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ELECTRICAL DOUBLE LAYER AT MANGANESE OXIDES/1:1 ELECTROLYTE SOLUTION INTERFACE

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Results of the investigations of the electrical double layer (edl) at manganese oxides/ aqueous solution of alkali metal chlorides interface are presented. The solid phase in the experiments consists of Mn_2O_3 or MnO_2. Dzeta potential (ζ) and surface charge (σ_0) measurements for the mentioned oxides were performed in 0.1- 0.001M solutions of LiCl, NaCl and CsCl. On the basis of surface charge density as a function of pH and ionic strength data the ionization and complexation constants of surface hydroxyl groups were calculated. The surface charge measurements and cation adsorption data indicated that the sequence of the adsorption of alkali metal cations is Li> Na>Cs.

Key words: electrical double layer, manganese oxides/electrolyte interface, pzc, iep

INTRODUCTION

Dispersions of manganese dioxide are present in environment as *pyrolusite*. Manganese hydroxy (oxides) form mineral component of soil. Manganese dioxide may be found in form of nodules on the bottom of the oceans. It finds vide application in numerous branches of industry. For example, it is common oxidant, and in ceramic, textile and rubber industry it is applied as a mineral dye. It is used also as a depolarizer of dry batteries in electronics (Surowce Mineralne Świata 1981). Recently, MnO aroused great interest as a promoter of Fe/Si-2 catalyst for olefin production (Xu et al. 1998), improving its activity and selectivity.

A stability of the dispersion and its rheologic properties are connected with the structure of the electrical double layer at the interface: metal oxide/aqueous solution of electrolyte. The electric charge at such interface is formed as a result of some reactions of acid-base hydroxyl group of metal oxide with electrolyte solution ions (Wiese et al. 1976, James and Parks 1982).

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$$\equiv SOH_2^+ \leftrightarrow \equiv SOH + H^+ \tag{1}$$

$$\equiv SOH \leftrightarrow \equiv SO^- + H^+ \tag{2}$$

The another determinant, influencing the charge magnitude and the structure of the double layer is concentration of the background electrolyte. The ions of this electrolyte take part in, so called, complexation reactions of the surface hydroxyl groups of the oxide, resulting in the increase of the surface charge density, on the other hand compensating the surface charge (James et al. 1978).

$$\equiv SOH_2^+ An^- \leftrightarrow \equiv SOH + An^- + H^+ \tag{3}$$

$$\equiv SOH + Ct \leftrightarrow \equiv SO^- Ct^+ + H^+ \tag{4}$$

Reactions (1-4) are described by thermodynamic constants defined as follows:

$$K_{a_1} = \frac{[H^+][\equiv SOH]}{[\equiv SOH_2^+]} \cdot \frac{\gamma_H \gamma_0}{\gamma_+} \cdot \exp\left(\frac{-e\Psi_0}{kT}\right) \tag{5}$$

$$K_{a_2} = \frac{[H^+][\equiv SO^-]}{[\equiv SOH]} \cdot \frac{\gamma_H \gamma_-}{\gamma_0} \cdot \exp\left(\frac{-e\Psi_0}{kT}\right) \tag{6}$$

$$K_{An} = \frac{[H^+][An^-][\equiv SOH]}{[\equiv SOH_2^+ An^-]} \cdot \frac{\gamma_H \gamma_{An} \gamma_0}{\gamma_\pm} \cdot \exp\left(\frac{-e(\Psi_0 - \Psi_\beta)}{kT}\right) \tag{7}$$

$$K_{Ct} = \frac{[H^+][\equiv SO^- Ct^+]}{[\equiv SOH][Ct^+]} \cdot \frac{\gamma_H \gamma_\mp}{\gamma_0 \gamma_{Ct}} \cdot \exp\left(\frac{-e(\Psi_0 - \Psi_\beta)}{kT}\right) \tag{8}$$

where:

K_{a_1} - dissociation constant of surface group $\equiv SOH_2^+$; K_{a_2} - dissociation constant of surface group $\equiv SO^-$; K_{An} - anion complexation constant; K_{Ct} - cation complexation constant; [.] - concentrations of specific surface forms or ions in the solution; Ψ_0 -surface potential; Ψ_β - potential of Inner Helmholtz Plane (IHP); T- temperature; k-Boltzman constant ($1.38 \cdot 10^{-23}$ J·K^{-1}), e- electron charge, γ_H - activity coefficient of H^+ ions, γ_0 - activity coefficient of ≡SOH groups, γ_+ - activity coefficient of $\equiv SOH_2^+$groups, γ_- - activity coefficient of $\equiv SO^-$groups, γ_{An} activity coefficient of anions, γ_{Ct} - activity coefficient of cations, $\gamma_\pm$ - activity coefficient of $\equiv SOH_2^+An^-$ groups, $\gamma_\mp$ - activity coefficient of $\equiv SO^-Ct^+$ groups.

