A C T A U N I V E R S I T A T I S L O D Z I E N S I S
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EFFECT OF THE FERRIC ION ADDITION ON THE DOUBLE LAYER CAPACITY IN UREA SOLUTIONS*

The method of determination of double layer capacity curves was used to study the adsorption of urea and that of Fe^{3+} and Fe^{2+} on mercury in aqueous solution of $HClO_4$. The effect of the addition of Fe^{3+} ions on the urea adsorption was also investigated. It was shown that Fe^{3+} ions, unlike Fe^{2+} ions, are not adsorbed at the interface electrode-electrolyte solution. In the system containing Fe (III) and urea there are adsorbed urea molecules as well as the complexes ions of the type $[Fe(H_2O)_{6-n}\,U_n]^{3+}$ and complexes containing, in the coordination sphere, adsorbed ligand M_{ads} of the type $[Fe(H_2O)_{5-n}\,U_n\,(U_{ads})]^{3+}$ and also aquacomplexes $[Fe(H_2O)_6]^{2+}$ formed by the reduction of Fe^{3+} to Fe^{2+}.

INTRODUCTION

Specific properties of urea associated with the adsorption at interface: air-aqueous solution have been first obserwed by F r u m k i n [1]. He has found that most organic substances are adsorbed at the interface solution-air and solution-mercury in a similar way. He has concluded that similar adsorption is determined first of all by the structure of water on the electrode surface and by the interactions between molecules of organic substances and water. Another reason for such a specific behaviour can be, according to Frumkin, occurrence of specific interactions between the adsorbed compound and mercury. In the case of thiourea, due to strong interactions sulphur-mercury, the latter cause, no doubt, plays a greater part (although the interactions between water and

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thiourea should not be overlooked since they are stronger than those between water and urea). In the case of urea adsorption, the specific behaviour associated with the adsorption is brought by different structure of water at the interface water-urea. For the first time extensive examination of the urea properties at the interface mercury-aqueous solution has been carried out by G o u y [2]. In adsorption studies, the structure of urea in water has turned out to be very interesting, particularly in comparision with thiourea and simple aminoacids [3-5]. The urea adsorption phenomenon belongs to the very complicated ones, which is associated with its specific properties such as: mesomerism, tautomerism, ability for protonation, high dipole moment and high viscosity [6].

Our investigation of the adsorption of urea at the interface: mercury dropping electrode-electrolite solution, carried out by the method of the drop time measurement [7], has shown that urea brings about decrease in surface tension and slight shift of pzc, which evidences its adsorption. The adsorption value was determined and found to be consistent with the isoterm of Frumkin. Following the adsorption of urea in the presence of Fe^{3+} and Fe^{2+} ions [8-10] and comparing it with the adsorption of urea itself, we have concluded that in the adsorption are involved urea molecules as well as the complexes: $[Fe(H_2O)_{6-n}U_n]^{2+}$, $[Fe(H_2O)_{6-n}U_n]^{3+}$ and the complexes containing adsorbed ligand (U_{ads}): $[Fe(H_2O)_{5-n}U_n(U_{ads})]^{2+}$ and $[Fe(H_2O)_{5-n}U_n(U_{ads})]^{3+}$ where U - urea.

The phenomena taking place at the interface electrode-solution in the presence of urea and ferric ions can be affected, besides the adsorption of urea and the complexes of Fe(II) and Fe(III) with urea, also by the adsorption of Fe^{2+} and Fe^{3+} ions as well as by the reduction of Fe^{2+} and Fe^{3+} and of their complexes with urea.

Due to complicated character of the phenomena taking place at the interface in the presence of urea and ferric ions and complexity of adsorption of urea itself, we have come to conclusion that the present method of the drop time measurement is not sufficiently accurate. So, we have decided to verify the results, obtained previously, with a more precise method - measurement of the double layer capacity. It seems that only with this measurement method, it is possible to draw certain conclusions in such a complicated system.

EXPERIMENTAL

Reagents and solutions

The urea used in the experiments was recrystallized twice from anhydrous ethanol and dried in vacuum. KNO_3 was recrystallized three times from threefold distilled water and dried in vacuum. $Fe(ClO_4)_3$ was prepared according to the description in paper [11]. All the remaining reagents were analar grade of POCh-Gliwice. The solutions were prepared with threefold distilled water. Mercury was chemically purrified and than distilled three times in vacuum.

