

EFFECT OF Fe(III) ON SPECIFIC ADSORPTION OF ALIPHATIC CARBAMIDE DERIVATIVES AT THE DROPPING MERCURY ELECTRODE*

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Received October 15th, 1982

The specific adsorption of carbamide and its aliphatic derivatives (L) was studied by the drop-time method in the system $\text{Fe}(\text{ClO}_4)_3\text{-L-HClO}_4\text{-H}_2\text{O}$ and the adsorption process was elucidated. From the calculated surface concentrations and adsorption isotherms, it was found that the adsorption of aliphatic carbamide derivatives is higher in the presence of Fe(III) ions than in their absence under the same conditions. In the presence of Fe(III) ions at the interface, free molecules of carbamide derivatives and the complexes $[\text{Fe}(\text{H}_2\text{O})_6 - n\text{L}_n]^{3+}$ as well as the complexes $[\text{Fe}(\text{H}_2\text{O})_{5-n}\text{L}_n\text{L}_{\text{ads}}]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_{5-n}\text{L}_n\text{L}_{\text{ads}}]^{2+}$ formed with the adsorbed ligand are adsorbed. The adsorption was found to proceed according to the Frumkin's isotherm.

Studies on the effect of adsorption of neutral molecules and ions at electrodes on the stability constants of metal complexes in solutions are still in an initial stage although several relevant papers have been published¹⁻⁸. Emelyanko and coworkers¹ found that of the ligands investigated, complexes of Cu(I) with thiocarbamide (nonionic ligand) are most strongly adsorbed, similarly as was observed in the case of mixed amino acid complexes of Cu(II)². Turyan and coworkers⁹ found that Fe^{2+} ions and Fe(II) complexes formed with either free or adsorbed ligand molecules at the electrode surface have a catalytic effect on the electrode process. In our polarographic investigations of Fe(II) complexes with carbamides¹⁰, the effect of adsorption of ligands and complexes on the complex formation taking place at the dropping mercury electrode has not been considered. In recent studies, we dealt with the specific adsorption of carbamide derivatives and with the effect of Fe(II) on the phenomena at the electrode-solution interface^{11,12}.

The present study deals with the effect of Fe(III) ions on the extent and course of specific adsorption of carbamide derivatives at the dropping mercury electrode. The investigations were carried out in systems $\text{Fe}(\text{ClO}_4)_3\text{-L-HClO}_4\text{-H}_2\text{O}$, where $\text{L} = \text{H}_2\text{NCONH}_2$ (U), $\text{CH}_3\text{NHCONH}_2$ (MtU), $\text{C}_2\text{H}_5\text{NHCONH}_2$ (EtU), $\text{CH}_3\text{NH}\cdot\text{CONHCH}_3$ (sym DMtU), and $\text{C}_2\text{H}_5\text{NHCONHC}_2\text{H}_5$ (sym DeU).

EXPERIMENTAL

Reagents and Solutions

The following "Analar" grade reagents, manufactured by POCH Gliwice, were used for the experiments: HClO_4 , NaClO_4 , H_2NCONH_2 , and $\text{CH}_3\text{NHCONH}_2$. In addition, we used $\text{C}_2\text{H}_5\text{HN}\cdot$

* Paper presented on the PTCh and SITPCh Meeting, September 1981, Gdańsk.

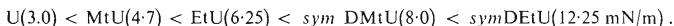
.CONH₂ of Lab Reagent, England, CH₃HNCONHCH₃ of Loba Chemic, Wien, and C₂H₅HN.CONHC₂H₅ of Fluka A. G. Buchs S. G., Switzerland. Solutions were prepared in 10 ml volumetric flasks. To a solution of HClO₄ and Fe(ClO₄)₃, the required quantity of a solution of a carbamide derivative was added and the volume was made up to the mark with water. The base electrolyte was 0.2M-HClO₄, the concentrations of the carbamide derivatives varied from 0.2 to 1.6 mol/dm³ and the concentration of Fe(ClO₄)₃ was $3.9 \cdot 10^{-4}$ mol/dm³. The ionic strength was maintained at 0.2.

Methods and Apparatus

Measurements were done on a square wave OH-105 type polarograph (Radelkis, Hungary) with a dropping mercury electrode. Purity of the investigated samples and nitrogen was checked polarographically on the same apparatus. The reference electrode was a saturated calomel electrode (s.c.e.), separated from the measured solution by a salt bridge filled with 1M-NaClO₄. The flow rate of mercury through the capillary was 1.00 mg/s. On the basis of the values given by Smolders¹³ for the surface tension of mercury in Na₂SO₄ solutions, the value of $\gamma = 426.2 \text{ mN/m}$ in the electrocapillary maximum at 25°C was used in all calculations. Oxygen was removed from the investigated solutions by bubbling nitrogen, purified by passing through a specially constructed apparatus¹¹. The temperature of measurements was $25 \pm 0.1^\circ\text{C}$, the potential was varied at 50 mV steps from -50 to -950 mV. After 4 min elapsed from the potential change, the drop time of 10 mercury drops was measured, and the drop time of 20 or 30 mercury drops was measured near the electrocapillary maximum. An average from five measurements was taken. The standard deviation was $\pm 0.12 \text{ mN/m}$ corresponding to $\pm 0.1 \text{ s}$ (for 10 drops).

