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Acid-Base Properties of 2-Morpholinoethanesulfonic Acid (MES), Complexation Reaction of Cu^{II}-MES, and Interaction of Hydrous Manganese Oxide Surface with Cu^{II} in MES Buffer

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Abstract: The acidity constants of 2-morpholinoethanesulfonic acid (MES) have been determined at various ionic strengths; $pK_{a1} = 1.99$ and $pK_{a2} = 6.21$ at ionic strength $I = 0.1$ M. The conditional stability constant of Cu^{II}-MES complex has been measured by means of a Cu^{II}-ion selective electrode: $\lg {}^{c}K_{Cu\text{-}MES} = 1.39 \pm 0.07$ at pH = 5.57. Furthermore the interaction between Cu^{II} and hydrous manganese oxide surface in MES buffer was studied by differential pulse polarography. Conditional stability constants for Cu^{II}-MnO_x complex (SCu) at three pH values were calculated by two methods: van den Berg-Ružić method as well as the Scatchard plot yield corresponding values for $\lg {}^{c}K_{SCu}$. Both methods indicated the presence of one class of equivalent binding sites. The results of this investigation corroborate that MES is a suitable buffer for studying metal-MnO_x interactions.

Trace metal ions present in aquatic systems are transported both in the dissolved and particulate forms. In these systems, they may exist in diverse forms[1], for instance:

- as «free» metal ion;
- complexed to «simple» inorganic and organic ligands;
- complexed to coordinating sites of naturally occuring organic macromolecules, colloids or mineral particles such as hydrous oxides.

Organic macromolecules such as humic substances, microorganism surfaces and their exudates, and hydrous oxide surfaces act as coordinating sites for metal ions. The interaction between metal ions and the coordinating sites is strongly pH-dependent as shown by the reaction in equation (1)[2,3]

$$a \equiv SH_n + M^{z\oplus} \rightleftarrows \equiv S_aM^{(z-an)\oplus} + na\,H^{\oplus} \quad (1)$$

The value of n is usually found to be either 1 or 2 indicating that the metal forms either 1:1 or 1:2 complexes with the coordinating sites (≡S).

Since reaction (1) is pH-dependent, complexation measurements have to be performed in a well-buffered medium. For this purpose, the chosen buffer should exhibit the following properties:

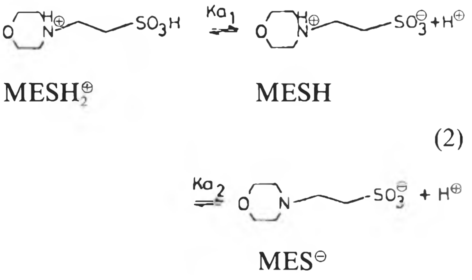
- it should have a good buffering capacity in the pH range of interest;
- it should not form complexes with the test metal ion.

Some buffers that have been used for biological studies[4] seem to exhibit these properties but very little information is available on their acid-base properties, e.g. the dissociation constants at various ionic strengths, and their complexing properties towards metal ions, particularly the heavy metal ions.

Thus the aim of this investigation was to determine:
(i) the acidity constants of the biological buffer 2-morpholinoethanesulfonic acid (MES);
(ii) the stability constant of Cu-MES complex;
(iii) the interaction of Cu^{II} with hydrous manganese oxide surface in MES buffer at constant ionic strength.

Acidity constants of MES

The dissociation equilibria of MES are given by



$MESH_2^{\oplus}$ MESH $MES^{\ominus}$ (2)

and the dissociation constants are defined as:

$$K_{a1} = \frac{[MESH]\,[H^{\oplus}]}{[MESH_2^{\oplus}]} \cdot \frac{\gamma_{H\oplus}}{\gamma_{MESH_2\oplus}} \quad (3a)$$

$$K_{a2} = \frac{[MES^{\ominus}]\,[H^{\oplus}]}{[MESH]} \cdot \gamma_{MES\ominus} \cdot \gamma_{H\oplus} \quad (3b)$$

the activity coefficients are denoted by γ. Equation (3b) can be rewritten as:

$$pK_{a2} = pH + \lg \frac{[MESH]}{[MES^{\ominus}]} \cdot \frac{1}{\gamma_{MES\ominus}} \quad (3c)$$

pK_{a1} cannot be determined directly from pH titration curve since RSO_3H is a strong acid. However, its value may be obtained if the pK_{a2} value and the isoelectric pH are known.

Evaluation of K_{a2}: MESH and $MES^{\ominus}$ concentration may be calculated from mass and charge balance equations.

