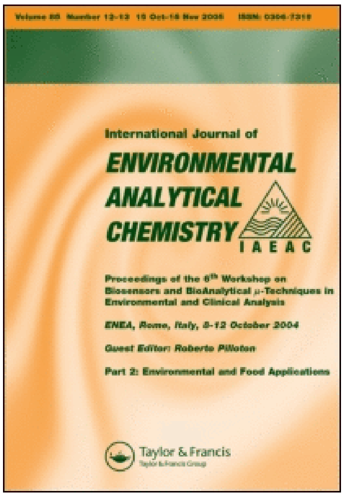

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Studies on Manganese Dioxide; Protolytic Behaviour of Some Synthetic Manganese Dioxides

A. Balikungeri[a]; W. Haerdi[a]
[a] Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Geneva, Switzerland

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Studies on Manganese Dioxide; Protolytic Behaviour of Some Synthetic Manganese Dioxides

A. BALIKUNGERI and W. HAERDI
Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Sciences II, 30 quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

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The pH_{zpc} and intrinsic acidity constants of manganese dioxide prepared by different methods have been determined by potentiometry. Amongst the factors affecting significantly the protolytic behaviour of these oxides are mode of drying and the extent of washing.

KEY WORDS: Manganese dioxide, protolytic behaviour, pH_{zpc}, intrinsic acidity constants.

INTRODUCTION

Manganese dioxide is one of the most important phases in controlling trace metal ions in natural water systems.[1] Adsorption of metal ions on hydrous manganese dioxide seems to be one of the mechanisms controlling the trace metal ions in solution.[2–6] Knowledge of the properties of solid–liquid interface is therefore necessary to understand phenomenon such as adsorption.

The interfacial properties of hydrous manganese dioxide, particularly the pH at zero proton condition, i.e. zero point of charge (pH_{zpc}) has been studied by several investigators.[2,5–12] The values of pH_{zpc} reported in the literature range from 1.4 to 7.4. Factors such as crystal structure, sample preparation and subsequent aging while in solution, method of drying and extent of washing of the sample may explain the cause of the observed differences in results. In our previous report,[13] it was shown that the stoichiometry of MnO_x ($1.93 \leq x \leq 1.98$) was unaffected by the mode of drying and method of preparation.

In this paper the effect of sample preparation, method of drying and the extent of washing on the pH_{zpc} and on the intrinsic acidity constants has been investigated. Only few studies[5,10] have been made to determine the acidity constants of surface sites of manganese dioxide and there is a wide variation in the reported intrinsic acidity constants. In this study the acidity constants of MnO_2 prepared under various experimental conditions have been determined.

EXPERIMENTAL

Preparation of samples

Samples of MnO_2 were prepared by the oxidation of Mn(II) by either MnO_4^- or $S_2O_8^{2-}$. For the sake of clarity, samples prepared by the oxidation of Mn(II) by $S_2O_8^{2-}$ are denoted by SF and SH and those by MnO_4^- are denoted by MF1, MF2, MH1 and MH2. F and H refer to the freeze and heat dried samples. Samples MF1 and MH1 differ from MF2 and MH2 in their extent of washing. The pH of washings of samples MF1 and MH1 was 3 whereas that of MF2 and MH2 was 6.

The I.R spectra of all these samples were essentially the same except that MF1 and MF2 showed vibrational bands due to H_2O.

X-ray analysis of samples showed that they were amorphous. The details of the mode of preparation and the I.R. characteristics of the samples are given elsewhere.[13]

pH_{zpc} and acidity constants

Unless otherwise stated, all measurements were made in solution thermostated at 25.0±0.5°C.

0.1 g of accurately weighed sample was suspended in 100 ml of 0.1 M or 0.05 M $NaClO_4$ solution ($pH = 7.0 \pm 0.2$) and left to equilibrate with the solution for 2 h under stirring conditions. 25 ml aliquots of the suspension was transferred into a titration cell, purged with nitrogen gas for 30 min and titrated with standard NaOH. After each addition of the base, the mixture was purged with N_2 gas for 5 min and then the steady value of pH was recorded in quiescent solution. Equilibrium was attained within 5 min in such a system.

