

ADSORPTION OF CARBAMIDE AND ITS ALIPHATIC DERIVATIVES ON THE DROPPING MERCURY ELECTRODE

Joanna MASŁOWSKA and Krystyna CEDZYŃSKA

*Institute of General Food Chemistry,
Politechnical University, 90-924 Łódź, Poland*

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The adsorption of carbamide and its aliphatic derivatives at the interphase mercury — electrolyte solution was studied, using the drop-time technique. The surface concentration Γ of carbamide and its derivatives has been calculated for a wide range of concentrations at the selected potential. The shape of the electrocapillary curves indicates that both carbamide and its derivatives are adsorbed at the interphase mercury-electrolyte solution.

During polarographic investigations of equilibrium reactions in solutions with Fe(III) and carbamides¹, we have found that these systems can be affected not only by complexation reactions but also by other phenomena associated with the properties of the electric double layer at the interphase mercury-electrolyte solution²). The main role is played here by the specific adsorption of molecules of carbamide or its derivatives.

Investigating the adsorption of carbamide on the mercury electrode in 1M solution of KNO₃ Parsons and coworkers³ have determined the surface carbamide concentration Γ the value being $24 \cdot 10^{-10}$ mol/cm². They have also proposed the mechanism of adsorption stating that the addition of carbamide molecules to the mercury surface is the same as that of the water dipole through the oxygen atom and that the addition of electrolyte components is here a competitive phenomenon. Similar relations have been found for the thiocarbamide adsorption in butyl alcohol⁴ and other solvents^{5,6} as well as for the adsorption of CH₃COOLi (ref.⁷) and 2-methylthioethanol⁸ versus the concentration of NaF as base electrolyte.

The aim of our study was to investigate the relation between the adsorption of carbamide and some of its derivatives on the mercury electrode and the polar effects of aliphatic substituents in carbamide on the oxygen atom of the carbonyl group as the center of adsorption.

EXPERIMENTAL

Reagents and Solutions

The following analar grade reagents, produced by POCH — Gliwice were used: HClO₄, NaClO₄, H₂NCONH₂ and CH₃HNCONH₂. C₂H₅HNCONH₂ was a product of Lab. Reagent, England; CH₃HNCONHCH₃ of Loba Chemie, Wien and C₂H₅HNCONHC₂H₅ of A.G. Buchs S.G., Switzerland. The base electrolyte in the studied solutions was HClO₄. The concentration of HClO₄

in each sample was 0.20 mol/dm^3 . A constant ionic strength ($I = 0.25$) of the solutions was maintained by the addition of a titrated NaClO_4 solution. The solutions were prepared as follows. To a definite volume of HClO_4 the carbamide derivative solution was added to obtain the required concentration both of HClO_4 and of the investigated compound after filling up with water to the mark.

Methods and Apparatus

Measurements were carried out on a Square wave type OH-104 polarograph produced in Hungary (Radelkis) as well as on hungarian polarograph (Radelkis) type OH-105, using a dropping mercury electrode. The polarographic vessel with the studied solution was kept at adequate temperature using a water jacket and it was tightly sealed (adequate tight fitting openings were left in the cover for the electrode, the nitrogen supply tube and for the thermometer). Oxygen was removed from the studied solutions by passing nitrogen purified in specially designed deoxygenating columns. Column I was filled with molecular sieves. Column II was filled with active copper to remove the emitted nitrogen oxides (heating). Column III was filled with active manganese placed on Al_2O_3 to remove additionally the oxygen residue below 0.5 ppm. A saturated calomel electrode was the reference electrode. It was connected with the investigated solutions through a salt bridge with 1M-NaClO_4 . The capacity of the capillary tube at a definite height was 1.00 mg/s . Measurements were carried out in $0.05\text{M-Na}_2\text{SO}_4$ standard solutions to determine the so-called capillary tube constant or the ratio of the mercury surface tension to the dura-