Apparatus

The double layer capacity was determined by measuring the impedance of interface: dropping electrode-electrolyte solution by the voltamperometric method [12, 13]. The following equipment was used: an impedance meter, type EIM 1, made at the University of Łódź (Poland), a potentiostat, type P-20/1 with a function generator, type LSS1, made at the University of Łódź (Poland), two selective nanowoltometers, type 237 and RG generator type PO-25 made in Poland and two X-Y recorders, type NE-240 of EMG (Hungary). Additionally, an oscilloscope, type DT-516A and a digital voltometer,

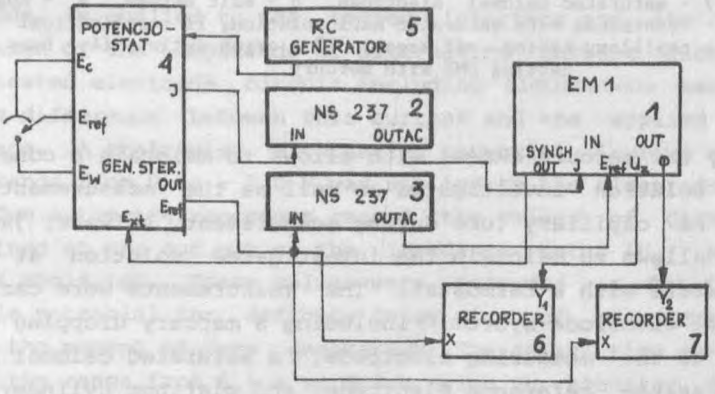

Fig. 1. Scheme of the measurement system for the Faradian impedance: 1 - an impedance meter, 2, 3 - selective nanovoltometers, 4 - a potentiostat with a generator, 5 - RC-generator, 6,7 - X,Y recorders

type V541, made in Poland, were used in the measurements. The scheme of measurement system is shown in Fig. 1 and the scheme of electrolytic cell-in Fig. 2. The cell has an autlet in its bottom

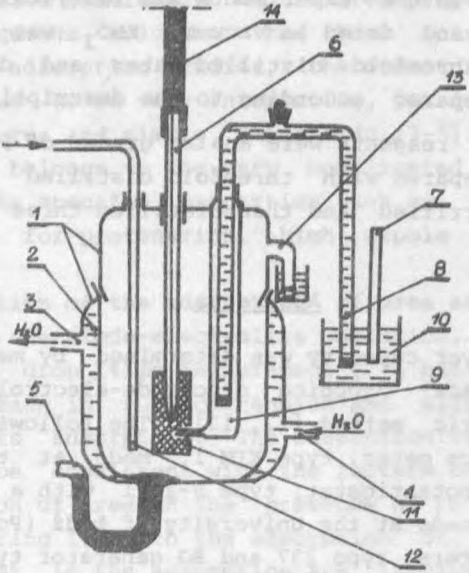

Fig. 2. Scheme of the electrolytic cell:
1 - a glass housing of the electrolytic cell, 2 - a water jacket, 3, 4 - connection with thermostat, 5 - outlet of mercury excess, 6 - dropping mercury electrode (DME), 7 - saturated calomel electrode, 8 - salt bridge, 9 - Ługin's capillary, 10 - containes with saturated NaCl solution, 11 - cylindrical platinum net, 12 - capillary taking off argon, 13 - argon outlet, 14 - hose connecting DME with mercury

to drain away the mercury exces, with allows to maintain a constant level of the solution investigated as well as the measurement of the capacity of capillary tube during measurement. A water jacket of the cell allows to maintain the investigated solution at constant temperature with a termostat. The measurements were carried out in a three-electrode system, including a mercury dropping electrode (MDE) as the measuring electrode, a saturated calomel electrode (SCE) as the reference electrode, and platinum cylinder net as the auxiliary electrode. The reference electrode with the investigated solution by a salt bridge through a Ługin capillary at the outlet of the mercury drop. The salt bridge was filled with

a 0.5 mole $HClO_4$ solution. The platinum net with a surface of 4.7 cm^2 enclosed cylindrically the mercury drop outlet and the Ługin capillary outlet. The glass capillary was silicone covered and ground so as to have a tapering end. The capillary wall thickness at its outlet was not higher than two diameters of its cappilary orifice. The grinding of capillary was caried out under a microscope, using suitable grinding powders. The capillary was connected with the mercury cell by an elastic PCV hose which was screened with a copper fail. The head of mercury from the capillary outlet to the mercury level in the cell was 1.0 m. Such a value of the mercury head eliminated the effects of back-pressure. Into the outlet of the Ługin capillary was introducted a platinum wire which was connected with the reference electrode through a capacitor so selected as to compensate the resistance of electrolyte in the measuring cell (4.7 μF). The measuring cell was feeded with argon to eliminate oxygen from the solution before measurements. The electrolytic cell and the mercury container were placed in a Faraday can and the wiring, taken outside the can, were screened.

Measurement Method

The interface measurements were carried out with the aid of apparatus developed and made at the University of Łódź [12, 13]. The measurement principle is as follows: in a potentiometric system, sinusoidally alternating voltage of low, precisely known amplitude, is applied to the tested interface and the measurement is taken of the amplitude of alternating current flowing within the tested electrode circuit including simultanous measurement of phase difference between this current and the applied alternating voltage. A stair-wise alternating potential (evry 5 min) within the range from 0 to - 1.0 V was applied to the electrodes.

