CROATICA CHEMICA ACTA CCACAA 47 (4) 577—585 (1975)

YU ISSN 0011-1643
546.57:541.183

CCA-902

Original Scientific Paper

Competitive Adsorption of Potential-determining Ions and Neutral Molecules by $(AgI)_n$

M. Tschapek and C. Wasowski

Casilla de Correo 30, Sucursal 19, Buenos Aires, Rep. Argentina

Received April 9, 1975

The density of the charges of $(AgI)_n$ is in direct relation with the concentration of the potential determining ions (Ag^+, I^-), reaching its maximum at 1.1 ions per nm^2, and is in inverse relation with the adsorption of neutral molecules (aliphatic alcohol). The adsorption of aliphatic alcohol (which reaches its maximum at 0.57 molecules per nm^2 on the left side of the pzc) is in inverse relation with the adsorption of the potential determining ions. The adsorption of 1 molecule of alcohol is accompanied by desorption of 2 ions and *vice versa.*

INTRODUCTION

The AgI sols have been the object of many studies. It would be no exaggeration to say that the electrochemistry of colloids has advanced on the basis of studies of $(AgI)_n$: ζ-potential, coagulation, pzc, adsorption, *etc.* Nevertheless, one property of $(AgI)_n$, namely its specific surface (a few $m^2\ g^{-1}$), is variable and difficult to determine and this may constitute a serious handicap in electrochemical studies.

It is a fact that determinations of specific surface, based on adsorption phenomena, are not precise[1]. A similar situation exists also with respect to the mean crystal size and density of charge. Lange and Berger[2] assumed that the density of charge is 80 $\mu C\ cm^{-2}$ or 5×10^{18} ions g^{-1}. Later Lyklema *et al.*[3] gave values $< 5\ \mu C\ cm^{-2}$ or $< 3.3 \times 10^{17}$ ions g^{-1} for dried preparations. Mirnik[4] gave values $5—8 \times 10^{18}$ ions g^{-1} (after authors 2—3 gequiv. per 10^3 *M* of (AgI)) for coagulated by counter ions and aged for 16 hours, *i. e.* close to the value assumed by Lange and Berger[2]. Obviously, the discrepancy between the values of different authors is due to the incorrect determination of the crystal size and specific surface and to different modes of preparation of $(AgI)_n$.

Frumkin and Obrucheva[5] were the first to establish that the maximum adsorption of neutral molecules (aliphatic acids: heptylic and caprylic) by $(AgI)_n$ from aqueous solution takes place at the negative side of pzc.

Later, Lyklema *et al.*[1,3] found the same phenomenon using as adsorbates aliphatic alcohols (butyl and propyl, *etc.*). Having available the specific surface values of $(AgI)_n$ these authors established the relationship between medium and electrical double layer properties: density of charge, pzc, *etc.*

The aim of this article is the quantitative study of the adsorption — desorption relations between 1-heptanol and the potential determining ions Ag^+ and I^-.

MATERIALS AND METHODS

All chemicals were of Analar grade and were used without further purification. The sediment was obtained by mixing of 50 cm^3 1 M $AgNO_3$ with 51 cm^3 of 1 M KI, and stirring. After being left in repose overnight, 2 cm^3 of 1 M $AgNO_3$ were added to the sediment which was then washed with bidistilled water up to pAg = = 5.2 — 5.3. Then, the sediment was transfered to a measuring cylinder of 100 cm^3 and the volume made up to 102 cm^3 (2 cm^3 = volume occupied by 11.73 g of $(AgI)_n$ with bidistilled water which contains determined quantities of alcohol and/or $AgNO_3$ and KI, *i. e.* AgI = 0.5 M. The supporting electrolyte (KNO_3) was added in a dry state.