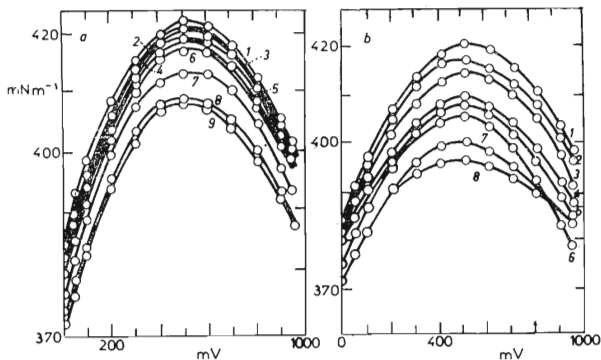


FIG. 1

Electrocapillary curves $\gamma = f(E)$ in the system $\text{L-HClO}_4\text{-NaClO}_4\text{-H}_2\text{O}$. $0.20 \text{ mol dm}^{-3} \text{ HClO}_4$; ionic strength $I = 0.25$; $298 \pm 0.1 \text{ K}$. *a* $\text{L} = \text{H}_2\text{N.CO.NH}_2$, conc. (mol dm^{-3}): 1.0; 2.0; 3.0; 4.0; 5.1; 6.2; 7.2; 8.3; 9.3. *b* $\text{L} = \text{CH}_3.\text{NH.CO.NH}_2$, conc. (mol dm^{-3}): 1.0; 2.0; 3.0; 4.0; 5.1; 6.1; 7.1; 8.2

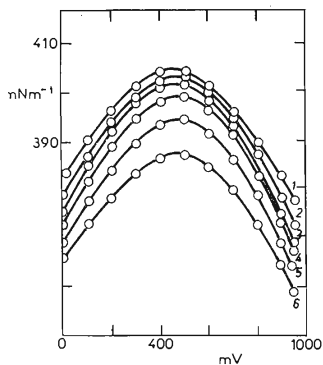


FIG. 2

Electrocapillary curves of the same system as in Fig. 1. $L = \text{CH}_3\text{NHCO.NHCH}_3$, conc. (mol dm^{-3}): 1 0.2; 2 0.3; 3 0.4; 4 0.6; 5 1.0; 6 1.6

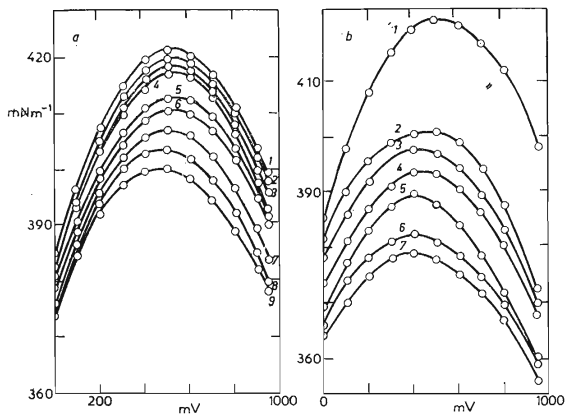


FIG. 3

Electrocapillary curves of the same system as in Fig. 1. *a* $L = \text{C}_2\text{H}_5\text{HNCO.NH}_2$, conc. (mol dm^{-3}): 1 0; 2 0.2; 3 0.6; 4 0.8; 5 1.0; 6 1.2; 7 1.6; 8 1.8; 9 2.0. *b* $L = \text{C}_2\text{H}_5\text{HNCO.NH.C}_2\text{H}_5$, conc. (mol dm^{-3}): 1 0; 2 0.2; 3 0.3; 4 0.4; 5 0.5; 6 1.0; 7 1.6

tion of mercury drop for a given level of mercury. We assume the value of surface tension in the maximum point of the electrocapillary curve to be $\max = 426.2 \text{ mN m}^{-1}$ (298 K), according to Smolders and Duyvis⁹. The drop-time data at all measurements were recalculated in relation to the above value. Measurements were made at a temperature of $298.0 \pm 0.1 \text{ K}$ changing the voltage values from -50 to -950 mV by steps of 50 mV . The scatter of the measured values was $\pm 0.1 \text{ s}$ for 10 drops ($\pm 0.12 \text{ mN m}^{-1}$). The duration of 10 drops of mercury was measured for each sample after about 5 min. We also measured the duration of 20 and 30 drops near the maximum of surface tension for each sample. A mean value of 5 results were taken for calculation.

RESULTS AND DISCUSSION

Figs 1 shows the electrocapillary curves $\gamma = f(E)$ for the investigated solution: *a* – carbamide (U); *b* – methylcarbamide (MtU); Fig. 2 sym. dimethylcarbamide (sym. DMtU). Fig. 3 shows the electrocapillary curves $\gamma = f(E)$ for: *a* – ethylcarbamide (EtU); *b* – sym. diethylcarbamide (sym. DEtU).

Comparison of the curves shows that even for low concentrations of U and of its derivatives, the surface tension of the mercury electrode is greatly decreased in relation to the same values of potential of the base electrolyte itself. The greatest lowering was found for sym. DEtU (at the studied potentials and concentrations).