Two automatic recorders record the values of direct voltage obtained at the out put of the impedance meter (U_z) and of phase shift angle (φ). These values were recorded as functions of variable potential for definite delay time of measurement counted from the moment of drop separation. The delay time can be changed with the range from 0.1 s to 9.9 s with an accuracy of $1 \cdot 10^{-4}$ s. The U_z measurement accuracy was ±0.2% and that of phase angle ±0.1 grad. The measurement system allows also to measure the drop time of mercury with an accuracy of $1 \cdot 10^{-3}$ s as well as to measure

the harmonic signal frequency (f). The moment of mercury drop separation is also signalized which is very useful for suitable regulation of the measurement delay time. The measurements were conducted at 120 Hz and an amplitude of 30 mV. It was found that within the range from 60 to 1000 Hz the double layer capacity from urea solutions is not dependent on the frequency. The capacity of capillary tube was determined each time after the measurement being completed. The drop time was about 6 s. The measurements were carried out for t_d = 1.7 s (where t_d - delay time) from the moment of drop - birth at constant temperature 25 ± 0.1°C under argon with which the tested solution was purged for 1 h before the measurement. The ionic strength of sclutions was constant μ = 0.5. A 0.5 mole $HClO_4$ solution was used as the basic electrolyte.

Calculation Procedure

The following data are obtained from measurements of the tested system: sinusoidal voltage ($U_\sim$), applied to the tested interface, direct Voltage (U_z) at the output from the impedance meter for the given value of potential and values of phase ample (φ) wersus applied potential. Due to same irregularities of amplification of the selective nanovoltometer, initial phase shif and long-term changes in the amplification of the impedance meter, it is desirable to carry out calibration measurements, using known calibrated resistor (R^o) before or after the actual measurement and to calculate the required values, taking into account the calibration results. The parameters (R^o, U_z^o, φ^o, $U_\sim^o$) of all the sygnals should be identical during the calibration measurement as well as in the actual one. The required value of impedance modulus of the tested system is calculated from the following equation [12, 13]:

$$|Z| = \frac{U_z^o \, U_\sim}{U_u \, U_\sim^o} R_o \qquad (1)$$

The double layer capacity (C) was calculated from the following relationships, at an assumption that the dropping electrode is ideally polarizable:

$$R = |Z| \cos \varphi \qquad (2)$$

$$\frac{1}{\omega C} = |Z| \sin \varphi \tag{3}$$

$$C = \frac{1}{\omega |Z| \sin \varphi} \tag{4}$$

where:

φ - phase shift angle, $\varphi = \varphi_M - \varphi^\circ$, grad

$\omega = 2\pi f$, f - harmonic signal frequency, Hz.

The value of double layer capacity was calculated per the mercury drop surface (A) according to eq.(5):

$$C = \frac{U_z \, U_\sim^\circ}{2\pi f \sin \varphi \, U_z^\circ \, U_\sim \, A} \tag{5}$$

The drop surface varies with time, hence it is important to control the time from the moment of drop detachment to the moment of measurement. The drop surface (A) is found from eq.(6):

$$A = 4\pi r^2 = \left(\frac{3m\,t}{4\pi d}\right)^{2/3} 4\pi = 0.8515 \, m^{2/3} \, t^{2/3} \tag{6}$$

where:

m - mercury flow rate, g/s,

t - time from the moment of previous drop detachment to the moment of measurement $t = t_d + kT$, t - the value of fixed delay, T - period of harmonic voltage applied, k - coefficient resulting from the time of reaction of the selective nanovoltometer and the liberating voltage U_T set at boundary value (found experimentally), T - period of harmonic voltage applied.

RESULTS AND DISCUSSION

The double layer capacity was determined for six concentrations of urea (0.1 to 1.8 mole/dm^3) in a 0.5 mole $HClO_4$ solution (Fig. 3) and for these solutions of urea and $HClO_4$ in the presence of $Fe(ClO_4)_3$ with a concentration of $3.921 \cdot 10^{-4}$ mole/dm^3 (Fig. 4). In follows from the obtained results (Fig. 3) that the increase in urea concentration is solution is accompanied by the increase in its adsorption at the interface electrode-solution. This is confirmed by the lowering of the differential capacity curves in relation to the capacity curve in the basic electrolyte with these