RESULTS AND DISCUSSION

The electrocapillary curves $\gamma = f(E)$ for all the carbamide derivatives studied are shown in Figs 1–3. By comparing the values of the surface tension obtained in systems with and without Fe(III) (ref.¹¹) for the same concentration of the investigated substances (1 mol/dm³) at the electrocapillary maximum, the following sequence is obtained for the decrease of the surface tension, $\Delta\gamma$, in the presence of Fe(III) ions with respect to that in their absence:



This suggests an increase in adsorption at the electrode-electrolyte interface in the presence of Fe(III) ions, both the derivative molecules and the complexes of the type $[\text{Fe}(\text{H}_2\text{O})_6 - n\text{L}_n]^{3+}$ being adsorbed at the mercury electrode. The growing values of $\Delta\gamma$ are in a close relation with the stability constants of Fe(III) complexes with carbamide derivatives, which increase in the same order¹⁰.

Fig. 4 shows examples of electrocapillary curves for solutions of 0.2M-EtU without (1) and with (2) Fe(II) ions as well as with Fe(III) ions (3). The greatest decrease of the electrocapillary curves is observed in the latter case.

Increasing the concentration of the derivative in the presence of Fe(III) ions results in a considerable shift of the zero charge potential, E^z , towards negative values, whereas in the presence of Fe(II) ions towards positive values¹². The adsorption of

carbamide derivatives themselves is associated with a slight shift of E^2 towards negative values¹¹. These changes suggest different mechanisms of the adsorption process.

To describe the specific adsorption process, the potential as an independent electrical variable was chosen¹⁴ and the values of the surface concentration, Γ , of the ad-

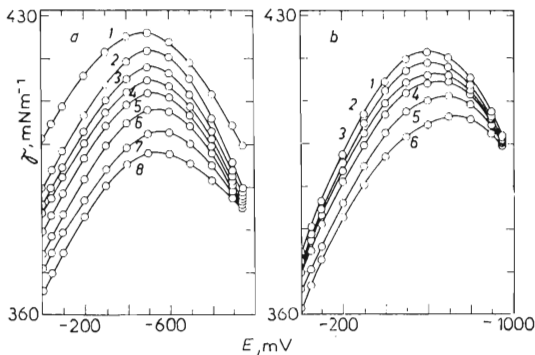


FIG. 1

Electrocapillary curves $\gamma = f(E)$ measured in the system $\text{Fe(III)}-\text{L}-\text{HClO}_4-\text{H}_2\text{O}$. 0.20M HClO_4 ; ionic strength 0.20 ; $3.9 \cdot 10^{-4}\text{M Fe(III)}$; $25 \pm 0.1^\circ\text{C}$. a $\text{L} = \text{CO(NH}_2)_2$, concentration (mol/dm^3): 1 0; 2 0.2; 3 0.4; 4 0.6; 5 0.8; 6 1.0; 7 1.2; 8 1.4; b $\text{L} = \text{CH}_3\text{NH.CO.NH}_2$, conc. (mol/dm^3): 1 0.2; 2 0.4; 3 0.6; 4 0.8; 5 1.0; 6 1.2

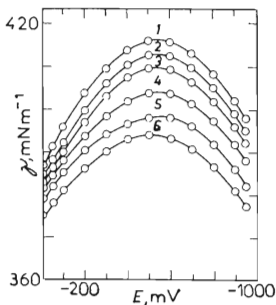


FIG. 2

Electrocapillary curves measured in the same system as in Fig. 1. $\text{L} = \text{C}_2\text{H}_5\text{NH.CO.NH}_2$, conc. (mol/dm^3): 1 0.2; 2 0.4; 3 0.6; 4 0.8; 5 1.0; 6 1.2

sorbed substances were calculated¹⁵. The results are presented in the form of adsorption isotherms, which illustrate the dependence of Γ on the volume concentration, c , for selected values of the electrode potential $E = -300, -500$, and -700 mV vs S.C.E. (Figs 5–7). The curves show that a full coverage was attained for *sym* DMtU and *sym* DEtU in the studied concentration range. For *sym* DMtU, the limiting relative surface excess, Γ_{∞} , was found to be equal to $1.143 \cdot 10^{-8}$ mol/cm², and for *sym* DEtU $1.061 \cdot 10^{-8}$ mol/cm² at -700 mV.