Mass balance:
$$[MES]_T = [MESH] + [MES^{\ominus}] \quad (4a)$$

Charge balance:
$$[MES^{\ominus}] + [OH^{\ominus}] = [H^{\oplus}] + [Na^{\oplus}] \quad (4b)$$

$[H^{\oplus}]$ and $[OH^{\ominus}]$ are given by:

$$[H^{\oplus}] = \frac{10^{-pH}}{\gamma_{H\oplus}}\,;\ [OH^{\ominus}] = \frac{10^{-(14-pH)}}{\gamma_{OH\ominus}} \quad (5)$$

Thus, by measuring the pH of the solution and substituting its value and the calculated values of MESH and $MES^{\ominus}$ in equation (3c), pK_{a2} can be evaluated.

Isoelectric pH: The pH at which MESH is solely present as uncharged MES is defined as the isoelectric pH. The net charge Q of MES in the solution is given by:

$$-Q = C_B + [H^{\oplus}] - [OH^{\ominus}]$$
$$= [MES^{\ominus}] - [MESH_2^{\oplus}] \quad (6)$$

where C_B is the total concentration of the base. Thus Q can be calculated as a function of pH. Extrapolation of pH vs Q curve to $Q = 0$ will yield the value of isoelectric pH (pH_{ie}). pH_{ie} can be written as:

$$pH_{ie} = \frac{1}{2}\,(pK_{a1} + pK_{a2}) \quad (7)$$

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Thus pK_{a1} can be computed from equation (7).

Stability constant of Cu^{II}-MES complex

The complex formation reaction between $Cu^{2\oplus}$ and $MES^{\ominus}$ can be described as follows:

$$Cu^{2\oplus} + MES^{\ominus} \overset{K}{\rightleftharpoons} CuMES^{\oplus} \qquad (8)$$

$$K = \frac{[CuMES^{\oplus}]}{[Cu^{2\oplus}]\,[MES^{\ominus}]} \qquad (9)$$

Since $H^{\oplus}$ also competes for $MES^{\ominus}$, the following equilibria should also be taken into account:

$$MES^{\ominus} + H^{\oplus} \rightleftharpoons MESH \qquad (10a)$$

$$MESH + H^{\oplus} \rightleftharpoons MESH_2^{\oplus} \qquad (10b)$$

The concentration of $MES^{\ominus}$ at a given pH may be calculated from the degree of complexation α^{H}_{MES} which is defined by *Ringbom*[5] as:

$$\alpha^{H}_{MES} = \frac{[MES]_T}{[MES^{\ominus}]} = 1 + \frac{1}{K_{a1}}[H^{\oplus}] + \frac{1}{K_{a1}\cdot K_{a2}}[H^{\oplus}]^2 \qquad (11)$$

and the conditional stability constant ${}^{c}K_{Cu\text{-}MES}$ can be written as:

$${}^{c}K_{Cu\text{-}MES} = \frac{[CuMES^{\oplus}]}{[Cu^{2\oplus}]\left(\dfrac{[MES]_T}{\alpha^{H}_{MES}} - [CuMES^{\oplus}]\right)} \qquad (12)$$

$[CuMES^{\oplus}]$ can be calculated from the mass balance for total copper ion concentration $[Cu]_T$:

$$[Cu]_T = [Cu^{2\oplus}] + [CuMES^{\oplus}] \qquad (13)$$

$[Cu^{2\oplus}]$ can be measured with a copper ion selective electrode.

Complex formation with hydrous manganese oxide surface

Hydrous oxides exhibit polyligand properties similar to those of the so-called humic and fulvic acids, algae, and biological cell surfaces. Therefore one may expect these oxides to show analogous types of interactions with trace metal ions[6]. Hence, conceptual models used for describing the organic macromolecules–metal ions interactions may be extended to hydrous manganese oxide. The binding parameters can be evaluated by several methods[7]. Two of the methods are described below.

1. *van den Berg-Ružić method*[8,9]: The interaction between Cu^{II} and surface binding sites, S, may be written as:

$$S + Cu^{2\oplus} \rightleftharpoons SCu \qquad (14)$$

Because $H^{\oplus}$ competes for S, conditional stability constants are used to describe the complexation at constant pH. In addition, if the buffer employed to keep the pH constant competes for $Cu^{2\oplus}$ as shown by equation (8), then this reaction has to be taken into account.

The conditional stability constant for surface complexation in MES buffer can be expressed as:

$${}^{c}K_{SCu} = \frac{[SCu]}{[Cu^{2\oplus}]'\,[S]} \qquad (15)$$

where

$$[Cu^{2\oplus}]' = [Cu^{2\oplus}] + [CuMES^{\oplus}] \qquad (16)$$

The mass balances for total $[Cu]_T$ and $[S]_T$ are given by:

$$[Cu]_T = [Cu^{2\oplus}]' + [SCu] \qquad (17a)$$

$$[S]_T = [S] + [SCu] \qquad (17b)$$

The concentration of Cu^{II}-hydroxo complexes would be negligible under the pH conditions chosen for this study.