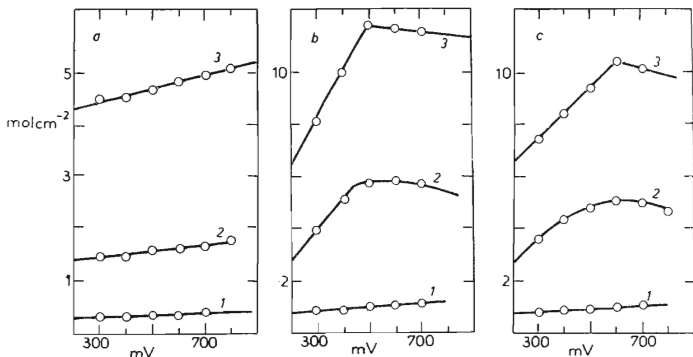


FIG. 4

Plots of adsorption charge (I) vs potential (E). *a* $\text{H}_2\text{N.CO.NH}_2$, conc. (mol dm^{-3}): 1 0.2; 2 1.0; 3 3.0, *b* $\text{CH}_3.\text{HN.CO.NH}_2$, conc. (mol dm^{-3}): 1 0.2; 2 1.0; 3 2.0; *c* $\text{C}_2\text{H}_5.\text{HN.CO.NH}_2$, conc. (mol dm^{-3}): 1 0.2; 2 1.0; 3 2.0; $0.20 \text{ mol dm}^{-3} \text{ HClO}_4$; $I = 0.25$; $298 \pm 0.1 \text{ K}$

Basing on the known Gibbs formulas¹⁰, we calculated the surface concentrations Γ of the investigated compounds at various concentrations and potentials. The values of derivatives ($dy/\partial c$) were determined graphically basing on the shape of curves $\gamma = f(c)$ and by the least square method.

The experimental dependence $\Gamma = f(c)$ at the selected potential (from -450 to -750 mV) is linear, growing with the increase in concentration of carbamide or its derivatives. Comparing the values of Γ (Fig. 4 and 5) obtained for the same concentration of all the compounds ($c = 1.6 \text{ mol dm}^{-3}$ at $E = -500$ mV) the following series was obtained in the order of increasing adsorption on the mercury electrode for the investigated carbamide derivatives:

$$U(2.4) < \text{sym. DMtU}(7.3) < \text{EtU}(7.7) < \text{MtU}(9.5) < \\ < \text{sym. DEtU}(10.2) \cdot 10^{-10} \text{ mol cm}^{-2}.$$

Our measurements show that carbamide and its derivatives evidently change the run of electrocapillary curves in 0.2M-HClO_4 as the result of their adsorption at the interphase mercury-electrolyte solution. Curves obtained for carbamide derivative are similar to electrocapillary curves obtained for the parent compound by us (Fig. 1a)

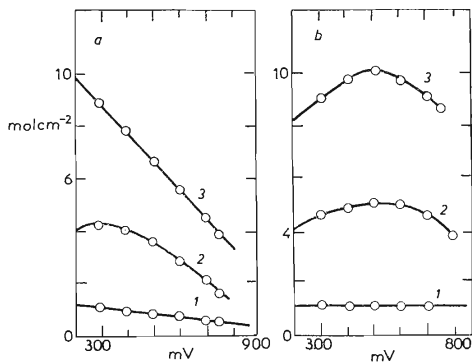


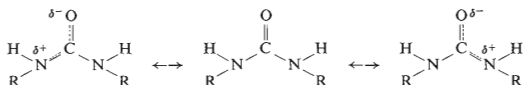
FIG. 5

Plots of adsorption charges (Γ) vs potential (E). *a* $\text{CH}_3\cdot\text{HN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_3$, conc. (mol dm^{-3}): 1 0.2; 2 0.8; 3 1.6. *b* $\text{C}_2\text{H}_5\cdot\text{HN}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_2\text{H}_5$, conc. (mol dm^{-3}): 1 0.2; 2 0.8; 3 1.6. Other data as in Fig. 3

and by other authors³ as well as for some other compounds containing a donor oxygen atom⁶).

The range of potentials and shape of the electrocapillary curves indicate that both carbamide and its derivatives are adsorbed on mercury, most probably, in the form of neutral molecules; adsorption potential of these compounds has a negative value since the maximum of obtained curves shifts to the negative values with the increasing concentration.

The molecule of carbamide and its derivative, being in a mesomeric equilibrium:



is a dipole with a negatively polarised oxygen atom and a positive nitrogen atom. According to papers¹¹⁻¹³, it should be expected that the carbonyl group oxygen atom as the negative pole of the dipole is pointed towards the positively charged mercury surface. The charge of the oxygen atom (δ^-) will decide about the adsorption of compounds at the interphase mercury electrolyte solution.

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