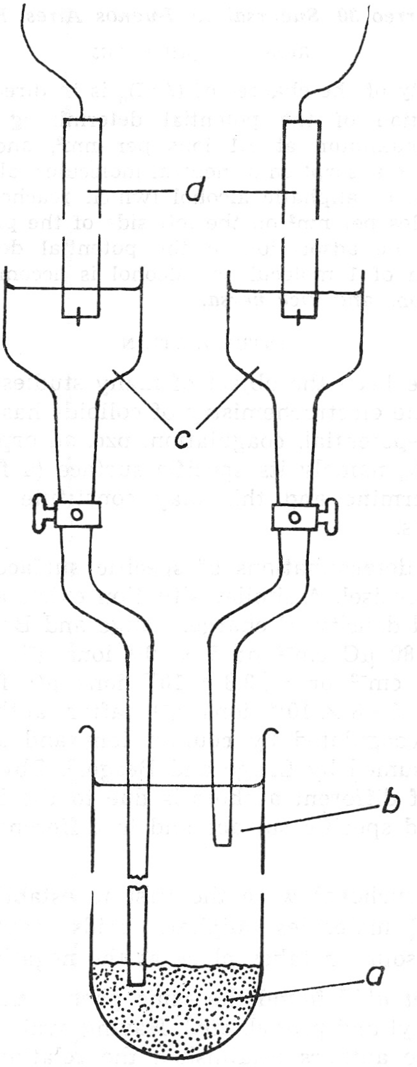

Fig. 1 Illustration of determining of the pzc by the suspensions effect measurements. a) sediment; b) decantate; c) bridges with 0.01 M KNO_3; d) calomel electrodes.

The changes of Ag^+ and I^- concentrations were determined by the use of calibration curves with the silver electrode 242 of Metrohm, and silver — silver iodide electrode made after De Bruyn[6] respectively. As a reference electrode the KCl saturated calomel electrode 204 of Metrohm was used, connected to the solution by a 0.01 M KNO_3 salt bridge.

The pzc of $(AgI)_n$ was determined by the suspension effect, measured with two calomel electrodes submerged, as shown in Fig. 1, in the sediment and the decantate obtained by centrifugation.

The EMF was measured with a Keithley Digital Electrometer 616 whose input impedance is $> 2.10^{14}$ ohms. The number of adsorbed ions per nm^2 was calculated from the difference in amount of Ag^+ in the decantate and in blank solutions. The specific surface, determined by Methylene Blue adsorption is $A/AgI = 3.6\ m^2\ g^{-1}$, *i.e.* the surface of 11.73 g of $(AgI)_n$ is 42.2 m^2.

The adsorption of 1-heptanol by (AgI) Ag^+ and (AgI) I^- was determined by measurements of the surface tension (γ) for decantate (γ_{dec}) and blank solution (γ_{bl}) by a De Noüy tensiometer, at 25 °C. From the calibration curve $\gamma = f(n)$, where n is the amount of 1-heptanol in mg per 100 cm^3, is found. The difference between the amount in the blank solution and in the decantate gave the amount of adsorbed alcohol, calculated in molecules per nm^2.

For a comparative study also the nonporous carbon black »Vulkan 3 — G (2700)″ $A/C = 71.3 - 2.7\ m^2\ g^{-1}$, manufactured by Teddington Physical Laboratory (England), was used.

RESULTS AND DISCUSSION

In order to obtain the cross — sectional area of the 1-heptanol molecule in the interface between the hydrophobic surface and water, its adsorption on the nonporous carbon black of known specific surface was studied. The curve in Fig. 2 shows the number of 1-heptanol molecules adsorbed by nonporous carbon black per nm^2, as a function of its concentration.

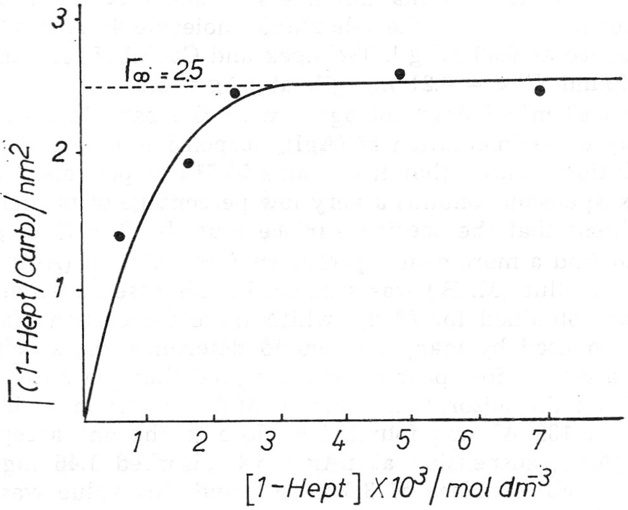

Fig. 2 Adsorption of 1-heptanol by carbon black as a function of its concentration (mol/dm^3). Ord: Γ (1-hept)/nm^2 = number of adsorbed molecules per nm^2; Absc: [1-hept] × 10^3/mol dm^{-3}.