$[Cu^{2\oplus}]'$ represents the reducible forms of copper and it may be measured by differential pulse polarography (DPP). Combining the equations (15)–(17b) and rearranging yield the following expression:

$$\frac{[Cu^{2\oplus}]'}{[Cu]_T - [Cu^{2\oplus}]'} = \frac{1}{[S]_T\cdot{}^{c}K_{SCu}} + \frac{1}{[S]_T}\cdot[Cu^{2\oplus}]' \qquad (18)$$

Thus a plot of the left hand side term vs $[Cu^{2\oplus}]'$ should give a straight line of slope equal to $1/[S]_T$ and intercept equal to $1/[S]_T\,{}^{c}K_{SCu}$

$${}^{c}K_{SCu} = \text{slope/intercept} \qquad (19)$$

provided 1:1 complex is formed.

2. *Scatchard plot method*[10,11]: Application of this method requires a knowledge of the total binding sites $[SOH]_T\cdot[SOH]_T$, i.e. the maximum exchange capacity[12] is defined as

$$[SOH]_T = [SOH_2^{\oplus}] + [SOH] + [SO^{\ominus}] \qquad (20)$$

If there are n_i non-equivalent class of sites per molecule of SOH, then the ith conditional stability constant ${}^{c}K^{i}_{SCu}$ for the complexation of a metal ion by ith site is given by:

$${}^{c}K^{i}_{SCu} = \frac{[SCu]}{[Cu^{2\oplus}]\,(n_i\,[SOH]_T - [SCu])} \qquad (21)$$

If we define $\bar{\nu}$ as:

$$\bar{\nu} = \frac{\text{bound metal}}{\text{total surface}} = \frac{[SCu]}{[SOH]_T} \qquad (22)$$

then equation (21) becomes:

$$\frac{\bar{\nu}}{[Cu^{2\oplus}]'} = {}^{c}K^{i}_{SCu}\cdot n_i - {}^{c}K^{i}_{SCu}\cdot\bar{\nu} \qquad (23)$$

For the simplest case, i.e. when there is only one class of binding sites, the Scatchard plot would yield a straight line of slope equal to $-K_i$ (i = l). From the intercept, the value of n_i can be calculated. However care should be taken when n_i is evaluated by this method, since its value may be underestimated. *Klotz*[13] has in fact shown that n_i determination by extrapolation of the Scatchard plot is only valid if the Klotz plot ($\bar{\nu}$ vs $\lg[Cu^{2\oplus}]'$ gives a S-shaped curve with an inflection point at the half maximum binding ($n_i = n = 1/2$), otherwise an underestimated value is obtained for the number of binding sites.

In general, Scatchard plots for Cu^{II}-fulvic acid system are found to be curved-upward indicating that more than one class of binding sites exist[14–18].

In this study, the conditional stability constants have been calculated using both these methods.

Experimental

Determination of pK_{a2} of MES: 10 mL of 0.1 M stock MES, 5 mL of 0.1 M NaOH, and varying amounts of 1.0 M $NaClO_4$ were pipetted into a series of 100 mL volumetric flasks and diluted up to 100 mL mark with bidistilled water. The final $NaClO_4$ concentration in these solutions varied between 0.005–0.25 M. All solutions were thermostated at 25.0 ± 0.1 °C. The 3 M internal reference solution of the glass combination electrode was replaced by 3 M NaCl in order to avoid $KClO_4$ precipitation.

Potentiometric determination of isoelectric pH of MES: 25 mL solutions containing 0.01 M MES and varying concentrations of $NaClO_4$ ($0.05 \leqslant I \leqslant 0.2$ M) were titrated with 0.1 M NaOH. 0.05 mL increments of the base were made and the corresponding pH were measured after 3 min. The total volume of the added base was 2 mL. These measurements were made at 4 different ionic strenghts.

Potentiometric determination of the stability constant of Cu^{II}-MES complex: 20 mL solution containing 10^{-2} M MES and 0.1 M $NaClO_4$ (pH = 5.57) was titrated with $5\cdot10^{-3}$ M $Cu^{2\oplus}$ and the free copper ion concentration was measured by means of a Tacussel $Cu^{2\oplus}$ ion-selective electrode. Stable potential readings were recorded after each titrant increment and the free $Cu^{2\oplus}$ concentration was calculated from Nernst equation:

$$E = E' + S\lg[Cu^{2\oplus}] \qquad (24)$$

where E is the measured potential, E' is a constant, S is the slope of the electrode ($S = 2.3\,RT/2F$, $T = 298$ K). E' and S were obtained from the calibration curve constructed prior to the Cu^{II}-MES titration. S and E' were found to be 29.8 mV and 195.4 mV, respectively (r = 1.000).