EVALUATION OF DATA

The charge due to the potential determining ions, i.e. H^+ and OH^-, corresponds to the difference between the protonated and deprotonated SOH groups. The pH_{zpc} corresponds to the pH where the surface is uncharged: $\{SOH_2^+\}=\{SO^-\}$. It is assumed that H^+ and OH^- ions are the only specifically adsorbable ions in an inert electolyte medium,[14] although the validity of this assumption has been questioned by some investigators.[15]

The determination of surface charge density is based on the electroneutrality condition:

$$\frac{C_B - C_A + [H^+] - [OH^-]}{a} = \{SO^-\} - \{SOH_2^+\} = -Q \qquad (1)$$

where

Q	charge on the surface ($mol.kg^{-1}$)
C_B and C_A	concentration of strong base and strong acid added ($mol.dm^{-3}$).
a	the quantity of the oxide in the suspension ($kg.dm^{-3}$)
[ ]	concentration of solute ($mol.dm^{-3}$)
{ }	concentration of surface species ($mol.kg^{-1}$)

The pH_{zpc} is conventionally determined relative to the intersection of the titration curves at different ionic strength.[16] For strong acid oxides, i.e. δ-MnO_2, the alkaline portion of titration curves is only operational[5,6,8] and the pH_{zpc} can be obtained by extrapolation to zero charge condition.

The protolytic behaviour of surface hydroxyl groups can be described by the following reactions:

$$SOH_2^+ \overset{Ka_1^{int}}{\rightleftharpoons} SOH + H^+$$

$$Ka_1^{int} = \frac{\{SOH\}[H^+]}{\{SOH_2^+\}} \cdot \frac{\gamma_0 \cdot \gamma_{H^+}}{\gamma_+} \exp(-F\psi_{H^+}/RT) \tag{2}$$

$$SOH \overset{Ka_2^{int}}{\rightleftharpoons} SO^- + H^+$$

$$Ka_2^{int} = \frac{\{SO^-\}[H^+]}{\{SOH\}} \cdot \frac{\gamma_- \cdot \gamma_{H^+}}{\gamma_0} \exp(-F\psi_{H^+}/RT) \tag{3}$$

where:

$\gamma_{H^+}, \gamma_+, \gamma_0, \gamma_-$	activity coefficients of H^+, SOH_2^+, SOH and SO^- respectively
ψ_{H^+}	potential at the location of H^+ on the surface

γ_{H^+} is a constant at constant ionic strength. Chan *et al.*[17] have assumed that $\gamma_+ = \gamma_0 = \gamma_-$, however a satisfactory theoretical basis for activity coefficients of surface species is still lacking[18] and they are usually taken as 1. In this case the above equations can be rewritten as:

$$Ka_1^{int} = Ka_1 \exp(F\psi_{H^+}/RT) \tag{4}$$

$$Ka_2^{int} = Ka_2 \exp(F\psi_{H^+}/RT) \tag{5}$$

where

$$Ka_1 = \frac{\{SOH\}[H^+]}{\{SOH_2^+\}} \tag{4a}$$

$$Ka_2 = \frac{\{SO^-\}[H^+]}{\{SOH\}} \tag{5a}$$

For the evaluation of intrinsic acidity constants, the coordination chemistry model of Schindler *et al.*[18–20] and Stumm *et al.*[4,14,21] have been adopted here. The microscopic acidity constants, Ka_i, can be experimentally determined and intrinsic acidity constants, Ka_i^{int}, can be obtained by extrapolation of Ka_i to zero charge condition. It must be kept in mind that the intrinsic acidity constants defined by the Eqs. (4) and (5) refer to a particular ionic strength. In the coordination chemistry model, the surface potential is assumed to be only a function of the surface charge σ: $\psi = f(\sigma)$, thus Eqs. (4) and (5) can be generalised as:

$$p\mathrm{Ka}_i = p\mathrm{Ka}_i^{\mathrm{int}} + bQ \tag{6}$$

where b is an empirically found slope from the plot $p\mathrm{Ka}_i$ vs Q.

