20. B.D. Nicol, R. Miles and R.T. Short, Electrochim. Acta, **28** (1983) 1285.

21. B.E. Conway, H. Angerstein-Kozlowska, W.B.A. Sharp and E.E. Cridle, Anal. Chem., **45** (1973) 1331.

22. M.Z. Hassan and S. Bruckenstein, Anal. Chem., **46** (1974) 1962.

23. R.M. Cervino, W.E. Triaca and J.A. Arvia, J. Electrochem. Soc., **132** (1985) 267.

24. E. Custidiano, A.C. Chialvo and A.J. Arvia, J. Electroanal. Chem., **196** (1985) 423.

25. J.C. Canullo, W.E. Triaca and A.J. Arvia, J. Electroanal. Chem., **175** (1984) 337.

26. A.J. Arvia, J.C. Canullo, E. Custidiano, C.L. Perdriel and W.E. Triaca, Electrochim. Acta, **31** (1986) 1359.

27. S. Gilman, J. Electroanal. Chem., **7** (1964) 382.

28. R. Woods, Electroanal. Chem., in A. Bard **9** (1976) 1.

29. M.W. Breiter, Electrochim. Acta, **8** (1963) 925.

(Received 18 December 1986)

ADSORPTION OF UREA FROM AQUEOUS SODIUM CHLORIDE SOLUTIONS

BY

FERNANDO SILVA* e M. ROSA BARBOSA
Departamento de Química
Faculdade de Ciências
Pr. Gomes Teixeira
4000 PORTO, PORTUGAL.

ABSTRACT

Measurements of the differential capacity of a Hg electrode in contact with six aqueous solutions of urea were made using a computer controlled system which sampled 75 times during the drop life. The parameters of the adsorption isotherm are determined under appropriate thermodynamic conditions. The results indicate that urea adsorbs much less strongly than thiourea.

I - INTRODUCTION

The electrochemical adsorption of urea has received considerably less attention than the similar compound, thiourea, in contact with the many physical chemistry studies of its biological influence[1,2,3,4]. Parsons and Peat[5] studied the electrochemical adsorption of urea from aqueous 1.0 M KNO_3 and found that urea was adsorbed on a Hg electrode

to a much smaller extent than thiourea and, as a consequence, not in a fixed orientation for all values of surface charge density. The influence of the chemical linkage between Hg and C=S on the characteristis of adsorption of thiourea was derived from the linear dependence of the surface excess of entropy on the amount of thiourea adsorbed.[6] It would be important to study the entropy of formation of the interface in the presence of thiourea and therefore a systematic study was carried out. Account is here given of the experimental details of the computer controlled system used to sample the capacity 75 times in a Hg drop, and the dependence of adsorption upon concentration at 298K. In a forthcoming paper the influence of temperature will be presented and the surface excess of entropy derived.

II - EXPERIMENTAL

The large body of experimental data required for a proper thermodynamic analysis of interfacial properties requires the use of automatic data acquisition systems. For an electrode with time dependent area, such as the DME, particular care has to be given to the triggering of the measuring system and to the value of the surface area at the moment of sampling. The system employed uses an interface to control time and convert the analog signals into digital words. The triggering signal was derived using the fact than when a drop falls the cell impedance goes to infinity and therefore an appropriate pulse can be produced.

To overcome the problem of the changing area with time the

assumption was made that the electrode was nearly spherical and therefore the total capacity and the capacity per unit area are related through

$$C_t = C \left(\frac{6\,m\,\pi}{\rho}\right)^{2/3} t^{2/3} - CA_o \tag{1}$$

where : m is the mass flow rate of Hg

ρ is the density of mercury

t is the time

C_t is the total capacity

C is the capacity per unit area

A_o is the non efective area, in contact with the capillary tip

Use of eq. 1 requires measurements of the total capacity in several instants in the drop life, preferably towards the end to avoid the initial instants when the rate of growth is at the highest.

The form of potential wave imposed to the electrode was of a staircase synchronised with the drop, i.e., each drop experimented a constant potential during its life, which differed from that of the previous drop by a controlled amount, the step height. Therefore at the beginning of the drop there will be current transients which require some time to dye down.