Polarographic measurements: Before investigating the adsorption of Cu^{II} on MnO_x, kinetic studies were performed to determine the optimal conditions for adsorption measurements. For this purpose, known amounts of $Cu^{2\oplus}$ were added to a solution containing MnO_x suspension, 0.02 M MESNa/MESH buffer (pH = 6), and 0.1 M $NaClO_4$ and polarograms were recorded at various intervals of time. The results showed that equilibrium was attained after 130 min for the highest Cu^{II} concentration (Fig. 1), i.e. the complexation/adsorption is a fairly slow process.

In this study, the sample of MnO_x was prepared according to *Gadde* et al.[19] and was freeze-dried. MnO_x has the following physico-chemical characteristics[20,21]: $x = 1.98 \pm 0.01$, surface area 181 ± 3

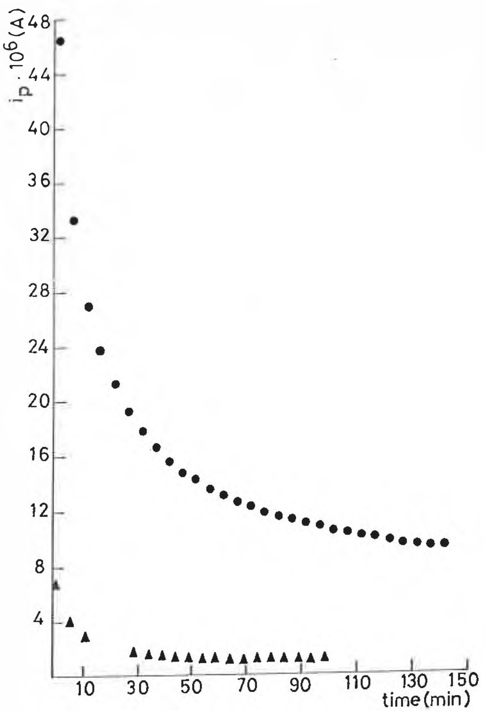

Fig. 1. Kinetics of complexation of Cu^{II} *by hydrous manganese oxide surface.* ● $[Cu^{2\oplus}]_T = 4.96\ 10^{-4}$ M, ▲ $[Cu^{2\oplus}]_T = 1.24\ 10^{-4}$ M; $[MnO_x] = 0.276\ g \cdot L^{-1}$; $I = 0.1$ M $NaClO_4$; $pH = 6$ *(buffer: MESNa/MESH 0.02* M*).*

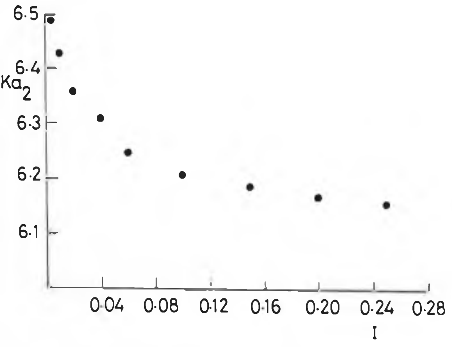

Fig. 2. pK_{a2} *as a function of ionic strength I.*

$m^2\ g^{-1}$, maximum exchange capacity 2.04 ± 0.03 mol kg^{-1}, $pH_{zpc} = 2.47 \pm 0.04$, $pK_{a1}^{int} = 0.66 \pm 0.01$ and $pK_{a2}^{int} = 4.28 \pm 0.01$.

The adsorption measurements were made using the batch method. Stock MnO_x suspension (0.2–0.25 g L^{-1}) was prepared in a solution containing 0.02 M MESNa/MESH buffer and 0.1 M $NaClO_4$. Its pH was adjusted to the appropriate value with $HClO_4$ or NaOH. 40 mL aliquots of the suspension were placed in polypropylene beakers and appropriate amounts of $Cu^{2\oplus}$ were added to each of these suspensions. The suspensions were stirred for 150 min on a shaker (Kotterman Mod. 4.031). Then the DPP polarograms were run after degassing the suspensions for 15 min with nitrogen (99.999%).

Polarograms were obtained with a Metrohm Polarecord E 506. Three electrode systems were used with Pt as the auxilliary electrode, dropping Hg as the working electrode, and Ag/AgCl/NaCl (3M) as the reference electrode. A pulse amplitude of 60 mV was used.

Results and Discussion

MES acidity constants and conditional stability constant of Cu^{II}*-MES complex:* pK_{a2} was calculated from pH titration curves and Fig. 2 shows its variation with ionic strength. pK_{a2} values were found to vary between 6.49 and 6.16 over the ionic strength range 0.005–0.25 M. The results illustrate the importance of ionic strength in pK_a determination and therefore the ionic strength of the working system should always be specified.