Equilibrium constants of ionization and complexation reactions allow, according to „site binding" theory, calculation of the concentrations of specific forms, bearing electric charge on the surface of the oxide and determination of the structure of the electrical double layer at metal oxide- electrolyte solution interface. These constants may be determined from the dependencies: surface charge density versus pH and concentration of the electrolyte solution (James et al. 1978, Janusz 1991, Janusz and Szczypa 1998).

It is well known from studies on the stability of dispersed system, that even monovalent ions of alkali metals reveal some differences in coagulation capacity, that is reflected in so called Hofmeister's lyotropic series ($Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$). Examinations of edl structure in metal oxide-electrolyte solution system and following studies on dispersion stability showed that for some system for example α-Fe_2O_3, γ-Al_2O_3 this series may be reversed (Lyklema 1995). What is more, even for the same oxide TiO_2 and alkali metal salt solutions the classic lyotropic series or reversed series may be noticed, depending on the preparation method of the solid. (Dumont 1987).

Ardizzone and Trassatti 1996 summarized information concerning the electrical double layer of the manganese oxides/electrolyte properties of manganese dioxides. From their review one can noticed those pzc and iep values scatter, even for the same crystallographic structure of the sample. They cited data of Tamura et al., for the γ-MnO_2/solution of $NaNO_3$, which indicated the dependence of the pzc on the concentration of background electrolyte.

In present paper the results of experiments on the structure of electrical double layer for manganese dioxide and Mn_2O_3 in LiCl, NaCl and CsCl solutions are presented. The investigations included following measurements: surface charge by potentiometric titrations, adsorption of alkali metal cations with application of radioactive isotopes and dzeta potential by electrophoresis. Obtained results were used to calculation of equilibrium constants of ionization and complexation of surface hydroxyl groups of metal oxides.

EXPERIMENTAL

MATERIALS

Aldrich, Milwakee, USA delivered manganese dioxide. Specific surface of the sample, determined by BET method (adsorption and desorption of nitrogen) was 38.14m^2/g and porosity analysis proved existence of micropores (total volume of pores from desorption 1,7nm <d< 300nm by BJH method was 0,046 cm^3/g and their average pore radius from desorption was 4.9nm). Grain size distribution of the sample determined by PCS method (Photo Correlation Spectroscopy) reveals relatively broad diameter, 150-550 nm, of grains.

Manganese oxide (III) was obtained following Ul Hag and E. Matijevic (1997) method. A mixture of carbamide (30.0279 g/l) and $MnSO_4$ (15.099g/l) solutions was heated in 85^{o}C during two hours, then cooled to room temperature. Next the obtained suspension was centrifuged; sediment was washed out with double distilled water and dried. Dry $MnCO_3$ was calcinated in 700°C during one hour in air. According to BET measurements, the specific surface of the obtained sample was 9.22 m^2/g and such as MnO_2 sample it was microporous (total volume of pores from desorption 1,7nm <d< 300nm by BJH method was 0,0184 cm^3/g and their average pore radius from desorption was 7.8nm). Grain size distribution of this sample demonstrated also broad range of the particle diameter (100-750 nm).

METHOD

Potentiometric titration was performed in Teflon vessel. Temperature of measurements, equal to 25°C was maintained by Julabo F10UC thermostat. Carbon dioxide, dissolved in solutions was removed from the system by flowing nitrogen. Such method provides neutral atmosphere during titration of the solutions and suspensions. The content of the titration vessel was stirred by propeller mixer. A pH measurement was carried out with Radiometer Copenhagen PHM 85 Precision pH Meter. A titrant (base solution) was added with Metrohm Dosimat 665 burette. Both the pH meter and the burette were connected to a computer for acquisition data (pH and titrant volume) and to control the addition of titrant. From obtained data the surface charge density values were computed.