The surface charge σ is related to Q by:

$$\sigma = \frac{QF}{S}(\mathrm{C\,.\,m^{-2}}). \tag{7}$$

F Faraday constant ($\mathrm{C\,.\,mol^{-1}}$).
S Specific surface area ($m^2\,.\,\mathrm{kg}^{-1}$).

If the electrostatic term bQ is expressed as $-\log[\exp(-F\psi/RT)] = F\psi/RT\ln(10)$, one can observe the relationship between the slope b and the differential capacity σ/ψ of the double layer. The differential capacity is assumed to be constant[4, 14, 18–21]:

$$\frac{\sigma}{\psi} = \frac{F^2}{2.303bSRT}(\mathrm{Farad.\,m^{-2}}). \tag{8}$$

For the evaluation of microscopic acidity constants Ka_i, the maximum exchange capacity (C_m) of the sample must be known. C_m is defined by:

$$C_m = \{\mathrm{SOH_2^+}\} + \{\mathrm{SOH}\} + \{\mathrm{SO^-}\}. \tag{9}$$

The C_m values reported in our previous paper[13] were used for the computation of Ka_i. The following limiting cases were considered:

i) For $\mathrm{pH} \ll \mathrm{pH_{zpc}}$ the surface is positively charged and the following approximation is justified:

$$C_m = \{\mathrm{SOH_2^+}\} + \{\mathrm{SOH}\}; \quad Q = \{\mathrm{SOH_2^+}\}$$

$$\mathrm{Ka}_1 = \frac{C_m - Q}{Q}[\mathrm{H^+}]. \tag{10}$$

ii) For $pH \gg pH_{zpc}$ the surface is negatively charged, thus:

$$C_m = \{SOH\} + \{SO^-\}; \quad \{SO^-\} = -Q$$

$$Ka_2 = \frac{-Q}{C_m + Q}[H^+]. \tag{11}$$

iii) For $pH = pH_{zpc}$ the surface is uncharged, thus:

$$\{SOH_2^+\} = \{SO^-\}$$

$$pH_{zpc} = \tfrac{1}{2}(pKa_1^{int} + pKa_2^{int}). \tag{12}$$

RESULTS AND DISCUSSION

pH_{zpc}

Figures 1–4 show the net adsorption curves for samples SF, SH, MF2 and MH2. One can observe the following:

i) a linear relationship between the pH and the charge on the surface of the oxides over the pH range ~4–8

ii) an intersection of net adsorption curves for $I = 0.05$ and 0.1 M at zero charge.

The pH_{zpc} were determined by extrapolation of the linear portion of the curve to zero charge condition and the results are given in Table I. The values reported in the literature have also been included for comparison purposes. The results show that the pH_{zpc} obtained in this study for samples SF, SH and MF2 are, within experimental errors, in good agreement with those previously reported by Morgan *et al.*[6] and Murray[8] but are less acidic than those reported by others.[2,5,7]. The pH_{zpc} reported by Gray *et al.*[9] is about 1 pH unit higher than the afore-mentioned. These differences may be due to the following factors:

i) the method of synthesis

ii) the extent of washing the sample to remove adsorbed ions, in particular H^+ evolved during synthesis; the H^+ concentration re-