Plots of pH vs net charge of MES at four different ionic strengths are shown in Fig. 3. The isoelectric pH was obtained by extrapolating the curve to $Q = 0$ and its value was found to be 4.1 ± 0.1. From

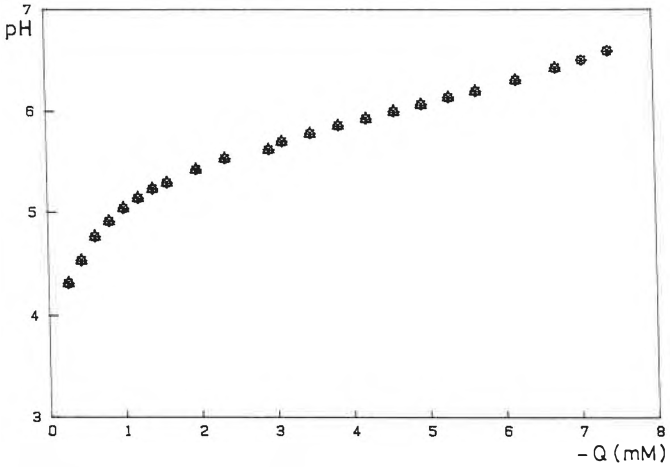

Fig. 3. Evaluation of isoelectric pH: pH vs net charge $-Q$ *at four ionic strengths;* $I = 0.05$, *0.10, 0.15, and 0.20* M $NaClO_4$.

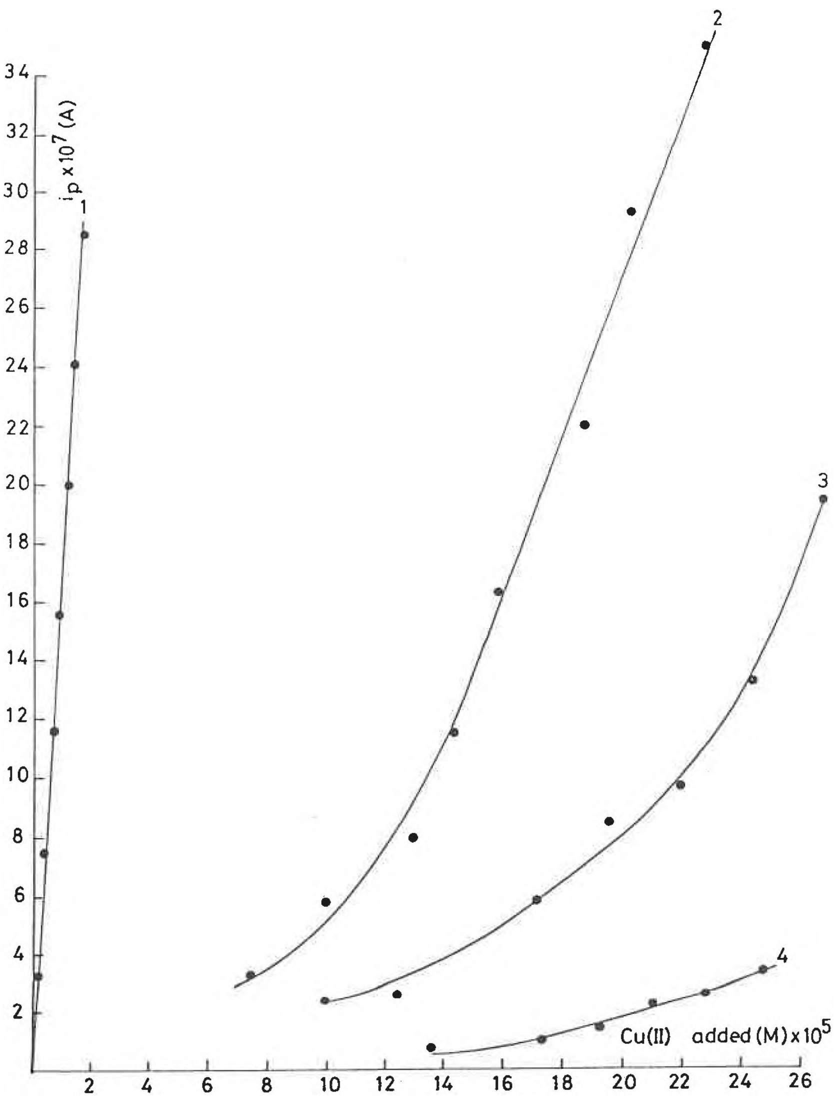

Fig. 4. DPP-titration curves of hydrous manganese oxide surface with $Cu^{2\oplus}$ *in MES buffer at* $I = 0.1$ M $NaClO_4$. *1: calibration curve; 2:* $[MnO_x] = 0.1992\ g \cdot L^{-1}$, $pH = 5.47 \pm 0.03$; *3:* $[MnO_x] = 0.2000\ g \cdot L^{-1}$, $pH = 5.96 \pm 0.03$; *4:* $[MnO_x] = 0.2479\ g \cdot L^{-1}$, $pH = 6.47 \pm 0.01$.