The adsorption of Na^+ or Cs^+ was determined by the isotope technique, by measurement of the ^{22}Na or ^{137}Cs activity uptake from the solution. Details of this procedure were described by Janusz 1996. The adsorption of Li^+ was calculated from uptake of the concentration of Li^+ ions from solution. The concentration of Li^+ was determined by means of AAS method.

Dzeta potential was determined by electrophoretic method with Zetasizer 3000 by Malvern.

RESULTS AND DISCUSSION

ELECTRICAL DOUBLE LAYER AT MnO_2/ ALKALI METAL IONS SOLUTIONS

As was mentioned earlier electrical charge at the interface of metal oxide/ electrolyte solution is formed as a result of the reactions of acid-base hydroxyl groups (Reactions 1 and 2) and due to complexation reactions of surface hydroxyl group with the background electrolyte ions (Reactions 3 and 4). In the case of specific adsorption of the electrolyte ions the increase of the electrolyte concentration results in the increase of the charge density.

Surface charge density versus pH and concentration of the electrolytes (LiCl, NaCl, and CsCl) dependencies are presented on Figures 1, 2 and 3 respectively. It can be noticed that pH_{pzc} equals nearly 4. For the MnO_2/CsCl solution system the pH_{pzc} is the same for all concentration of background electrolyte. Small shift of pH_{pzc} with electrolyte concentration was noticed for LiCl solution. Unexpectedly high shift of

pH_{pzc} was observed for NaCl solutions; for 0.001M solution it moves to pH=5.5. Such shift of pH_{pzc} is characteristic for specifically adsorbing cations. These results confirm results of Tamura et al. (Ardizzone and Trasatti 1996). On the other hand, a comparison of surface charge for the greatest concentrations of the electrolyte suggests that adsorption sequence should be as follows:

Li> Na > Cs

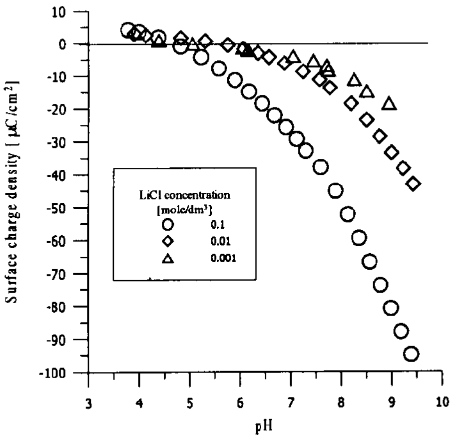

Fig. 1. Surface charge density as a function of pH and electrolyte concentration for the MnO_2/LiCl solution system

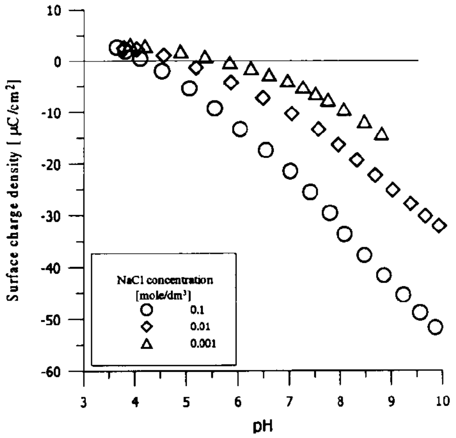

Fig. 2. Surface charge density as a function of pH and electrolyte concentration for the MnO_2/NaCl solution system

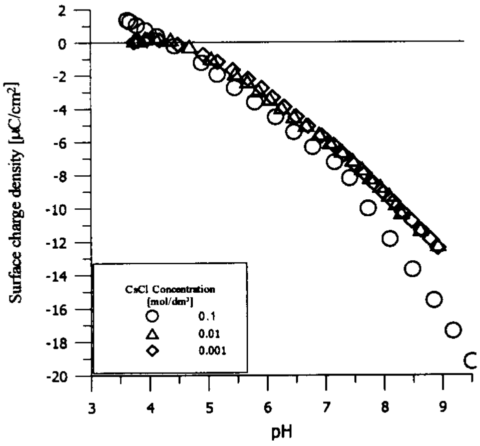

Fig. 3. Surface charge density as a function of pH and electrolyte concentration for the MnO_2/CsCl solution system