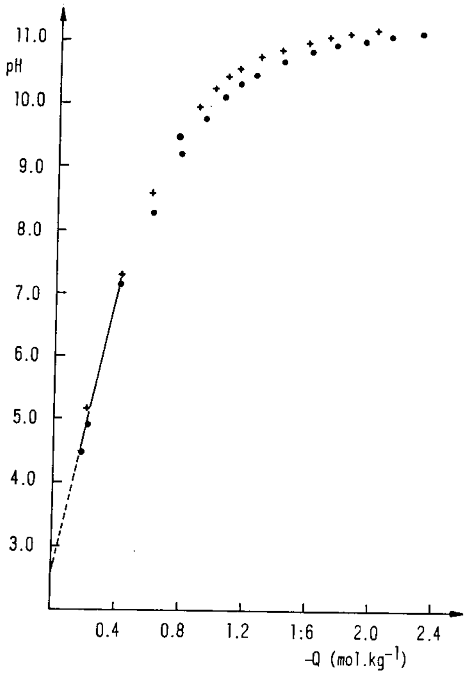

FIGURE 1 Sample SF: pH as a function of surface charge Q; (●) $I=0.1$ M, (+) $I=0.05$ M, $r=0.9910$ (r: correlation coefficient).

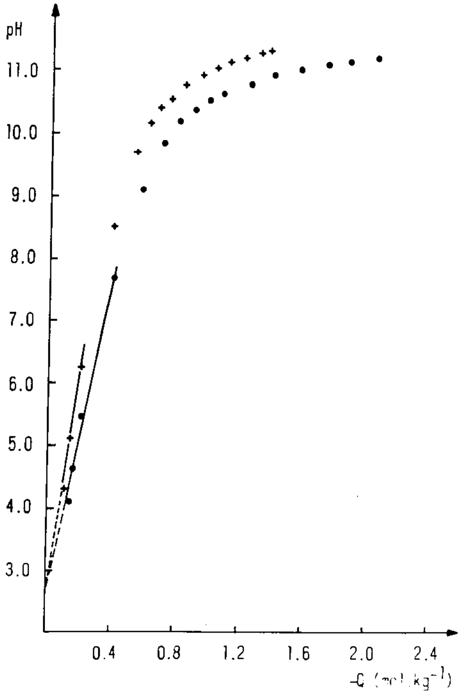

FIGURE 2 Sample SH: pH as a function of surface charge Q; (●) $I=0.1$ M $r=0.9932$, (+) $I=0.05$ M $r=0.9948$.

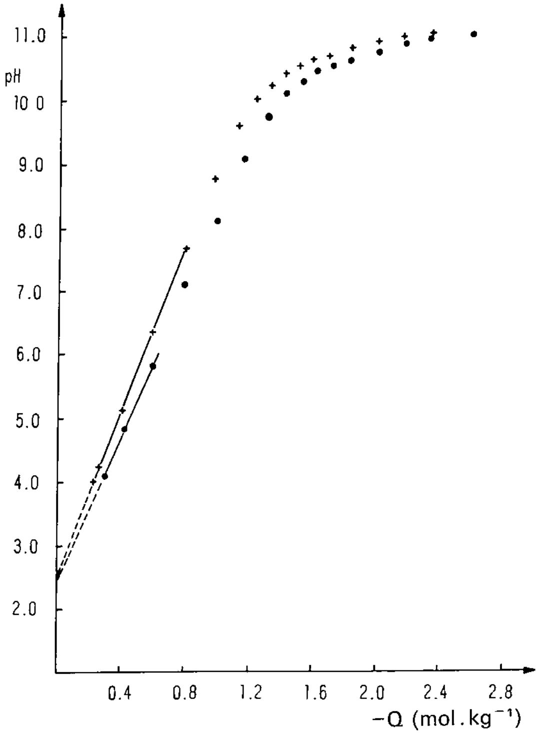

FIGURE 3 Sample MF2: pH as a function of surface charge Q; (●) $I=0.1\,\mathrm{M}$ $r=0.9999$, (+) $I=0.05\,\mathrm{M}$ $r=0.9998$.