Fig. 3, it can be seen that pH_{ie} is independent of the ionic strength. From the value of pH_{ie} and pK_{a2}, pK_{a1} was computed using equation (7). The values of pK_a thus obtained are listed in Table 1. Also included in the table is lg ${}^cK_{Cu\text{-}MES}$ at pH = 5.57; lg ${}^cK_{Cu\text{-}MES}$ value reported in Table 1 seems to be reasonable when compared with lg $K_{Mn\text{-}MES}$[4]. However, its value is not negligible as stated by *Good* et al[4].

Table 1. Acidity constants of MES and the conditional stability constant Cu-MES; $I = 0.1$ M, $T = 25.0 \pm 0.1$ °C.

pK_{a1}	pK_{a2}	lg ${}^cK_{Cu\text{-}MES}$
1.99	6.21	1.39 ± 0.07 (pH = 5.57)
	6.15[4]*)	

*) $T = 20$ °C, I = not specified.

Using the data given in Table 1, the buffering intensity of MES at various pH and for $[MES]_T = 4.10^{-2}$ M was evaluated using *Synoeyink* et al.'s method[22]. Values of $5 \cdot 10^{-3}$, $2 \cdot 10^{-2}$ and 10^{-2} M were found for pH 5, 6 and 7, respectively. From these results one can conclude that:

(i) MES acts as a good buffer in this pH range. Therefore, adsorption studies were carried out in the pH range $5.5 \leqslant pH \leqslant 6.5$ using MES buffer.

(ii) MES being a weak complexant, it will not compete significantly with hydrous manganese oxide surface for $Cu^{2\oplus}$, since the latter is expected to form fairly strong complexes. The conditional stability constant of Pb^{II}-MnO_x complex, lg K is reported to be 6.2 at pH = 5.0[3] and hence the value of Cu^{II}-MnO_x complex would be roughly the same order of magnitude.

Cu^{II} complexation with hydrous manganese oxide surface: Cu^{II}-DPP titration curves of hydrous manganese oxide surface at three different pH values (5.5, 6.0, 6.5) are shown in Fig. 4. The decrease in the peak current with increase in pH (Fig. 4) reflects that Cu^{II} binds more strongly to MnO_x surface with increasing pH.

The conditional stability constant was calculated by van den Berg-Ružić[8,9] and Scatchard[10,11] plot methods. Both methods yielded straight line plots (Fig. 5 and Fig. 6) indicating that:

(i) 1:1 complex is formed.

(ii) There is only one class of equivalent binding sites on hydrous manganese oxide surface. This result confirms the validity of *Gonçalves* et al.'s[3] assumption that «the hydrous oxide surface consists of an uniform polymeric network of repeating energetically equivalent surface sites».

(iii) No kinetic effects are observed, since the presence of such an effect will cause deviation from linearity in the van den Berg-Ružić and Scatchard plots[7,23,24].

The average number of binding sites per molecule of the complexant can be quantified [14,15] and n was found to be 0.57 at pH = 5.47 for MnO_x surface. This result suggests that 1:2 rather than 1:1 complex is formed. However, as mentioned already, care should be taken while interpreting n values obtained from Scatchard plots. Klotz plot (Fig. 7) does not show either an inflection point or levelling-off effect and these results clearly illustrate how misleading results for n may be obtained. In any case, 1:1 complex is formed between Cu^{II} and MnO_x confirming that 1:1 complex model proposed by *Gonçalves* et al.[25] for Pb^{II}-MnO_x fits also for Cu^{II}-MnO_x complex.

The conditional stability constants computed by the two methods as well as the

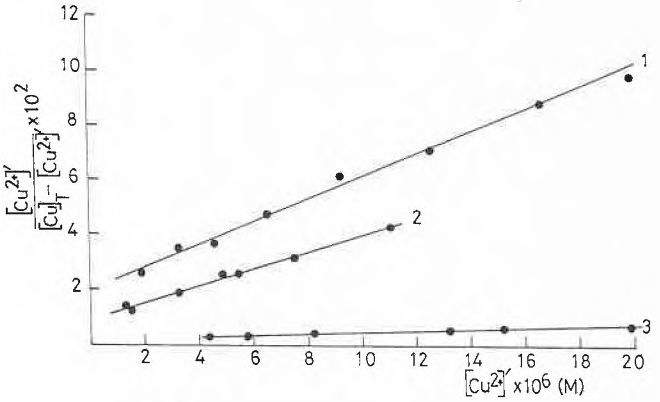

Fig. 5. Van den Berg-Ružić plots of the data obtained from Fig. 4. 1: $[MnO_x] = 0.1992$ $g \cdot L^{-1}$, $pH = 5.47 \pm 0.03$; 2: $[MnO_x] = 0.2000$ $g \cdot L^{-1}$, $pH = 5.96 \pm 0.03$; 3: $[MnO_x] = 0.2479$ $g \cdot L^{-1}$, $pH = 6.47 \pm 0.01$.