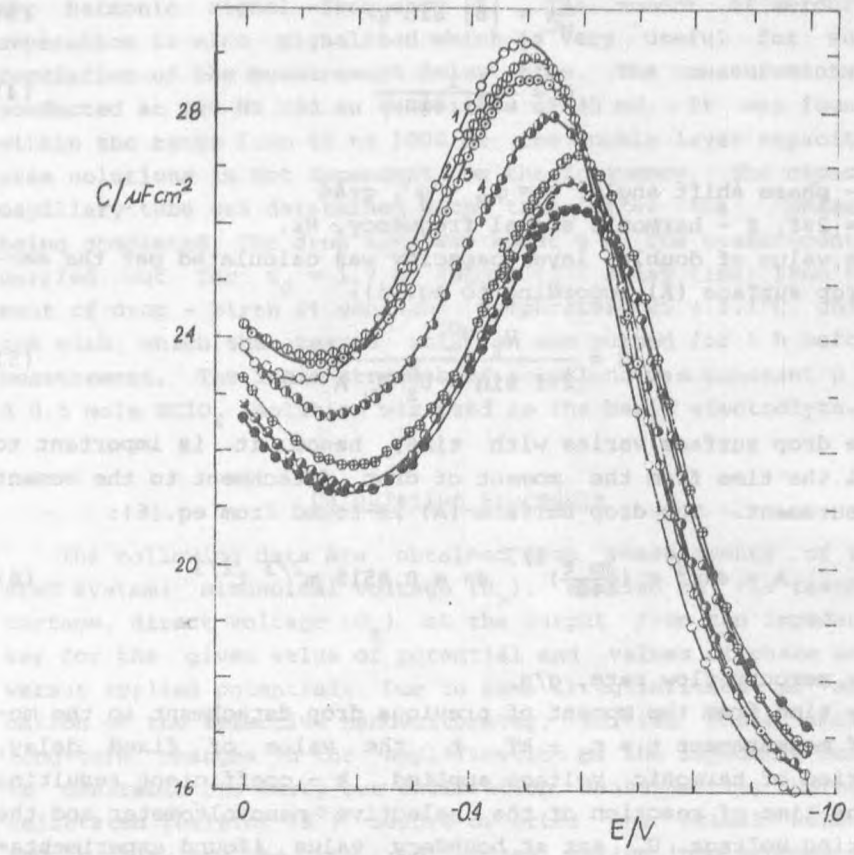

Fig. 3. Differential capacity of mercury electrode in 0.5 mole/dm^3 $HClO_4$ in the presence of NH_2CONH_2: 1 - 0, 2 - 0.1, 3 - 0.2, 4 - 0.4, 5 - 0.8, 6 - 1.2 and 7 - 1.8 mole/dm^3. The potential was measured in relation to saturated calomel electrode, t = 25°C, μ = 0.5

curves being shifted towards negative potentials. Comparing the values of double layer capacity in urea solutions (Fig. 3) with those obtained in these solutions containing Fe^{3+} ions (Fig. 4) e.g. for the concentration of urea 0.2 mole/dm^3 at a mercury electrode potential of - 0.2 V, there is a decrease in the differential capacity by 1.0 μF/cm^2, and at potential of - 0.5 V by 1.05 μF/cm^2. Once can deaw a conclusion from this observation that the addition of Fe^3 ions brings about increase in the adsorption of

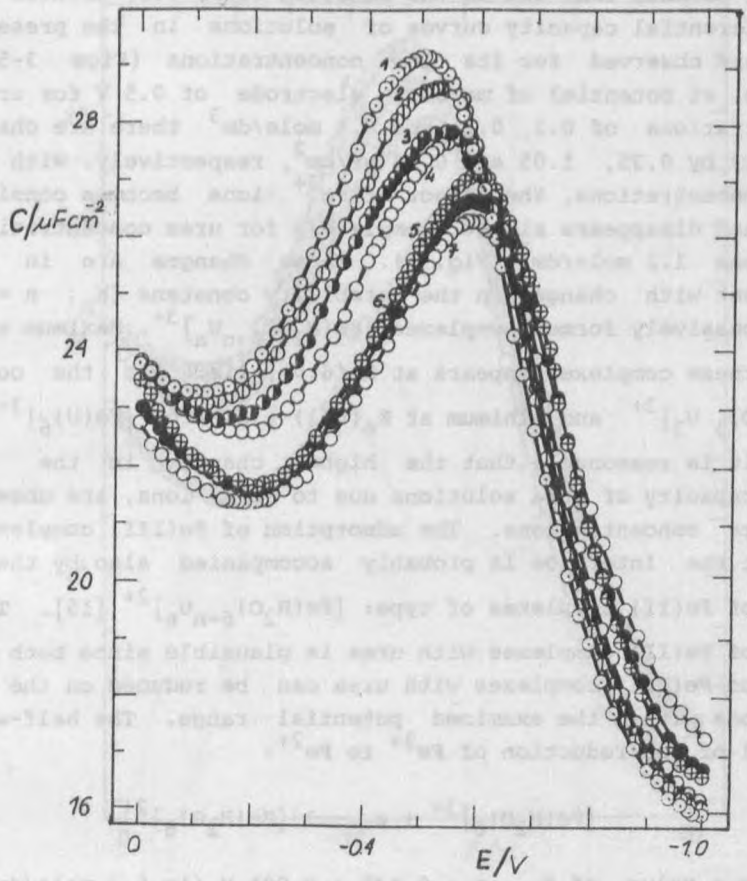

Fig. 4. Differential capacity of mercury electrode in 0.5 mole/dm^3 $HClO_4$ in the presence of NH_2CONH_2 and of $3.921 \cdot 10^{-4}$ mole/dm^3 $Fe(ClO_4)_3$. Concentrations of urea and measurement conditions as in Fig. 3

