 cm^3 humic acid solutions were performed with 0.1 mol/dm^3 NaOH in solutions containing 0 or 10 mmol/dm^3 NaCl, respectively, with exclusion of atmospheric CO_2. The equilibrium pH and conductivity values were read 3 min after the addition of each aliquot of titrant. Radelkis (Hungary) OP-205/1 and OK-102 instruments were used.

The number average molar masses of humic acid and Na–humate were determined at 5 and 500 mmol/dm^3 NaCl concentrations by membrane osmometry. Measurement in a dilute solution of a neutral salt was necessary to screen the charges of polyions (Morawetz, 1966). The low gradient of the reduced osmotic pressure (π/c_p) vs humic acid or humate concentration (c_p) curves (Fig. 4) show clearly the quasi-ideal behavior of these solutions. An extrapolation procedure (Morawetz, 1966) for polyelectrolytes was used to calculate the molar masses. The dependence of the reduced osmotic pressure (π/c_p) of the polyelectrolyte solution on the polymer concentration (c_p) is given by the equation:

$$\frac{\pi}{c_p} = RT\left(\frac{1}{M} + \frac{c_p}{4a^2c_s}\right) \tag{1}$$

where R = gas constant, T = temperature, M = molar mass of polyelectrolyte, c_s = salt concentration and $a = M/z$, i.e. the molecular mass per charge number of the molecule. According to equation (1), the reduced osmotic pressure is a linear function of the polymer concentration. The number average molar mass can be calculated from the intercept of the straight line on the π/c_p axis. Osmotic pressure values were determined in the humic acid and Na–humate concentration range 0.125–1.0 g/100 cm^3, at 310 K, using a Knauer (West Berlin) membrane osmometer and a Sartorius (N 11539) superfine membrane.

Coagulation values of humic acid (2 and 0.5 g/100 cm^3) and Na–humate (0.4 g/100 cm^3) solutions were determined by using NaCl as coagulating electrolyte. After standing for 24 h, samples with increasing NaCl concentrations were centrifuged (5000 rpm, 30 min) and the extinctions of the resulting supernatant liquids, which contained only the non-coagulated portion of humics, were measured at 450 nm. The percentage of the humic acid or humate which remained in the dissolved state, after coagulation, was calculated on the basis of calibration curves for humic acid and Na–humate, respectively.

RESULTS

With regard to the application of an ionization model, humic colloids can be considered, to a first approximation, as substances with bifunctional surfaces, since they contain two main acidic groups with different dissociation constants (Gamble, 1972; Burch *et al.*, 1978; Tombácz *et al.*, 1988b). Contemplating more than two intrinsic dissociation constants (Sposito, 1977; Paxéus and Wedborg, 1985; Perdue and Lytle, 1983) would complicate this calculation and simple analytical solutions of the equations would be impossible. Only the acidic groups of humic substances are considered because these are the most important pH-dependent charges on soil organic matter (Sparks, 1986).

The protolytic reactions for the ionization of the assumed functional groups are:

$$\text{S—COOH} \rightleftharpoons \text{S—COO}^- + \text{H}_\text{S}^+ \quad \text{(site type 1)}$$

$$\text{S—OH} \rightleftharpoons \text{S—O}^- + \text{H}_\text{S}^+ \quad \text{(site type 2)}$$

where H_S^+ denotes the protons (in reality hydronium ions) in the surface layer. The difference in electrical potential between surface and solution (ψ_0) results in a difference in the chemical potential of the protons, and hence in their activity; thus:

$$\{\text{H}_\text{S}^+\} = \{\text{H}^+\}\exp(-y_0) \tag{2}$$

where $\{\text{H}_\text{S}^+\}$ is the activity of protons in the surface layer, $\{\text{H}^+\}$ is the corresponding activity in the bulk, and y_0 is the reduced potential, i.e. $y_0 = ve\psi_0/kT$, where v = valence of the ions, ψ_0 = surface potential, $kT = 4.04 \quad 10^{-21}$ J at room temperature and e = electronic charge.