A comparison, based on the dimensionless parameter Θ , of the isotherms for *sym* DMtU and *sym* DEtU with the theoretical isotherm^{16,17} shows that the adsorption is governed by the Frumkin isotherm, the value of the molecular interaction coefficient a being equal to -2.00 for *sym* DMtU and -1.81 for *sym* DEtU at -700 mV. The values of the equilibrium constant for the adsorption process, $\log \beta'$, are -0.78 for *sym* DMtU and -0.62 for *sym* DEtU at the same potential. Similarly, the adsorption isotherms obtained for all the investigated carbamide derivatives in the presence of Fe(III) ions allow us to conclude that the adsorption proceeds in these systems in accordance with the Frumkin isotherm.

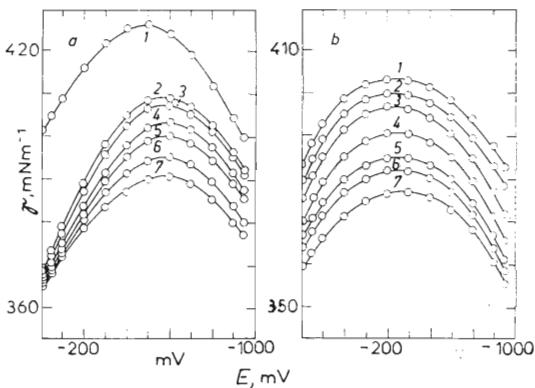
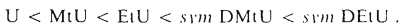


FIG. 3

Electrocapillary curves measured in the same system as in Fig. 1. *a* $L = \text{CH}_3\text{NH.CO.NH.CH}_3$, conc. (mol/dm³): 1 0; 2 0.2; 3 0.4; 4 0.8; 5 1.0; 6 1.2; 7 1.6; *b* $L = \text{C}_2\text{H}_5\text{NH.CO.NH.C}_2\text{H}_5$, conc. (mol/dm³): 1 0.2; 2 0.4; 3 0.6; 4 0.8; 5 1.0; 6 1.2; 7 1.4

The values of the surface concentration Γ in systems containing Fe(III) increase in the following sequence



The increase of the adsorption of carbamide derivatives in the presence of Fe(III) ions is connected with the change of the effects of polar alkyl substituents ($\sum\sigma^*$) causing, in the same sense, changes in the electron density (δ^-) on the oxygen atom. This corresponds to changes in the dipole moment of carbamide and its derivatives in aqueous solutions. The dipole moment of the derivatives increases (under the same conditions) in the same sequence. The adsorption of carbamide derivatives at the mercury electrode depends on the charge, δ^- , of the negative end of the dipole, *i.e.* the oxygen atom in the CO group, which probably is directed towards the positively charged mercury surface¹¹.

The addition of Fe(III) ions brings about a higher increase in the adsorption of carbamide derivatives than the addition of Fe(II) (ref. ¹²). This is associated with higher values of the stability constants of the Fe(III) carbamide complexes as compared to analogous complexes of Fe(II), as well as with a different course of the specific ad-

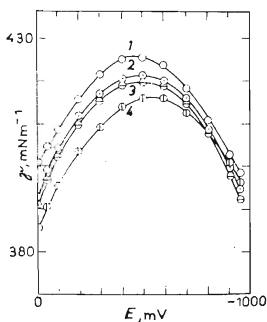


FIG. 4

Electrocapillary curves $\gamma = f(E)$ measured in the systems: 1 $\text{HClO}_4\text{--H}_2\text{O}$; 2 $\text{L--HClO}_4\text{--H}_2\text{O}$; 3 $\text{Fe(II)--L--HClO}_4\text{--H}_2\text{O}$; 4 $\text{Fe(III)--L--HClO}_4\text{--H}_2\text{O}$. 0.20M--HClO_4 , $0.20\text{M--C}_2\text{H}_5\text{NH.CO.NH}_2$ (L), $7.0 \cdot 10^{-3}\text{M--Fe(II)}$, $3.9 \cdot 10^{-4}\text{M--Fe(III)}$, $25 \pm 0.1^\circ\text{C}$

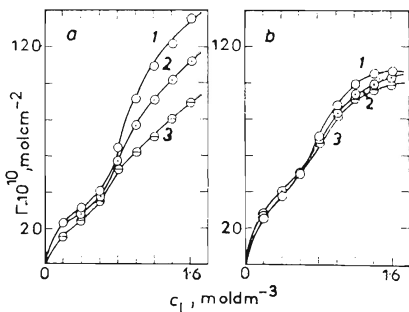
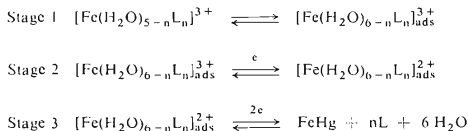