From the curve presented in Fig. 2 it can be concluded that the cross — sectional area of the 1-heptanol molecule in the interface between hydrophobic solid and water is 40 Å² (= 0.4 nm^2). Now, assuming that the cross-sectional area of the 1-heptanol molecule in the interface $(AgI)_n$ — water is the same as in the interface carbon-water, it is possible to determine the specific surface of $(AgI)_n$. In Fig. 3 change of adsorption of 1-heptanol by $(AgI)_n$, at $pAg = 5.4$, as a function of its concentration is given.

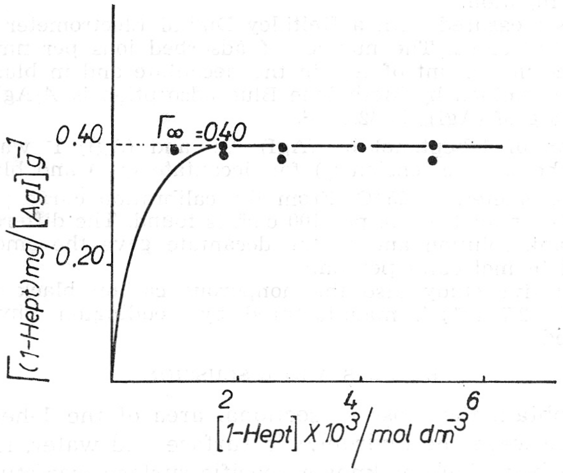

Fig. 3. Adsorption of 1-heptanol by $(AgI)_n$ as a function of its concentration at $pAg = 5.4$. Ord: Γ (1-hept)/mg g^{-1} = adsorbed 1-heptanol in mg per g^{-1}; Absc: [1-hept] $\times 10^3$/mol dm^{-3}.

As may be estimated, the maximum adsorption, $\Gamma\infty$ is 0.40 mg g^{-1}, which at a cross — sectional area of the 1-heptanol molecule 40 Å^2 (= 0.4 nm^2) gives the specific surface as 0.83 m^2 g^{-1}. Tschapek and Caviglia[7] for similar sediment of (AgI) Ag^+ found $\Gamma\infty = 0.21$ mg g^{-1}, at $pAg = 3$.

The value 0.83 m^2 g^{-1} does not agree with the particle distribution curve of $(AgI)_n$. Study of sedimentation of $(AgI)_n$ suspension, obtained by interaction of 1 molar solutions, shows that it contains 53.7% of particles $< 3 \times 10^{-5}$ cm. Although the suspension contains a very low percentage of particles $< 1 \times 10^{-5}$ cm, it was evident that the specific surface must be > 0.83 m^2 g^{-1}.

In order to find a more exact specific surface value of $(AgI)_n$, the adsorption of Methylene Blue (M. B.) was studied. In this case an attempt was made to compare data obtained for $(AgI)_n$ whith those for carbon black. The M.B. method has been used by many authors to determine the specific surface of disperse minerals[1,8–12]. Most people have accepted that the cross-sectional area was 132 Å^2. From the adsorption curve of M.B. by carbon — blask the cross — sectional area 132 Å^2 was found, *i. e.* close to the one accepted by many authors. The $(AgI)_n$ suspension at $pAg = 5.4$ adsorbed 1.46 mg g^{-1} of M.B., which gives a specific surface of 3.6 m^2 g^{-1}, and this value was accepted for the present study.