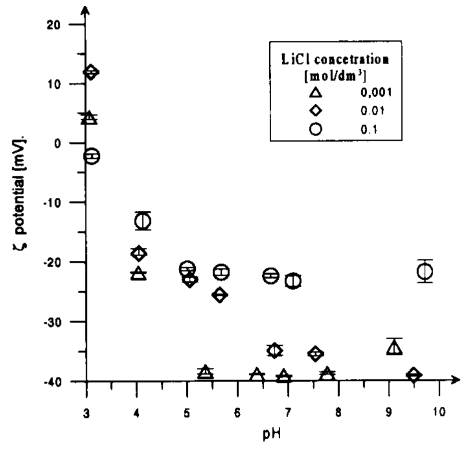

Fig. 4. Zeta potential as a function of pH and electrolyte concentration for th MnO_2/LiCl solution system

This sequence is in good agreement with observation for many oxides, for example TiO_2, Fe_2O_3 (Lyklema 1995) nevertheless it should be noticed that for lithium the charge density at pH=9 is two times higher than for sodium which is also higher than for cesium.

In presented sequence of electrolytes the decrease of the influence of the electrolyte concentration on the charge density is well visible. Considering above it seems that titration by NaOH and CsOH leads, beside acid base reactions also to neutralization of some substances that contaminate the surface. LiOH as week base does not take part in such type reactions.

Potential dzeta versus pH dependence for discussed electrolytes is presented on Fig 4, 5 and 6 for LiCl, NaCl and CsCl solutions, respectively. For all studied systems pH_{iep} is lower than 4.

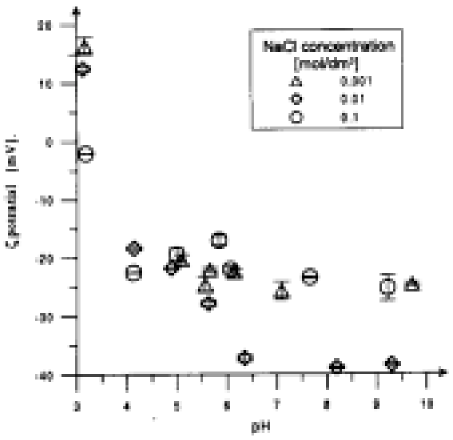

Fig. 5. Zeta potential as a function of pH and electrolyte concentration for the MnO_2/NaCl solution system

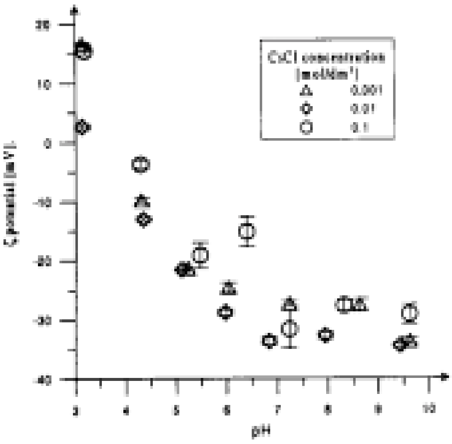

Fig. 6. Zeta potential as a function of pH and electrolyte concentration for the MnO_2/CsCl solution system.

Only for MnO_2/LiCl system the relationship of the ζ potential as a function of background electrolyte concentration is typical for oxide systems relation. Dzeta decreases when the electrolyte concentration increases. The less pronounced dependence is observed for MnO_2/CsCl. For MnO_2/NaCl system the highest ζ is observed for concentration 0.01M. This effect seems to be difficult to explain and may be caused by porosity of the solid.

Figure 7 demonstrates dependence of the adsorption of alkali cation on pH of the 0.001M solutions. A plot of these dependencies is in agreement with reaction 4 that is adsorption increases with the pH increase, however observed increase of the adsorption as a function of pH is not uniform. For Na^+ and Li^+ sharp increase of the adsorption is observed at pH=7 whereas for Cs^+ the increase of the adsorption starts at pH_{iep}. The greatest adsorption is noticed for sodium ions. It may be explained by low value of dzeta potential in the case of MnO_2/NaCl system.