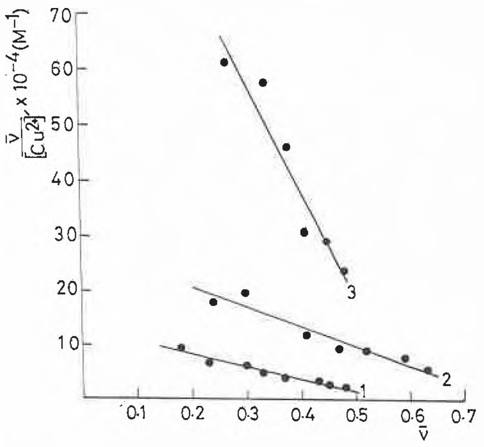

Fig. 6. Scatchard plots of the data obtained from Fig. 4 (experimental conditions used are the same as those given in Fig. 5).

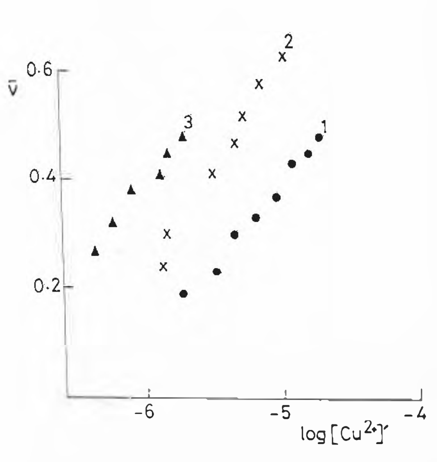

Fig. 7: Klotz plots of the data of Fig. 4 (for experimental conditions used see Fig. 5).

complexing capacity $[S]_T$ evaluated by the van den Berg-Ružić method are given in Table 2. The maximum exchange capacity $[SOH]_T$, is also included in the table for comparison purposes.

Table 2. Conditional stability constants of Cu^{II}-MnO_x surface complex and the complexing capacity $[S]_T$.

	Method			
	van den Berg-Ružić		Scatchard	
pH	$[S]_T^* \cdot 10^4$	lg $^cK_{SCu}$	$[SOH]_T^* \cdot 10^4$	lg $^cK_{SCu}$
5.47 ± 0.03	2.39 ± 0.07	5.32 ± 0.06	4.06	5.36 ± 0.09
5.96 ± 0.03	3.2 ± 0.1	5.54 ± 0.05	4.08	5.55 ± 0.06
6.47 ± 0.01	3.0 ± 0.1	6.30 ± 0.07	5.06	6.29 ± 0.07

* Complexing capacity and the maximum exchange capacity in mol · L^{-1} of binding sites.

lg $^cK_{SCu}$ values obtained by the two methods were in good agreement within experimental errors, and its value was found to increase with increase in pH in both the methods. *Kramer* [24] reported that Scatchard plot method systematically yields lower conditional stability constant values than van den Berg-Ružić plot method. This may be due to the fact that the experimental points are more widely scattered in the Scatchard plot method. In fact, we observed similar phenomenon and the correlation coefficients obtained from linear regression analysis: $0.996 \leqslant r \leqslant 0.998$ for van den Berg-Ružić plot, and $0.95 \leqslant r \leqslant 0.98$ for Scatchard plot, reveal a larger scattering for the latter.

The most disturbing feature of the results given in Table 2 is the large difference in the values of complexing capacity and the maximum exchange capacity. For fulvic acid it is well established that the complexing capacity is sensitive to change in pH, ionic strenght, and FA concentration [26]. Furthermore, the complexing capacity varies with the interacting metal ion [27,28]. The results of this study indicate that $[S]_T$ represents 58–78% of the total binding sites expressed as $[SOH]_T$. In some cases it could be as low as 0–20% of the total binding sites [29].

There is no doubt that complexing capacity is an useful operational parameter but from thermodynamics standpoint, it is not devoid of criticism.

Conclusion

The values of acidity constants of 2-morpholinoethanesulfonic acid suggest that $-SO_3H$ is indeed a strong acid and the amino group is a weak acid as predicted by theory. MES fulfills the conditions required for a good buffer:

- good buffering capacity in the pH range of interest;
- MES is a weak complexant, lg $^cK_{Cu\text{-}MES}$ is small and hence would not interfere in Cu^{II}-hydrous MnO_x oxide surface complexation reaction.