In Fig. 4 the curve of Ag^+ adsorption by $(AgI)_n$ as a function of its concentration is given. As may be seen, the density of charge reaches 1.1 ions per nm^2, *i. e.* 17.6 $\mu C\ cm^{-2}$ or 4×10^{18} ions g^{-1}. This value agrees with that given by Mirnik[4] for I^- coagulated on fresh $(AgI)_n$ ($I^-/(AgI) = 2 - 3 \times 10^{-3}$), but is higher than that given by Lyklema *et al.*[3] for dried $(AgI)_n$.

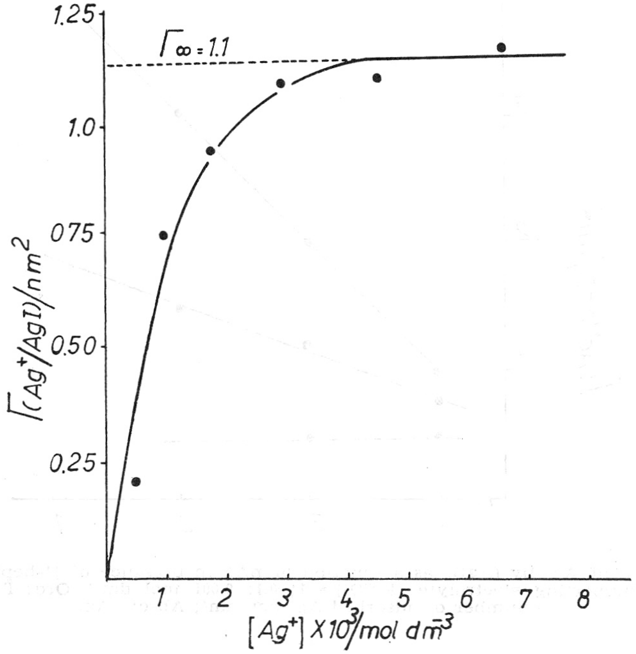

Fig. 4 Adsorption of Ag^+ by $(AgI)_n$ as a function of its concentration. Ord: Γ $(Ag^+)/nm^2$ = number of adsorbed Ag^+ per nm^2; Absc: $[Ag^+] \times 10^3/mol\ dm^{-3}$.

In Fig. 5 the adsorption curve of Ag^+ as a function of pAg in the presence of the supporting electrolyte (KNO_3) and 1-heptanol is given. As may be seen, adsorption of Ag^+ at high concentrations, in the presence of 1-heptanol increases only at high concentration of supporting electrolyte. At zero or at low concentrations of KNO_3, the surface of $(AgI)_n$ is occupied principally by 1-heptanol molecules.

The studies of Frumkin and Obrucheva[5] as well as those of Lyklema *et al.*[1,3] show that maximum adsorption of neutral molecules takes place on the left side of pzc, which, as shown by Lyklema *et al.*, shifts to the right. In order to establish the pzc of $(AgI)_n$ sediment in the presence of 3×10^{-3} M of 1-heptanol and 1 M 1-butanol, the pzc was determined by measurements of the suspension effect. In Fig. 6 the results of the study of pzc are given. As may be seen, the pzc shifts to the right from pAg = 5.57 to pAg = 5.30 (from 235 to 247 mV) in presence of 3×10^{-3} M of 1-heptanol and from pAg = = 5.57 to pAg = 3.62 in presence of 1 M of 1-butanol.

The adsorption — desorption reactions between 1-heptanol and potential — determining ions were carried out as follows. To 11.73 g/100 cm³ of $(AgI)_n$ (= 42.2 m²), which contained constant quantities of 1-heptanol (3×10^{-3} M) and supporting electrolyte ($[KNO_3]$ = 0.5 M), increasing stepped quantities of $AgNO_3$ or KI were added. After 15 min. of stirring, the concentrations of 1-heptanol and Ag^+ or I^- were determined. In Tables I and II the results of these experiments are given.