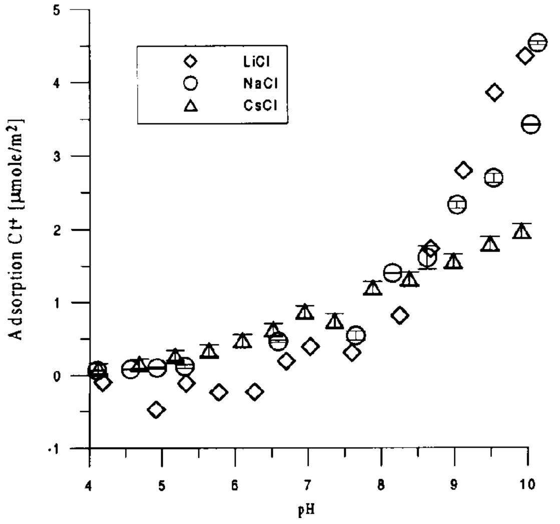

Fig 7. Adsoption of cations (Ct = Li, Na, Cs) vs pH at the MnO_2/0,001 M. CtCl electrolyte interface

Equilibrium constants for ionization and complexation of surface hydroxyl groups were calculated according to Davies et al. 1978 method, basing on potentiometric titration data. Obtained constants for LiCl, NaCl and CsCl solutions are listed in Table 1. It may be noticed that values of the constants of positively charged groups are similar. Only for NaCl the higher stability of ionized, positively charged groups is observed. Considered cations arrange in the following sequence: the lowest ionization tendency reveals CsCl solutions and the highest LiCl.

Table 1. Ionization and complexation constants of surface hydroxyl groups for MnO_2/Ct (Ct = Li, Na, Cs)Cl system.

Constants	Elektrolyte		
	LiCl	NaCl	CsCl
pK_{a1}	2.93±0.65	4.12±0.97	3.02±1.34
pK_{a2}	8.70±0.07	8.38±0.82	7.62±0.30
pK_{Cl}	2.62±1.14	1.20±0.66	0.26±1.09
PK_{Ct}	6.20±1.03	5.44±0.42	5.96±1.06

Analysis of the value of the cation complexation constants indicates that the strongest complexes are formed by sodium ions, weaker for cesium and the weakest for lithium ions in observed system. These results are in agreement with ion adsorption studies – Fig. 7. It may be concluded from the above that in lithium chloride solutions the ionization reactions has the greatest share in the charge formation whereas complexation reactions does the same in MnO_2/NaCl system.

ELECTRICAL DOUBLE LAYER AT Mn_2O_3/ALKALI METAL IONS SOLUTIONS

Surface charge density versus pH dependence for Mn_2O_3/LiCl solution system is presented on Figure 8, Mn_2O_3/NaCl solution system on Figure 9 and for Mn_2O_3/CsCl solution system on Figure 10. For Mn_2O_3/LiCl and Mn_2O_3/NaCl systems pH_{pzc} equals to 6 whereas for Mn_2O_3/CsCl small shift to pH=6.4 was noticed. On Figure 8 small dependence of charge density on the concentration of the background electrolyte may be noticed. For the remaining two cases (Figs 9 and 10) this dependence is typical for the oxides, although its character is different for each system. For Mn_2O_3/NaCl solution system pronounced dependence of surface charge density on electrolyte concentration is visible up to pH=7, whereas for Mn_2O_3/CsCl system this dependence is relatively higher below pH_{pzc}. In the first example the higher influence of the cation adsorption on the charge density is visible.

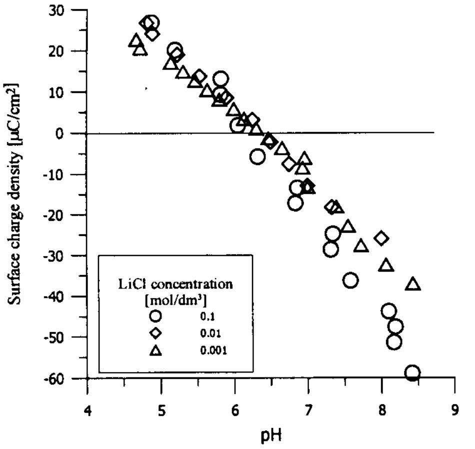

Fig. 8. Surface charge density as a function of pH and electrolyte concentration for the Mn_2O_3/LiCl solution system