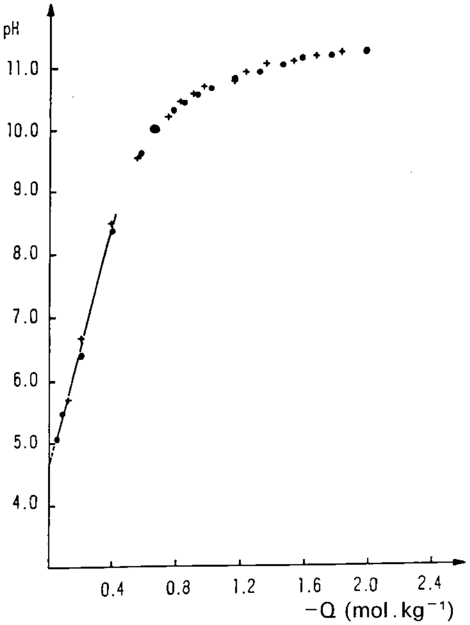

FIGURE 4 Sample MH2: pH as a function of surface charge Q; (●) $I=0.1\,\mathrm{M}$, (+) $I=0.05\,\mathrm{M}$, $r=0.9976$.

TABLE I

pH_{zpc} of various MnO_2 samples

Sample[a]	pH_{zpc}	Method	References
SF	2.5 ± 0.2	Titration	This work
SH	2.6 ± 0.2	Titration	This work
MF2	2.47 ± 0.04	Titration	This work
MH2	4.60 ± 0.06	Titration	This work
δ-MnO_2	2.8 ± 0.3	Titration	6
δ-MnO_2	1.5 ± 0.5	Coagulation	7
δ-MnO_2	2.40	Electrophoresis	8
δ-MnO_2	1.40	Electrophoresis	2
δ-MnO_2	3.3 ± 0.5	Titration	9
δ-MnO_2	1.5 ± 0.2	Titration and cation adsorption	5

[a] SF and SH: samples prepared by oxidation of Mn(II) with $S_2O_8^{2-}$. MF2 and MH2: samples prepared by oxidation of Mn(II) with MnO_4^-. *F* and *H* refer to freeze and heat-dried samples respectively.

maining on the sample after washing has been referred to as residual acidity[13]

iii) the way of handling the sample, i.e. drying or keeping the sample in aqueous suspension.

Although samples MF1 and MH1 differ from MF2 and MH2 only in the extent of washing, their pH_{zpc} could not be located. The high residual acidity of these samples[13] makes the extrapolation to zero charge condition difficult. However, with the exception of MH2, the results of this study show that the pH_{zpc} is not affected by both chemical method of synthesis and mode of drying. MH2 sample yielded systematically high values of pH_{zpc}. The cause of this is unknown at present. It must be pointed out that some investigators[5,8] store the sample in solution to avoid surface dehydration by drying the sample but in this case the results may be hampered by aging effect[8] while in contact with the solution.

Acidity constants

The microscopic acidity constants ($I = 0.1$ M $NaClO_4$) for the alkaline region are plotted in Figures 5 and 6. The intrinsic acidity constants pKa_2^{int} are obtained by extrapolation to zero charge

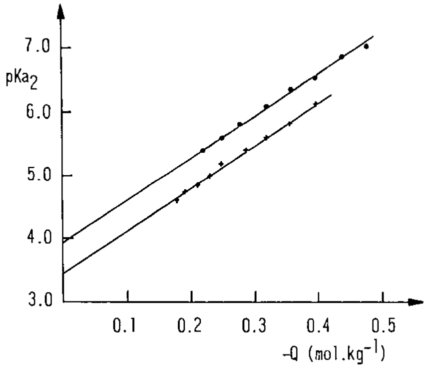

FIGURE 5 Microscopic acidity constants, pKa_2 as a function of surface charge Q; (●) Sample SF $r=0.9977$, (+) Sample SH $r=0.9971$.