The intrinsic ionization constants are:

$$K_{\text{a}1}^{\text{int}} = \frac{\{\text{S—COO}^-\}}{\{\text{S—COOH}\}}\{\text{H}^+\}\exp(-y_0) \tag{3}$$

$$K_{\text{a}2}^{\text{int}} = \frac{\{\text{S—O}^-\}}{\{\text{S—OH}\}}\{\text{H}^+\}\exp(-y_0) \tag{4}$$

The surface densities (sites/m^2) of the different type sites are N_1 = type 1 and N_2 = type 2, with $N_\text{S} = N_1 + N_2$, the number of all the ionizable sites.

The following expression was deduced (Tombácz *et al.*, 1988b) for the fractional surface ionization or degree of dissociation as a function of concentrations instead of activities:

$$\alpha = \frac{\dfrac{K_1^{\text{int}}}{[\text{H}^+]}\exp y_0 + \dfrac{N_2}{N_1}\left(\dfrac{K_1^{\text{int}}}{[\text{H}^+]}\exp y_0 + 1\right)\left(\dfrac{K_2^{\text{int}}}{[\text{H}^+]}\exp y_0 + 1\right)^{-1}\dfrac{K_2^{\text{int}}}{[\text{H}^+]}\exp y_0}{1 + \dfrac{K_1^{\text{int}}}{[\text{H}^+]}\exp y_0 + \dfrac{N_2}{N_1}\left(\dfrac{K_1^{\text{int}}}{[\text{H}^+]}\exp y_0 + 1\right)} \tag{5}$$

This equation considers only the inner part of the electrical double-layer (edl) formed by surface ionization. A fraction α' can be defined for the diffuse part of the edl, if exponential distribution of the counter ions is presumed in accordance with the Gouy–Chapman theory:

$$\alpha' = \frac{0.1174}{eN_\text{S}}c^{1/2}\sin h(y_0/2) \tag{6}$$

where c is the concentration of counter-ions in mol/dm^3. On the surface at a given pH and electrolyte concentration, only one ionization state (i.e. one surface potential) exists which fulfils both conditions, i.e. $\alpha = \alpha'$.

The above model takes into consideration simultaneously the effects of pH and electrolyte concentration on the structure of the edl, which determines the stability of aqueous colloids.

The constants of this model, i.e. the intrinsic ionization constants and the density of the surface sites, can be calculated from experimentally-determined data, and hence the individual features of the stability of a given humic acid–humate system can be defined.

We consider humic substances as small, planar colloids with two pH-dependent surface sites. In the similar model of Dempsey and O'Melia (1983), used for the estimation of surface and zeta potential as a function of pH and ionic strength, fulvic acid was considered as consisting of small, spherical, monofunctional colloids.

The total density of ionizable sites (N_s) was calculated from the specific surface of humic acid following the method of Tan and McGreery (1976), by supposing a disc shape with a thickness of 0.465 nm (Tombácz *et al.*, 1984) and using a specific amount of functional groups (5.974 meq/g), as measured by conductometric titration [see Fig. 1(a)]. The N_s value is influenced by the choice of the shape and dimensions of humic molecules. It has previously been shown by X-ray diffraction of long chain alkyl ammonium humate intercalculation complexes for the brown coal (Tatabánya) humic acid (Tombácz