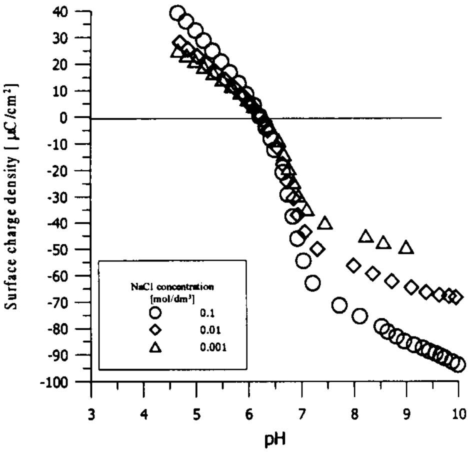

Fig. 9. Surface charge densit as a function of pH and electrolyte concentration for the Mn_2O_3/NaCl solution system

Dzeta potential versus pH dependences for three concentrations of the background electrolyte for systems Mn_2O_3/LiCl Mn_2O_3/NaCl and Mn_2O_3/CsCl are presented in Figures 11, 12 and 13 respectively. It may be noticed that pH_{iep} value for Mn_2O_3/LiCl and Mn_2O_3/NaCl systems equal to 3.2 whereas for Mn_2O_3/CsCl it is 3.5. A comparison of both values, pH_{pzc} and pH_{iep}, reveals difference in all systems bigger than three units. The reason for such difference may be significant adsorption of the anion, which shifts pH_{pzc} towards higher values, presence of contamination or porosity of the solid.

Examination of the structure of the solid by BET method (adsorption and desorption of the nitrogen) can not exclude the latter factor in principle. The lack of this shift for higher ionic strengths proves the same adsorption of the electrolyte ions at pH_{pzc} vicinity, so for any noticed shift alkali contamination such as NaOH or KOH should be responsible. On the other hand, the process of the sediment preparation excludes their presence. The precipitation of $MnCO_3$ is performed in the presence of carbamide and obtained sediment is washed with doubly distilled water until the conductivity of supernatant was constant. A difference between pH_{pzc} and pH_{iep} may results from neglecting the sediment solubility. Titration of the sediment with various weighed portion of the solid, to take the solubility into account, gave shift towards lower values about 0.5 pH unit. Because mentioned difference between pH_{pzc} and pH_{iep} was too big the washing out the solid with acid is necessary.

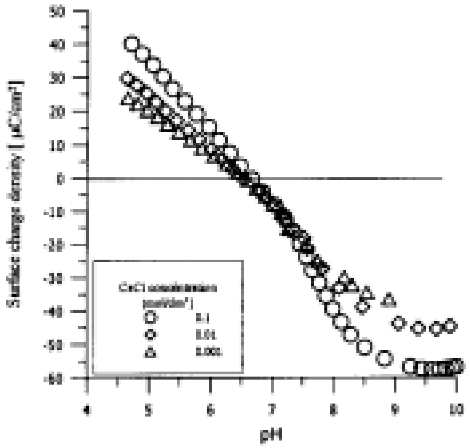

Fig. 10. Surface charge density as a function of pH and electrolyte concentration for the Mn_2O_3/CsCl solution system

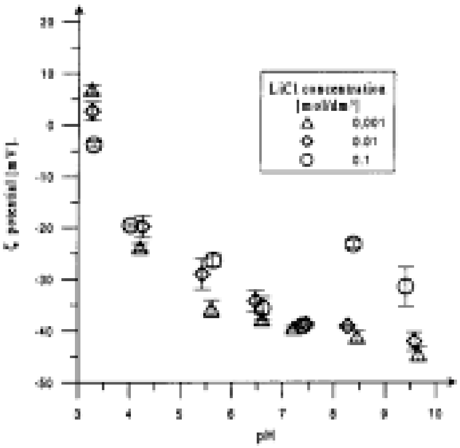

Fig. 11. Zeta potential as a function of pH and electrolyte concentration for the Mn_2O_3/LiCl solution system

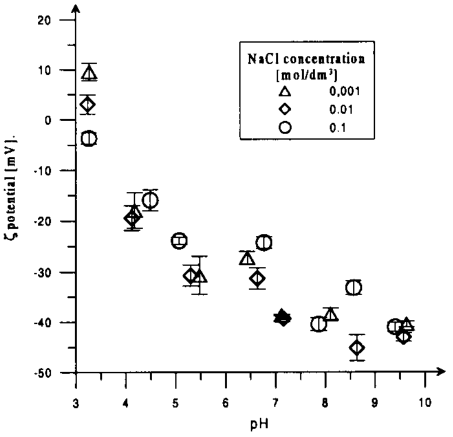

Fig. 12. Zeta potential as a function of pH and electrolyte concentration for the Mn_2O_3/NaCl solution system