DPP seems to be a suitable voltammetric method for determining the distribution of electroactive metal species between the dissolved and particulate phases without separation of the solid phase. The results of DPP-Cu^{II} titration of MnO_x show that 1:1 non-labile complexes are formed between Cu^{II} and MnO_x.

The conditional stability constants calculated by van den Berg-Ružić method and Scatchard plot were found to be in good agreement. However, the complexing capacity is not representative of the total number of available binding sites, since there is a disparity in values of complexing capacity and the maximum exchange capacity.

The stability constants for the complexation of Cu^{II} with MnO_x surface suggest that MnO_x is one of the complexing agents of natural water that is capable of regulating the transport and bioavailability of heavy metal ions in natural aquatic systems.

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[1] J. Buffle, R.S. Altmann, in W. Stumm (Ed.): *Aquatic Surface Chemistry, Chemical Processes at Particulate-Water Interface*, Wiley-Interscience, New York (1987), p. 352.
[2] J. Buffle, in H. Sigel (Ed.): *Metal Ions in Biological Systems*, Vol. *18*, Marcel Dekker, New York (1984), p. 165.
[3] M.L. Gonçalves, L. Sigg, M. Reutlinger, W. Stumm, *Sci. Total. Environ. 60* (1987) 105.
[4] N.E. Good, G.D. Winget, W. Winter, T.N. Connolly, S. Izawa, R.M.M. Singh, *Biochemistry 5* (1966) 467.
[5] A.J. Ringbom: *Les Complexes en Chimie Analytique*, Dunod, Paris (1967), p. 35.
[6] J.O. Leckie, *Life Sci. Res. Rep. 33* (1986) 237.
[7] I. Ružić, in C.J.M. Kramer, J.C. Duinker (Ed.): *Complexation of Trace Metals in Natural Waters*, Nijhoff and Junk, The Hague (1984), p. 131.
[8] C.M.J. van den Berg, J.R. Kramer, *Anal. Chim. Acta 106* (1979) 113.
[9] I. Ružić, *Anal. Chim. Acta 140* (1982) 99.
[10] G. Scatchard, *Ann. N.Y. Acad. Sci. 51* (1949) 660.
[11] G. Scatchard, J.S. Coleman, A.L. Schen, *J. Am. Chem. Soc. 79* (1957) 12.
[12] P.W. Schindler, B. Fürst, R. Dick, P.U. Wolf, *J. Colloid Interface Sci. 55* (1976) 469.
[13] I.M. Klotz, *Science 217* (1981) 1247.
[14] R.F.C. Mantoura, J.P. Riley, *Anal. Chim. Acta 78* (1975) 193.
[15] W.T. Bresnahan, C.L. Grant, J. Weber, *Anal. Chem. 50* (1979) 1675.
[16] G. Sposito, *Environ. Sci. Technol. 15* (1981) 396.
[17] G. Sposito, K.M. Holtzclaw, C.S. LeVesque-Madore, *Soil Sci. Soc. Am. Proc. 43* (1979) 1148.
[18] J.R. Tuschall, P.L. Brezonik, *Anal. Chim. Acta 149* (1983) 47.
[19] R.R. Gadde, H.A. Laitinen, *Anal. Chem. 46* (1974) 2022.
[20] A. Balikungeri, W. Haerdi, *Chimia 39* (1985) 145.
[21] A. Balikungeri, W. Haerdi, *Int. J. Environ. Anal. Chem. 23* (1986) 239.
[22] V.L. Synoeyink, D. Jenkins: *Water Chemistry*, Wiley, New York (1980), p. 153.
[23] I. Ružić, S. Nikolić, *Anal. Chim. Acta 140* (1982) 331.
[24] C.J.M. Kramer, *Mar. Chem. 18* (1986) 335.
[25] M.L. Gonçalves, L. Sigg, W. Stumm, *Environ. Sci. Technol. 19* (1985) 141.
[26] C.H. Langford, D.S. Gamble, A.W. Underdown, S. Lee, «Interaction of metal ions with well-characterized fulvic acid», in R.F. Christman, E.T. Gjessing (Ed.): *Aquatic and Terrestrial Humic Materials*, Ann Arbor Science Publ. (1983), p. 219.
[27] R.A. Saar, J. Weber, *Environ. Sci. Technol. 16* (1982) 510A.
[28] A. Castetbon, M. Carrales, M. Astruc, M. Dotin, *Environ. Technol. Lett. 7* (1986) 495.
[29] J.H. Reuter, E.M. Perdue, *Geochim. Cosmochim. Acta 41* (1977) 325.