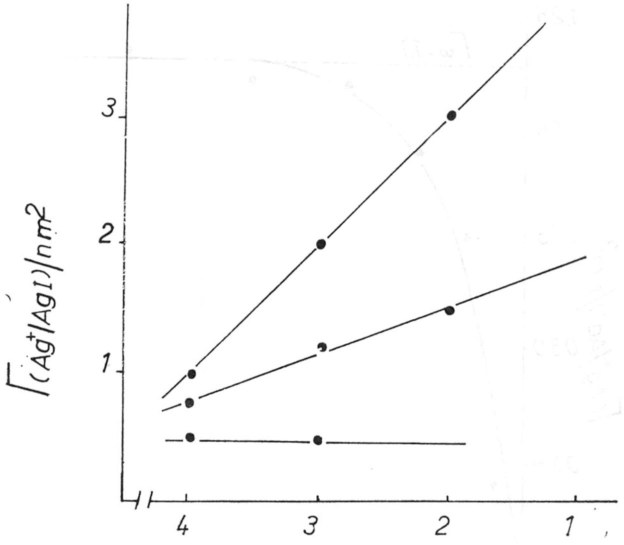

Fig. 5 Adsorption of Ag^+ by $(AgI)_n$ as a function of pAg in presence of [1-heptanol] = 2.7×10^{-3} mol dm^{-3} and supporting electrolyte [KNO_3] = 1; 0.1; 0.001 mol dm^{-3}. Ord: Γ $(Ag^+/AgI)/nm^2$ = = number of adsorbed Ag^+ per nm^2; Absc: pAg.

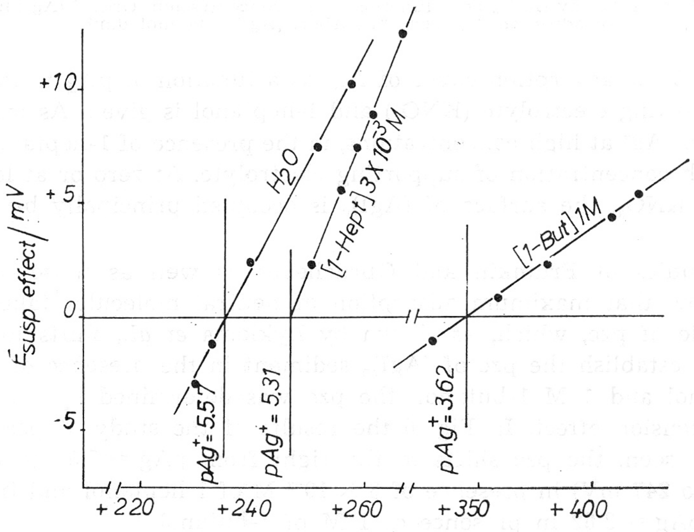

Fig. 6 The pzc of $(AgI)_n$ in presence of alcohols. Ord: $E_{susp.\ effect}$, mV = EMF of cell: calomel electrode — calomel electrode; Absc: EMF/mV of cell: calomel electrode — Ag^+ electrode.

As may be estimated from data presented in Tables I and II, the adsorption of Ag^+ and I^- from one side and alcohol molecules from the other side are incompatible.

TABLE I

Adsorption of Ag^+ *and 1-heptanol on* $(AgI)_n$ Ag

1 dm³ *contains:* $[AgI]_n = 0.5$ M; $A = 42.4$ m²; $[KNO_3] = 0.5$ M; $[\text{1-Heptanol}] = 3 \times 10^{-3}$ M

1-Heptanol by calibration curve: EMF—C_{Ag+}					1-Heptanol by calibration curve: γ—C_{Hept}			
c/mol dm⁻³		pAg in equilibrium	adsorbed		*c*/mg dm⁻³		adsorbed amount	
blank sol.	with $(AgI)_n$ Ag^+		10^5 mol/42.2 m²	ions/nm²	blank sol.	with $(AgI)_n$ Ag^+	mg/42.2 m²	molec./nm²
pAg = 5.2	pAg = 5.2	5.2	0	0	35.5	30.8	4.7	0.57
1.70×10^{-6}	1.00×10^{-6}	5.10	0.07	0.10	35.5	30.8	4.7	0.57
3.23×10^{-5}	4.48×10^{-5}	4.35	0.11	0.16	35.5	31.2	4.3	0.52
4.48×10^{-5}	2.63×10^{-5}	3.58	1.85	0.26	35.5	31.8	3.7	0.45
2.88×10^{-4}	2.40×10^{-4}	2.62	4.8	0.68	35.5	32.6	2.9	0.35
6.31×10^{-4}	5.63×10^{-4}	2.25	6.8	0.97	35.5	33.6	1.9	0.23
8.60×10^{-4}	7.82×10^{-4}	2.20	7.8	1.11	35.5	33.9	1.6	0.20