urea at the interface electrode-electrolyte solution. This observation is interesting and can be a proof that besides urea molecules, the Fe(III) complexes with urea can also be adsorbed at the interface. Based on previous polarographic examinations of the complexation proces in the system Fe^{3+} - urea [14], we can state that the lowering of capacity curves in urea solutions due to the addition of Fe^{3+} ions is brought about by the adsorption of complexes $[Fe(H_2O)_{6-n}U_n]^{3+}$, where n = 1 - 6, U-urea. It is also inte-

resting to note that due to the addition of Fe(III) greater changes in differential capacity curves of solutions in the presence of urea, are observed for its low concentrations (Figs 3-5). For example, at potential of mercury electrode of 0.5 V for urea with concentrations of 0.1, 0.2 and 0.4 mole/dm^3 there are changes in capacity by 0.35, 1.05 and 0.13 μF/cm^2, respectively. With growing urea concentrations, the effect of Fe^{3+} ions becomes considerably lower and disappears almost completely for urea concentrations higher than 1.2 mole/dm^3 (Fig. 5). These changes are in a good agreement with changes in the stability constans (K_n; n = 1 - 6) of successively formed complexes $[Fe(H_2O)_{6-n}U_n]^{3+}$. Maximum stability of these complexes appears at $K_1(6.0)$, i.e. for the complexes $[Fe(H_2O)_5\ U_1]^{3+}$ and minimum at $K_6(0.1)$ i.e. for $[Fe(U)_6]^{3+}$ [14]. Hence it is reasonable that the highest changes in the double layer capacity of urea solutions due to Fe^{3+} ions, are observed at low urea concentrations. The adsorption of Fe(III) complexes with urea at the interface is probably accompanied also by the adsorption of Fe(II) complexes of type: $[Fe(H_2O)_{6-n}U_n]^{2+}$ [15]. The presence of Fe(II) complexes with urea is plausible since both Fe(III) ions and Fe(III) complexes with urea can be reduced on the mercury electrode within the examined potential range. The half-wave potential of the reduction of Fe^{3+} to Fe^{2+}:

$$[Fe(H_2O)_6]^{3+} + e \rightleftharpoons [Fe(H_2O)_6]^{2+}$$

assumes a value of $E_{1/2}$ = + 0.145 ± 0.001 V (in 0.2 mole/dm^3 $HClO_4$) [14]. With the increase in urea concentration the $E_{1/2}$ value shifts towards negative potentials. On the others hand, the reduction of Fe^{2+} to Fe^{o}:

$$[Fe(H_2O)_6]^{2+} + 2e \rightleftharpoons Fe + 6H_2O$$

corresponds to $E_{1/2}$ = 1.375 ± 0.001 V (in 0.2 mole/dm^3 $NaClO_4$) [15], and with growing urea concentration shifts towards negative potentials.

The examinations of double layer capacity for several concentrations of $Fe(ClO_4)_3$ solutions in 0.5 mole/dm^3 $HClO_4$ (Fig. 6) show that aquacomplexes $[Fe(H_2O)_6]^{3+}$ are not adsorbed at the in-