FIG. 5

Adsorption isotherms $\Gamma = f(c)$ measured in the system $\text{Fe(III)--L--HClO}_4\text{--H}_2\text{O}$. 0.20M--HClO_4 , $3.9 \cdot 10^{-4}\text{M--Fe(III)}$, $25 \pm 0.1^\circ\text{C}$; potential vs S.C.E. (mV): 1 — 500; 2 — 300; 3 — 700. a L = $\text{CO(NH}_2)_2$, b L = $\text{CH}_3\text{NH.CO.NH}_2$

sorption. In the presence of Fe(III) ions, not only free molecules of carbamide derivatives, but also their complexes with Fe(III) are adsorbed either directly or with the participation of the adsorbed ligand. On the other hand, the adsorption of the Fe(II) complexes takes place only with the participation of the adsorbed ligand¹². The adsorption of the Fe(III) complexes proceeds according to the following schemes:



SCHEME 1

Scheme 1 comprises direct adsorption of the complexes $[\text{Fe}(\text{H}_2\text{O})_6 - n\text{L}_n]$ at the electrode-electrolyte interface (stage 1), which in stage 2 can be reduced to the complexes $[\text{Fe}(\text{H}_2\text{O})_6 - n\text{L}_n]^{2+}$ and in stage 3 to Fe^0 with the liberation of the ligand molecules.

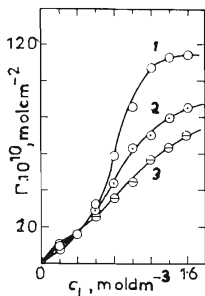


FIG. 6

Adsorption isotherms measured in the same system as in Fig. 5. $\text{L} = \text{CH}_3\text{NH.CO.NH.CH}_3$, E vs S.C.E. (mV): 1 — 700; 2 — 500; 3 — 300

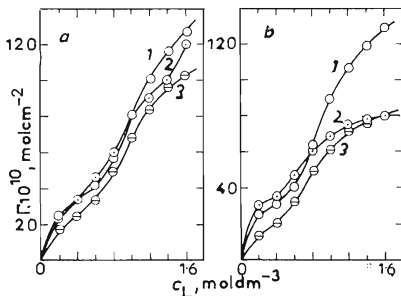
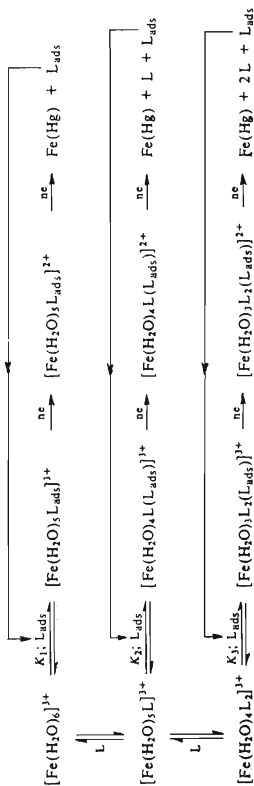


FIG. 7

Adsorption isotherms measured in the same system as in Fig. 5. $\text{a } \text{L} = \text{C}_2\text{H}_5\text{NH.CO.NH.C}_2\text{H}_5$, E vs S.C.E. (mV): 1 — 700; 2 — 500; 3 — 300; $\text{b } \text{L} = \text{C}_2\text{H}_5\text{NH.CO.NH.C}_2\text{H}_5$, E (mV): 1 — 700; 2 — 300; 3 — 500

It is assumed in Scheme 2 that in the initial stage of the interface, free molecules of the carbamide derivatives are adsorbed (L_{ads}), having a catalytic effect on the adsorption of the complexes. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions as well as the complexes $[\text{Fe}(\text{H}_2\text{O})_5 \cdot \text{L}]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_4 \text{L}_2]^{3+}$, *etc.* can participate in further complexation processes with the ligand molecules adsorbed at the electrode surface, giving complexes of the



SCHEME 2

type $[\text{Fe}(\text{H}_2\text{O})_5\text{L}_{\text{ads}}]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_4\text{L}(\text{L}_{\text{ads}})]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_3\text{L}_2\text{L}_{\text{ads}}]^{3+}$, etc. The complexes adsorbed at the mercury electrode can be decomposed by reduction, whereby a portion of the ligand molecules remains at the electrode surface, while another portion is set free into the solution. The Fe(II) complexes formed by reduction (Schemes 1 and 2) can be adsorbed at the electrode surface with the participation of the adsorbed ligand¹².

The process of specific adsorption depends on the concentrations of the ligand molecules and the Fe(III) and Fe(II) complexes, on their stability constants, and on the kinetics of the complexes formation with the adsorbed ligand.

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Translated by K. Micka.