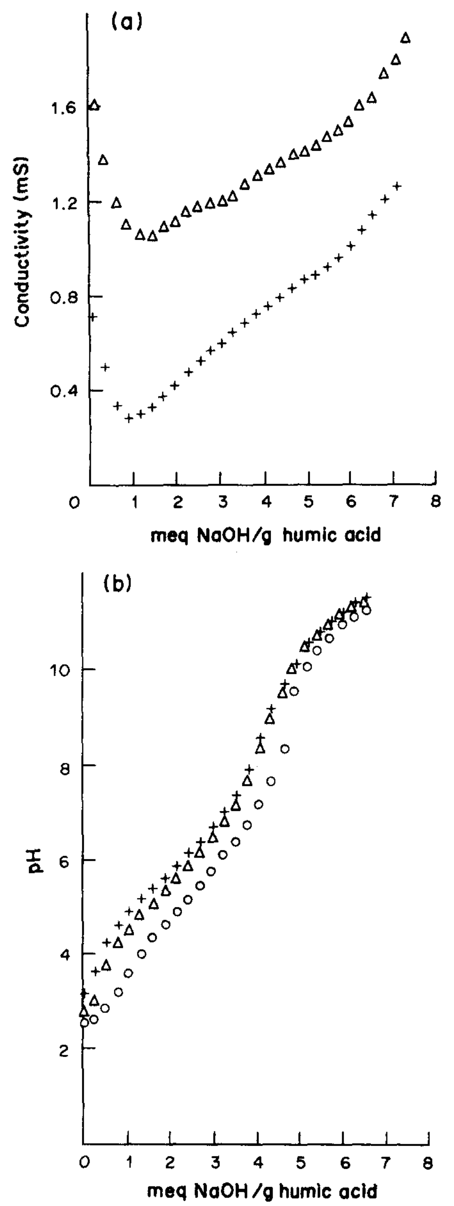

Fig. 1. Conductometric (a) and potentiometic (b) titrations in distilled water (+) and in 10 mmol/dm^3 NaCl solution (Δ).

et al., 1984) and some other samples with different origins (Tombácz *et al.*, 1988a) that the original humate units have a layer structure; the thickness of layer determined by an extrapolation method was between 0.45 and 0.84 nm depending on the origin of the samples. A disc model is the most probable shape in the case of layer structure materials. The ratio of the two kinds of acidic functional groups (N_1/N_2) was calculated from the equivalent amounts relating to the given end-points of the conductometric curve [see also Fig. 1(a)] which is generally used to determine the amounts of functional groups in this type of model calculation (Stone-Masui and Watillon, 1975; James and Parks, 1982).

The intrinsic ionization constants were determined on the basis of an extrapolation procedure (Stone-Masui and Watillon, 1975; James *et al.*, 1978) devised primarily for polymer latexes. At each point of the titration, the acidity quotients ($pQ = pH - \log \alpha/(1-\alpha)$, where α is the fractional surface charge) can be calculated from the potentiometric and conductometric experimental data (see Fig. 1). The intrinsic ionization constants relating to two dissociation steps can be determined by extrapolation of the points for the given steps, as theoretically the following equation can be deduced for the first step:

$$pK_1^{int} = pH - \log\frac{\alpha}{1-\alpha} + \frac{y_0}{2.3} + \log\left[\frac{1}{C} + \left(1 - \frac{1}{C}\right)\left(\frac{[S\text{—}COOH]}{[S\text{—}COOH] + [S\text{—}OH]}\right)\right] \qquad (7)$$

and for the second step:

$$pK_2^{int} = pH - \log\frac{\alpha}{1-\alpha} + \frac{y_0}{2.3} + \log\left[1 + \frac{[S\text{—}COOH]}{[S\text{—}COOH] + [S\text{—}OH]}(C-1)\right] \qquad (8)$$

where $C = K_1^{int}/K_2^{int}$ and its probable value is greater than 10^3 (James and Parks, 1982), and [S—COOH] and [S—OH] are the activities of unionized groups. If we plot the negative logarithm of the acidity quotients ($pQ = pH - \log\alpha/(1-\alpha)$) as a function of the fractional surface charge (α) and extrapolate the points of the two steps separately to zero charge (i.e. when $y_0 = 0$), we can evaluate the pK^{int} values. pK_1^{int} can be calculated from the extrapolated value relating to the points of the first step if we correct this according to equation (7). At zero charge, the last term in equation (7) can be calculated from the amounts of the two kinds of functional groups [the first endpoint of the conductometric curve which belongs to the stronger acidic sites gives the amount of [S—COOH] and the second one the sum of [S—COOH] and [S—OH], Fig. 1(a)], since the value of $1/C$ is negligibly small, this term then being

$$\log\frac{[S\text{—}COOH]}{[S\text{—}COOH] + [S\text{—}OH]} \qquad (9)$$

The value of this is $\log(0.977/5.974) = -0.786$.