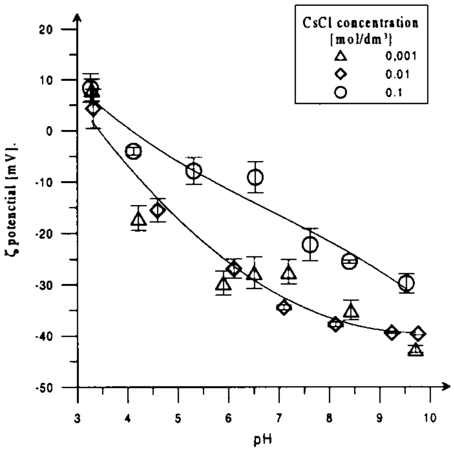

Fig. 13. Zeta potential as a function of pH and electrolyte concentration for the Mn_2O_3/CsCl solution system

Ionization and complexation constants of surface hydroxyl groups were determined from the dependence - surface charge density versus pH, according to Davies et al. These constants are listed in Table 2, for studied electrolytes.

Table 2. Ionization and complexation constants of surface hydroxyl groups for Mn_2O_3/Ct (Ct=Li, Na, Cs)Cl system

Constant	Electrolyte		
	LiCl	NaCl	CCl
pK_{a1}	4.77±0.01	5.02±0.20	4.97±0.07
pK_{a2}	7.85±0.08	7.80±0.22	8.28±0.08
pK_{Cl}	4.99±0.06	5.02±0.35	5.54±0.32
pK_{Ct}	7.50±0.01	7.52±0.28	8.15±0.09

For this oxide, some small differences of ionization constants are connected with positively charged groups (0.2 pH units) and a little bigger with negatively charged (0.4 pH units). The greatest differences are visible for cations. From the above data it may be concluded that lithium cations are the stronger complexing agent whereas cesium cations are the weakest one. This sequence is different than that of for previously mentioned MnO_2 and may result from ordered state of water layer at the surface of the oxide. For oxides with firmly hydrated surface the adsorption of hydrated ions is favored, whereas for the oxides with poorly hydrated surface the adsorption of ions hydration shield for example cesium. To prove above assumption the calculation of hydration degree of both oxides seems to be very helpful.

CONCLUSIONS

The following conclusions may be drawn from calculations based on potentiometric titrations, ion adsorption and dzeta potential measurements of the systems manganese oxide/ alkali metal chlorides:

1. pH_{pzc} and pH_{iep} of MnO_2 in solutions of alkali metal chlorides is lower than 4.
2. Obtained sequence of the adsorption of alkali metal cations is Li> Na>Cs. It should be noticed that the highest charge density was obtained for LiCl and the smallest one for CsCl solution. It is caused by a considerable contribution of the ionization of surface hydroxyl groups in LiCl solution.
3. Examination of the systems with Mn_2O_3 revealed big difference between pH_{pzc} (6.5) and pH_{iep} (3.8), which is difficult to explain on the base of the performed experiments.
4. Sequence of cations adsorption on Mn_2O_3 surface is Li> Na>Cs.

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Janusz W., Gałgan W., *Podwójna warstwa elektryczna na granicy faz tlenki manganu/roztwór elektrolitu 1:1,* Fizykochemiczne Problemy Mineralurgii, 35, 2001, 31-41 (w jęz. ang.).

Przedstawiono wyniki badań podwójnej warstwy elektrycznej na granicy faz tlenki manganu/wodny roztwór chlorków metali alkalicznych. Badania prowadzono nad właściwościami granicy faz w których fazę stałą stanowiły tlenki manganu; Mn_2O_3 i MnO_2. Pomiary ζ i ładunku powierzchniowego (σ_0) dla wyżej wymienionych tlenków przeprowadzono w 0.1-0.001M roztworach LiCl, NaCl, CsCl. W oparciu o zależności gęstości ładunku powierzchniowego, potencjału ζ od pH i stężenia elektrolitu obliczono stałe jonizacji i kompleksowania powierzchniowych grup hydroksylowych tlenków. Na podstawie pomiarów ładunku powierzchniowego oraz przez bezpośredni pomiar adsorpcji kationów określono następująca sekwencję adsorpcji kationów Li>Na>Cs.