TABLE II

Adsorption of I^- *and 1-heptanol on* $(AgI)_n$ I

1 dm³ *contains;* $[AgI]_n = 0.5$ M; $A = 42.4$ m²; $[KNO_3] = 0.5$ M; $[\text{1-Heptanol}] = 3 \times 10^{-3}$ M

I^-, by calibration curve: EMF — C_{I^-}					1-Heptanol by calibration curve: γ — C_{Hept}			
c/mol dm⁻³		pI in equilibrium	adsorbed amount		*c*/mg dm⁻³		adsorbed amount	
blank sol.	with $(Ag)_n$ I^-		10^5 mol/42.2 m²	ions/nm²	blank sol.	with $(AgI)_n$ I^-	mg/42.2 m²	molec./nm²
pAg = 5.2	pAg = 5.2	10.6	0	0	33.7	29.0	4.7	0.57
5.62×10^{-6}	1.00×10^{-6}	5.0	0.46	0.06	33.7	30.0	3.7	0.45
3.23×10^{-5}	1.10×10^{-5}	4.96	2.13	0.32	33.7	30.6	3.1	0.37
2.34×10^{-4}	1.90×10^{-4}	2.7	4.40	0.62	33.7	31.6	2.1	0.25
8.91×10^{-4}	8.13×10^{-4}	2.1	7.80	1.11	33.7	32.4	1.3	0.15

Becuase from Tables I and II it is not evident that maximum adsorption takes place on the left side of pzc, additional experiments were performed for the range $4 < pAg < 8$ or $91 < EMF/mV < 323$. To 11.73 g of $(AgI)_n$ (= 42.2 m^2) in 100 cm^3, at pAg = 4, were added 35 mg of 1-heptanol, 5 g of KNO_3 and increasing quantities of KI. After each addition of KI the sediment was shaken for 15 min. and there the EMF of the silver electrode — calomel electrode cell and the surface tension, were measured.

The results of this experiment are given in Fig. 7.

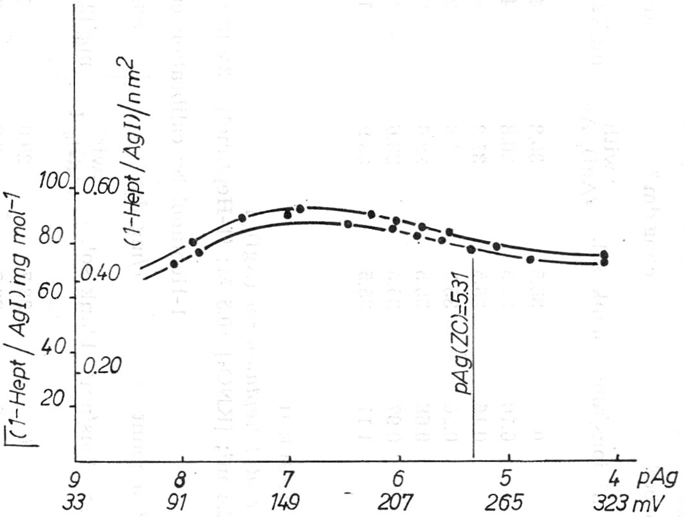

Fig. 7 Adsorption, Γ of 1-heptanol by $(AgI)_n$ as a function of pAg and EMF of cell: calomel electrode — Ag^+ electrode. Ord: Γ (1-hept/AgI) mg/mol $(AgI)_n$ = adsorbed 1-heptanol in mg per mol of AgI; Γ (1-hept/AgI)/nm^2 = number of adsorbed molecules per nm^2; Absc: pAg (EMF). Curves: two reproduced experiments.

This experiment shows that the maximum adsorption of 1-heptanol takes place at pAg = 6.9 — 7.0, *i. e.* on the left side of pzc, which in the presence of 1-heptanol is at 250 mV, *i. e.* at pAg = 5.3.