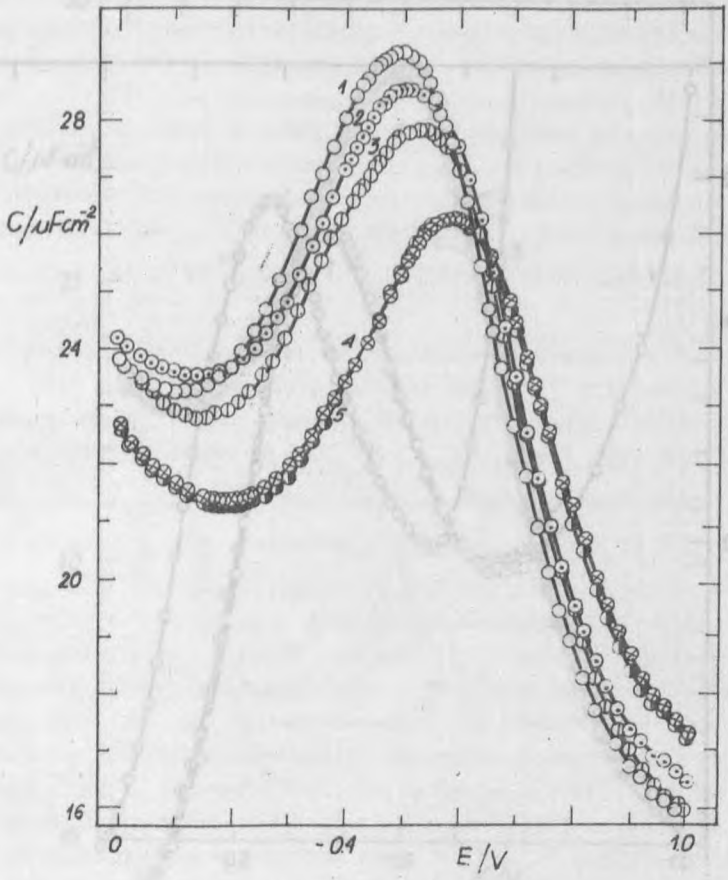

Fig. 5. Differential capacity of mercury electrode in 0.5 mole/dm^3 $HClO_4$ in the presence of NH_2CONH_2 and of $3.921 \cdot 10^{-4}$ mole/dm^3 $Fe(ClO_4)_3$: 1 - 0.5 mole/dm^3 $HClO_4$, 2 - 0.2 mole/dm^3 NH_2CONH_2, 3 - 0.2 mole/dm^3 NH_2CONH_2 + $Fe(ClO_4)_3$, 4 - 1.8 mole/dm^3 NH_2CONH_2, 5 - 1.8 mole/dm^3 NH_2CONH_2 + $Fe(ClO_4)_3$. Measurement conditions as in Fig. 3

terface electrode-electrolyte solution (there is no lowering of capacity curves). The presence of Fe^{3+} ions of a concentration of $3.89 \cdot 10^{-4}$ mole/dm^3 brings about only the shift capacity curve (2) towards negative potentials in relation to curve (1) from a 0.5 mole/dm^3 $HClO_4$ solution. In the presence of higher concentration of Fe^{3+} (curve 3), the effect of reduction of Fe^{3+} to Fe^{2+} is

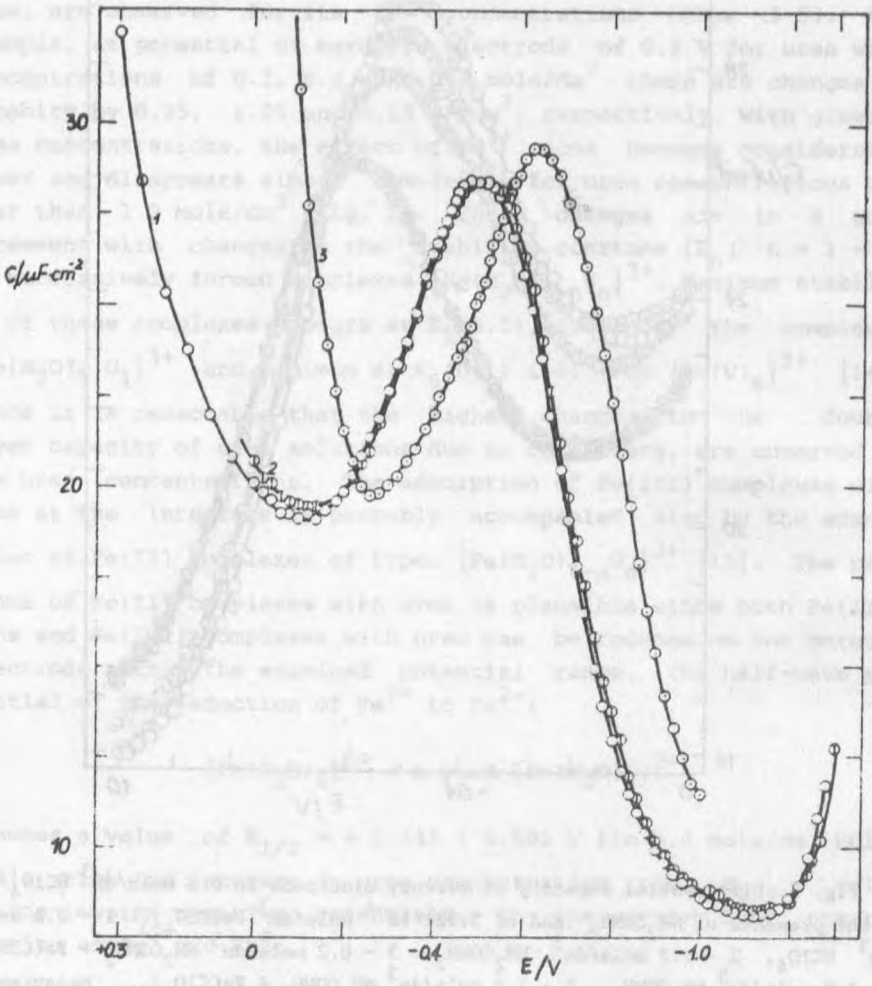

Fig. 6. Differential capacity of mercury electrode in 0.5 mole/dm^3 $HClO_4$ in the presence of $Fe(ClO_4)_3$: 1 - 0, 2 - $3.8976 \cdot 10^{-4}$, 3 - $3.6782 \cdot 10^{-3}$ mole/dm^3. Measurement conditions as in Fig. 3

cleary shown and that curve is considerably disorted. The concentration of $Fe(ClO_4)_3$ used in our investigations ($3.921 \cdot 10^{-4}$ mole/