pK_2^{int} can be calculated directly from the extrapolated value relating to the points of the second step, since when the weak acidic groups are ionizing (the second ionization step), the strong acidic groups are already fully ionized, i.e. [S—COOH] is zero, so the last term of equation (8) will be zero. The pH-$\log\alpha/(1-\alpha)$ vs α functions and the extrapolated pK^{int} values are shown in Fig. 2. These pK values relating to the dissociation of carboxyl groups ($pK_1 = 3.38$) and phenolic hydroxyls ($pK_2 = 6.08$) fall

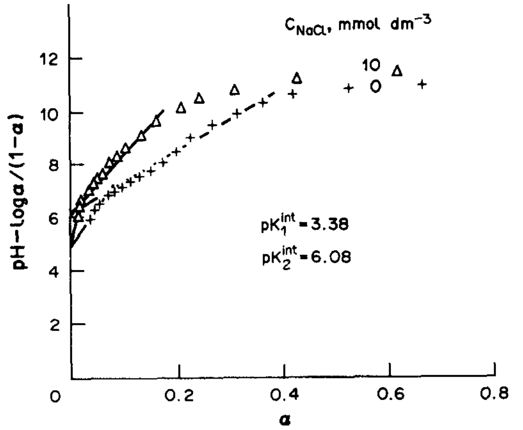

Fig. 2. Variation of surface acidity quotient with fractional surface charge (α).

in the range of values published in the literature (Sparks, 1986), i.e. for carboxyl groups $pK_a = 0.2$–6.2 and for phenolic hydroxyls $pK_a = 4$–10.

We calculated the dependences of the surface potential of the humic acid–humate systems on pH and 1:1 electrolyte concentration (see Fig. 3) by using equations (5) and (6), and the measured and calculated constants as follows:

$$N_s = 9.2 \times 10^{17} \text{ sites m}^{-2} \qquad K_1^{int} = 4.17 \times 10^{-4}$$

$$N_2/N_1 = 5 \qquad K_2^{int} = 8.34 \times 10^{-7}$$

The changes are very great with respect to both the pH and the electrolyte concentration and the curves form two steps. This latter is the result of a considerable difference between the ionization abilities of the two kinds of functional groups. The sensitivity of humic acid and humate solutions to the effects of pH and electrolyte concentration, i.e. their colloidal stability, can be explained on the basis of the ionization model. It is well known from the DLVO theory that the surface potential must be above a certain value for an electrically stabilized system; the higher its value, the greater the repulsion between the particles. On the basis of model calculations, it is to be expected that the repulsion between the particles decreases with both decreasing pH and increasing electrolyte concentration, i.e. the degree of aggregation increases; on the other hand it is to be expected that the precipitation of humic acid and humate solutions takes place at electrolyte concentrations differing considerably from each other, but at approximately the same surface potential.

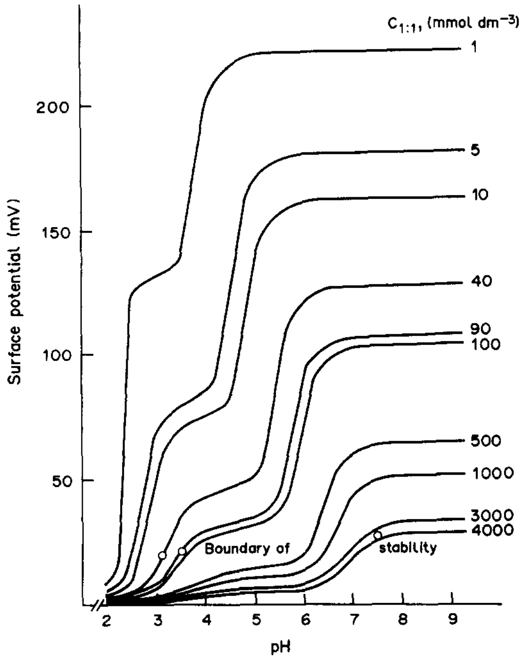

Fig. 3. Variation of surface potential (ψ_0) calculated from ionization model with pH at different 1:1 electrolyte concentrations.