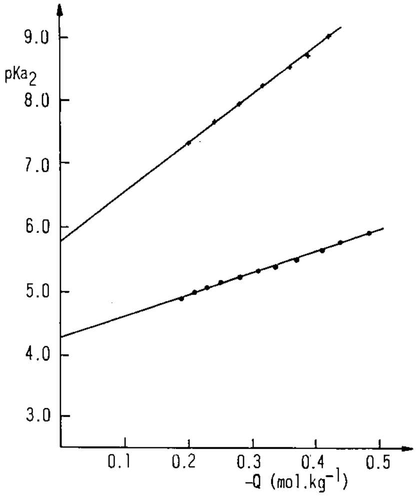

FIGURE 6 Microscopic acidity constants, pKa_2 as a function of surface charge Q; (●) Sample MF2 $r=0.9995$, (+) Sample MH2 $r=0.9989$.

condition and the intrinsic acidity constants for the first ionisation step pKa_1^{int} are computed from Eq. (12). The results are given in Table II.

These results show that freeze-dried samples are more acidic than heat-dried ones as far as pKa_1^{int} is concerned. The pKa_i^{int} values of

TABLE II
Intrinsic acidity constants of MnO_2 samples

Sample	pKa_1^{int}	pKa_2^{int}	$Ka_1^{int}/Ka_2^{int}(\alpha)$
SF	1.05 ± 0.09	3.95 ± 0.04	794
SH	1.8 ± 0.2	3.44 ± 0.03	44
MF2	0.66 ± 0.01	4.28 ± 0.01	4,169
MH2	3.40 ± 0.06	5.80 ± 0.03	251

MH2 differ markedly from other samples despite the fact that the maximum number of exchangeable OH groups per unit area is comparable with other samples.[13] As for pH_{zpc}, pKa_2^{int} could not be determined for samples MF1 and MH1 owing to their high residual acidity.

The protolytic behaviour of surface hydroxyl groups can be reasonably compared, at least qualitatively, with the ionisation of dicarboxylic acids. For dicarboxylic acids where the two acidic groups are sufficiently far apart in the molecule so that they do not influence each other, the ratio of the two acidity constants (Ka_1/Ka_2) should be 4.[22] Alternatively if the carboxylic groups are close to each other, there is a possibility of hydrogen bonding which would ease the first ionisation step and make the second one more difficult, thereby increasing the Ka_1/Ka_2 ratio.[22,23] The electrostatic effects can also be responsible of Ka_1/Ka_2 ratio.[23,24]

The values of Ka_1^{int}/Ka_2^{int} are given in Table II. It is observed that samples freeze-dried exhibit higher Ka_1^{int}/Ka_2^{int} ratio than heat-dried samples. It is interesting to note that the ratios α_{SF}/α_{SH} and $\alpha_{MF2}/\alpha_{MH2}$ are the same (17 ± 1) regardless of the method of preparation indicating the importance of the degree of hydration. Moreover IR spectra of MF2 showed the presence of adsorbed water.[13] Thus hydrogen bonding may be expected in this sample, which in turn would enhance the acidity of hydroxyl groups as previously reported.[25] As could be expected from IR spectra,[13] the effect of hydrogen bonding is less marked in SF than in MF2, thus $Ka_2^{int}(MF2) > Ka_1^{int}(SF)$. For samples heat-dried, such bonds are either very weak or non-existent.

CONCLUSION

The values of pKa_i^{int} of different preparations of MnO_2 compared with the protolytic behaviour of other oxides[19,20] show that the acidity increases in the order:

$$\gamma\text{-}Al_2O_3 < \alpha - FeOOH < ThO_2 \sim ZrO_2 < TiO_2 < SiO_2(am) < \delta - MnO_2.$$

Thus MnO_2 is a very acidic oxide which under natural water conditions will be almost completely deprotonated. The intrinsic acidity constants allows to compute the degree of deprotonation of the oxide and at pH of natural waters i.e. 8.2, the results show that more than 99.6% of the oxide surface is negatively charged (SO^-). This will favour the transport of trace metal ions by complexation at the surface sites.

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