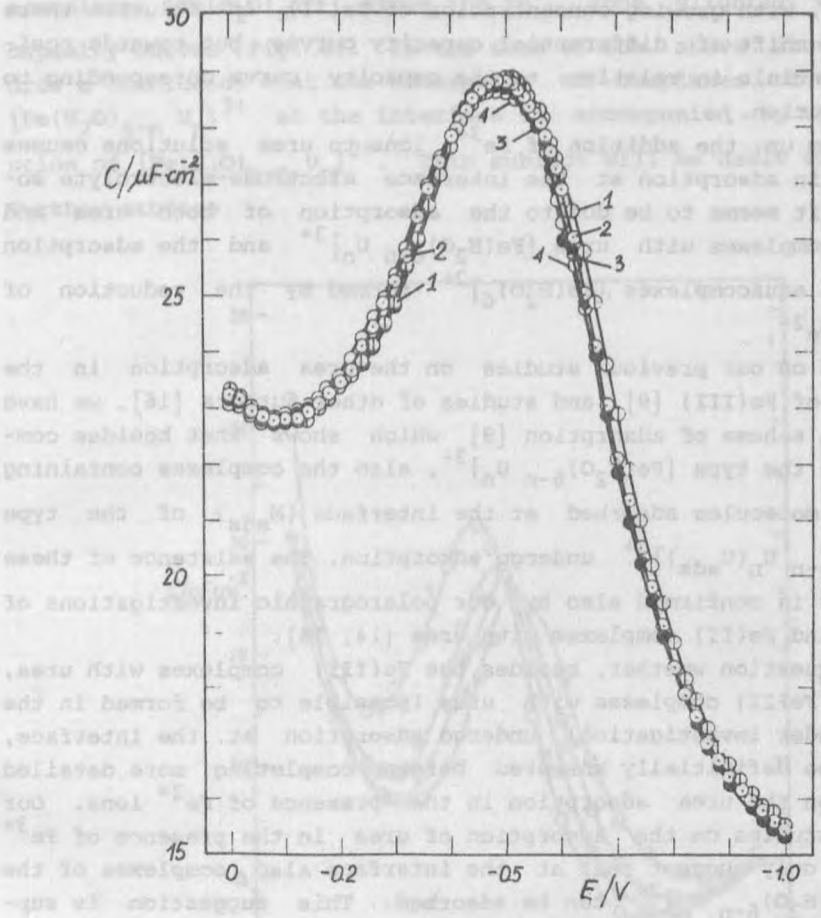

Fig. 7. Differential capacity of mercury electrode in 0.5 mole/dm^3 $HClO_4$ in the presence of $FeSO_4 \cdot 7H_2O$: 1 - 0, 2 - $1.4387 \cdot 10^{-4}$, 3 - $7.80496 \cdot 10^{-4}$, 4 - $1.30058 \cdot 10^{-3}$ mole/dm^3. Measurement conditions as in Fig. 3

/dm^3) could not have affected the change in the double layer capacity if there were no adsorption of Fe(III) complexes with urea. Figure 7 shows the double layer capacity curves for several concentrations of $FeSO_4$ solutions in 0.5 mole/dm^3 $HClO_4$. It follows from these curves that the addition of Fe^{2+} ions to $HClO_4$ solution brings about decrease in the double layer capacity and consequently also the adsorption of aquacomplexes $[Fe(H_2O)_6]^{2+}$ at the

interface. With growing concentration of Fe(II) in solution there is also a shift of differential capacity curves but towards positive potentials in relation to the capacity curve coresponding to $HClO_4$ solution.

To sum up, the addition of Fe^{3+} ions to urea solutions causes increase in adsorption at the interface electrode-electrolyte solution. It seems to be due to the adsorption of both urea and Fe(III) complexes with urea $[Fe(H_2O)_{6-n}\ U_n]^{3+}$ and the adsorption of Fe(II) aquacomplexes $[Fe(H_2O)_6]^{2+}$ formed by the reduction of Fe^{3+} to Fe^{2+}.

Based on our previous studies on the urea adsorption in the presence of Fe(III) [9] and studies of other authors [16], we have assumed a scheme of adsorption [9] which shows that besides complexes of the type $[Fe(H_2O)_{6-n}\ U_n]^{3+}$, also the complexes containing the urea molecules adsorbed at the interface (M_{ads}) of the type $[Fe(H_2O)_{5-n}\ U_n(U_{ads})]^{3+}$ undergo adsorption. The existence of these complexes is confirmed also by our polarographic investigations of Fe(III) and Fe(II) complexes with urea [14, 15].

The question whether, besides the Fe(III) complexes with urea, also the Fe(II) complexes with urea (possible to be formed in the system under investigation) undergo adsorption at the interface, can not be definitially answered before completing more detailed studies on the urea adsorption in the presence of Fe^{2+} ions. Our present studies on the adsorption of urea in the presence of Fe^{3+} ions can only suggest that at the interface also complexes of the type $[Fe(H_2O)_{6-n}\ U_n]^{2+}$ can be adsorbed. This suggestion is supported by the following facts observed: the half-wave potential of reduction of Fe^{3+} to Fe^{2+} in the presence of urea varies within the potentials of mercury electrode from +0.145 to -0.382 V, respectively for urea concentrations from 0 to 1.6 mole/dm^3 [14]. If the lowering of differential capacity curves were affected only by the adsorption of the Fe(III) complexes, these changes would be observable only within the potential range from 0 to about -0.4 V. The lowering of the differential capacity curves from urea solutions due to the addition of Fe^{3+} ions takes place, however, within the whole potential range under investigation (from 0 to -1.0 V).