It is interesting to point out that an inverse relation exists between adsorption — desorption of the potential determining ions and 1-heptanol molecules: desorption of two ions is accompanied by adsorption of one molecule and *vice versa*. Naturally, it is not an equivalent exhange, but is like a competition for surface sites, although it is not clear why the competition takes place when sites are unlike and besides surface coverage is too low: the area occupied by one ion is ≈ 0.9 nm^2 and by one molecule ≈ 1.8 nm^2 (0.4 mg per g). The competition would be easy to understand if the surface coverage was higher.

CONCLUSIONS

1. The coverage of $(AgI)_n$ surface by 1-heptanol even at pzc (by vertical orientation of the molecule) is 0.3.

2. The maximum measured adsorption of the potential determining ions (Ag^+ and I^-) reaches 1.1 ions per nm^2, *i. e.* 17.6 μC cm^{-2} or 4×10^{18} inos per g of $(AgI)_n$ or 1.57 ions per 1000 AgI, at pI = 2 and pAg = 2.

3. The maximum measured adsorption of the 1-heptanol reaches 0.57 molecules per nm^2, *i. e.* 0.78 × 10^{-3} mol per mol of $(AgI)_n$, at pAg = 6.9 — 7.0 and pI = 8.9 — 8.8 on the left side of pzc, which in presence of 1-heptanol shifts from pAg = 5.57 to pAg = 5.3.

4. The adsorption — desorption relation between potential determining ions and 1-heptanol molecules is inverse: adsorption of one molecule provokes desorption of ≈ 2 ions and *vice versa*. Although it is not an equivalent exhange, the coefficient ≈ 2 is maintained.

5. The potential determining ions compete with 1-heptanol only in the presence of supporting electrolyte.

Acknowledgment. The authors thank the Consejo Nacional de Investigaciones Cientificas y Tecnicas for their support in the course of this study.

REFERENCES

1. H. J. Van den Hul and J. Lyklema, *J. Amer. Chem. Soc.* **90** (1968) 3010.
2. E. Lange and R. Berger, *Z. Electrochem.* **36** (1930) 171.
3. J. Lyklema and J. Th. G. Overbeek, *J. Colloid Sci.* **16** (1961) 595; B. H. Bijsterbosch and J. Lyklema, *J. Colloid Interface Sci.* **37** (1971) 171.
4. M. Mirnik *Croat. Chem. Acta* **42** (1970) 161.
5. A. N. Frumkin and A. Obrucheva, *Biochem. Z.* **182** (1926) 220.
6. H. De Bruyn, *Rec. Trav. Chim. Pays-Bas* **61** (1942) 5.
7. M. Tschapek and A. M. Caviglia, *J. Electroanal. Chem.* **46** (1973) 131.
8. U. Hofmann and I. Dammler, *Chimia* **23** (1969) 476.
9. J. J. Kipling and R. B. Wilson, *J. Appl. Chem.* **10** (1960) 109.
10. G. M. Darr and U. Ludvig, *Mater. Constr.* **6** (1973) 233.
11. C. S. Broocs, *Koloid-Z Z. Polym.* **199** (1964) 31.
12. P. T. Hang and G. W. Brindley, *Clays and Clay Miner.* **18** (1970) 203.

SAŽETAK

Kompetitivna adsorpcija iona koji određuju potencijal i neutralnih molekula pomoću $(AgI)_n$

M. Tschapek i C. Wasowski

Gustoća naboja $(AgI)_n$) u izravnoj je vezi s koncentracijom iona (Ag^+, I^-) koji određuju potencijal, a najveća je kod 1,1 iona po nm^2. Ona je obrnuto proporcionalna adsorpciji neutralnih molekula (alifatski alkohol). Ova posljednja postiže maksimum kod 0,57 molekula po nm^2. Adsorpcija jedne molekule alkohola je popraćena desorpcijom dvaju iona.

CASILLA DE CORREO, 30,
SUCURSAL 19, BUENOS AIRES
ARGENTINA

Prispjelo 9. travnja 1975.