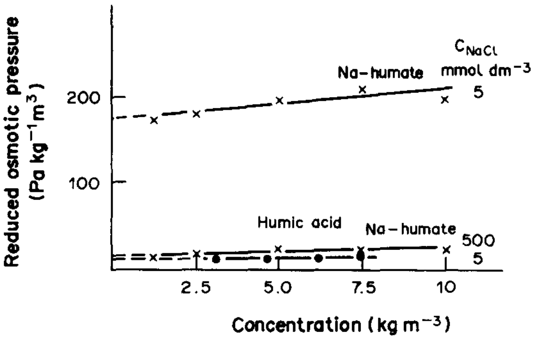

Fig. 4. Dependence of reduced osmotic pressure of humic acid and Na–humate solutions on their concentrations at 310 K.

We performed molar mass determination and coagulation experiments to verify the theoretical predictions. Molar masses of humic acid and Na–humate, calculated from reduced osmotic pressure vs concentration functions (see Fig. 4), are shown in Table 1 together with the experimental pH and electrolyte concentration data, and the surface potentials derived from model calculations (see Fig. 3). It can be seen that the molar masses of Na–humate determined in 5 and 500 mmol/dm^3 NaCl solution differ from each other considerably, in parallel with the difference between the ψ_0 values. On the other hand, the molar masses of humic acid in 5 mmol/dm^3 NaCl solution and of Na–humate in 500 mmol/dm^3 NaCl solution are similar in magnitude, in parallel with slightly different ψ_0 values.

The coagulation values of humic acid and humate solutions were determined on the basis of Fig. 5. They were given as the salt concentrations which precipitated more than 95% of humic colloids. The

Table 1. Comparison of surface potentials calculated from ionization model with experimental number average molar masses under the same conditions

Sample	ψ_0 (mV)	pH	c_{NaCl} (mmol/dm^3)	M_n (g/mol)
Na–humate	170	8	5	14,500
	60	8	500	203,000
Humic acid	50	2.5	5	260,000

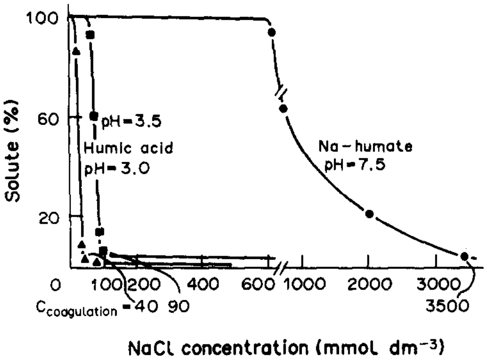

Fig. 5 Determination of coagulation value ($c_{coag.}$): percentage of non-coagulated humic acid and Na–humate after electrolyte treatment as a function of NaCl concentration.

coagulation of colloids or their stability domains are frequently presented in terms of their removal by either settling or filtration, measuring the turbidity or the optical density of the supernatant liquids as a degree of destabilization (Dental, 1988). Dempsey *et al.* (1984) published data on the coagulation of fulvic acid which was characterized in the same way. With regard to the electrolyte concentrations, 40, 90 and 3500 mmol/dm^3 depending on the pH of solutions, and the pH values relating to them, the surface potential existing under these conditions according to the model calculations are given in Fig. 3. It can be seen that they lie between 20 and 25 mV. This indicates the boundaries of stability for this humic acid–humate system. Under such conditions (pH and 1:1 electrolyte concentration), when the surface potential is greater than 25 mV, this humic material will be in the dissolved state; however, when the potential is smaller than 20 mV, the material will be precipitated. This stability/instability border can be reached reversibly from both sides by changes either in the pH of humate solutions or in their neutral electrolyte content.

CONCLUSION

It seems that the application of the simple ionization model to humic substances is a relatively good theoretical approach for the explanation of their sensitivity to pH and neutral electrolytes. This model could be refined if more dissociation steps, the presence of amino groups and the specific effects of electrolyte were also taken into account.

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