Such great changes in the differential capacity within the range over -0.4 V can not be caused only by the adsorption of aqu-

acomplexes $[Fe(H_2O)_6]^{2+}$ since the Fe^{2+} ions slightly change the capacity curves (Fig. 4). In the face of the above facts, we can draw a conclusion that the adsorption of complexes of the type $[Fe(H_2O)_{6-n}\ U_n]^{3+}$ at the interface is accompanied by the adsorption of $[Fe(H_2O)_{6-n}\ U_n]^{2+}$. This subiect will be dealt with in our further studies.

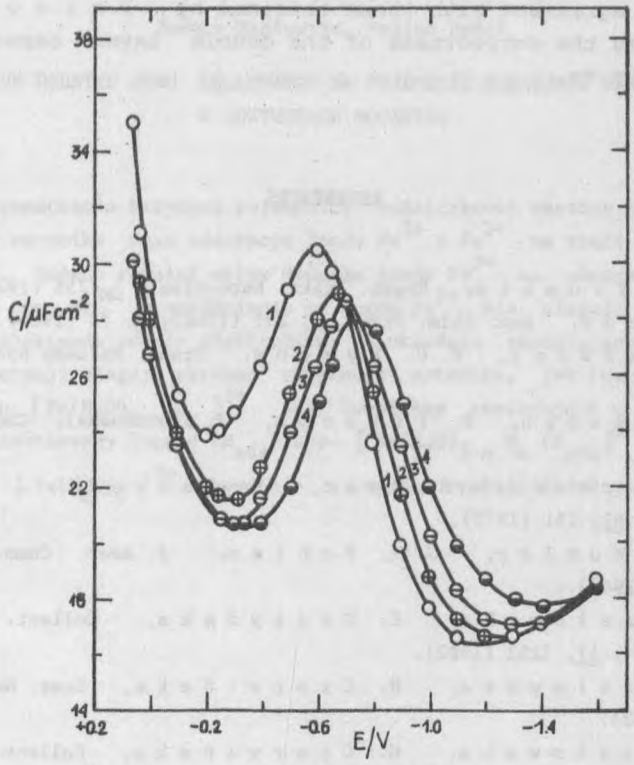

Fig. 8. Differential capacity of mercury electrode in 1.0 mole/dm^3 KNO_3 in the presence of NH_2CONH_2: 1 - 0, 2 - 0.63, 3 - 1.6, 4 - 4.0 mole/dm^3. The points in the particular curves correspond to the literature data [5]. The potential was measured relation to a 0.1 mole/dm^3 KCl calomel electrode t = 25°C.

In order to verify our results of the determination of the double layer capacity, we carried out measurements in urea solu-

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tions with the same concentrations and under the same conditions as those used by Parsons and coworkers [5]. Their concentrations of urea were from 0.1 to 4.0 mole/dm^3 in 1.0 mole/dm^3 KNO_3. The potential was measured by them in relation to a 0.1 mole/dm^3 KCl calomel electrode at a temperature of 25°C.

The results of our measurements of the double layer capacity of urea solutions with concentrations 0.63, 1.6 and 4.0 mole/dm^3 in a 1.0 mole/dm^3 KNO_3 solution are given in Fig. 8. The results are in good agreement with those obtained by P a r s o n s [5]. This confirms the correctness of the double layer capacity valuea determined by us.

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WPŁYW DODATKU JONU ŻELAZOWEGO NA POJEMNOŚĆ PODWÓJNEJ WARSTWY W ROZTWORACH MOCZNIKA

Metodą wyznaczania krzywych pojemności różniczkowej warstwy podwójnej badano adsorpcję mocznika oraz adsorpcję jonów Fe^{3+} i Fe^{2+} na rtęci w wodnym roztworze $HClO_4$. Badano również wpływ dodatku jonów Fe^{3+} na adsorpcję mocznika. Wykazano, że jony Fe^{3+} w odróżnieniu od jonów Fe^{2+} nie ulegają adsorpcji na granicy faz elektroda-rozwór elektrolitu. W układzie zawierającym Fe(III) i mocznik, adsorpcji ulegają zarówno cząsteczki mocznika, jak również jony kompleksowe typu $[Fe(H_2O)_{6-n}M_n]^{3+}$ oraz kompleksy zawierające w sferze koordynacyjnej zaadsorbowany ligand (M_{ads}) typu $[Fe(H_2O)_{5-n}M_n(M_{ads})]^{3+}$, a także akwokompleksy $[Fe(H_2O)_6]^{2+}$ powstałe w wyniku reakcji redukcji Fe^{3+} do Fe^{2+}.