A study was then undertaken to optimize i) the time in the drop life after which measurements should start, hereafter designated by DL (delay), ii) the number of samples to be taken in order to perform linear regression fit over C and t (time of measurement).

Measurement of the capacity was made using a lockin technique

and the relation

$$C_t = (1/w) \ K[V''(t) \ (1 + (V'(t)/V''(t)))]$$

where: V' and V'' are, respectively, the inphase and out of phase components of the ac current, and K is a constant determined by appropriate calibration with a dummy cell, which include w, the frequency of the perturbating ac signes.

In the optimization procedure, and due to constraints of the sampling rate of the ADC used, samples were taken every 50ms. The temporal programme followed is schematically represented in fig. 1.
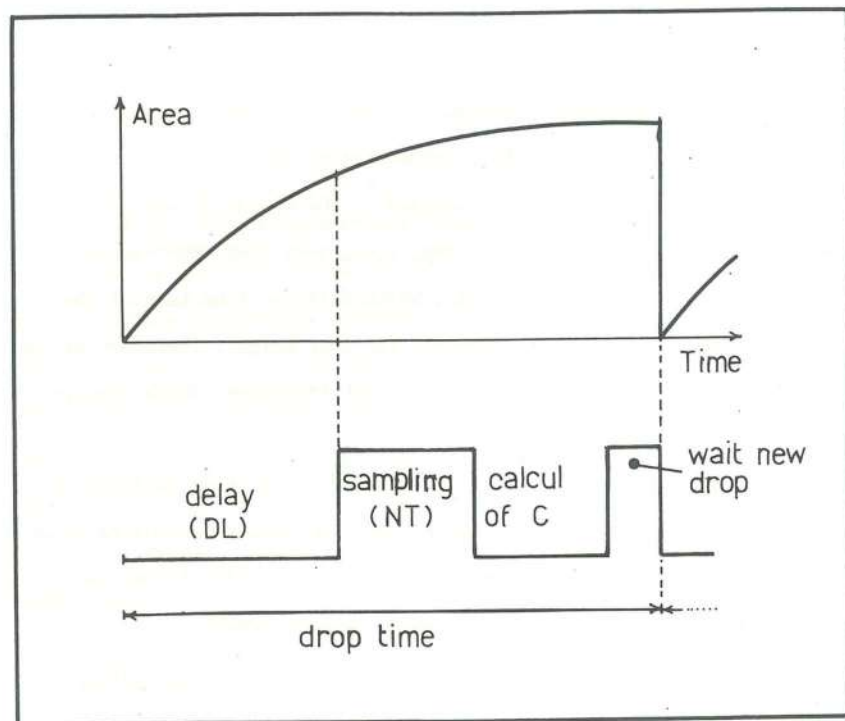

FIGURE 1 - Temporal programme, synchronized with the drop time, employed for the measurements of the capacity.

Five values of DL were tested 0,1,2,3,4 and 5 seg for three different number of samples 35,50 and 75. These values correspond to the maximum possible with the drop time used 20 seg at -1.500V(SCE).

Fig. 2 and 3 show, respectively, typical results obtained for the effect of the number of measurements at two values of delay, and the effect of the value of delay, at a fixed number of measurements, for some values of electrode potential. The observed effect of the delay time, especially at low number of measurements, may be connected with the existence of current transients at the beginning of the drop life due to the potential pulse applied, and due to the fact that the drop area, and therefore the components of the ac current, varies very rapidly with time at the beginning of the drop life.

A comparison of the values of the differential capacity with similar values in the literature[7] indicated that, for the experimental conditions used, the best results were obtained for delay times equal or above 3 seg with 50 or more measurements, and, therefore, the choice was made to use as a delay of 3 seg and measure the ac components of the ac current 75 times during the drop life.

An important parameter that can be used to check the quality of the results is the value of A_o, the non effective area of the electrode.

According to equation 1, the value of A_o should be independent of DL, NT and electrode potential (E), and close to the value estimated from the diameter of the capillary bore (3.14×10^{-4} cm). The value of A_o, in table 2, were obtained by linear regression on plots of C_t vs $(t + DL)^{2/3}$ where t is the time elapsed after the delay at which the measurement of C_t was made. A typical example of such plot is given in
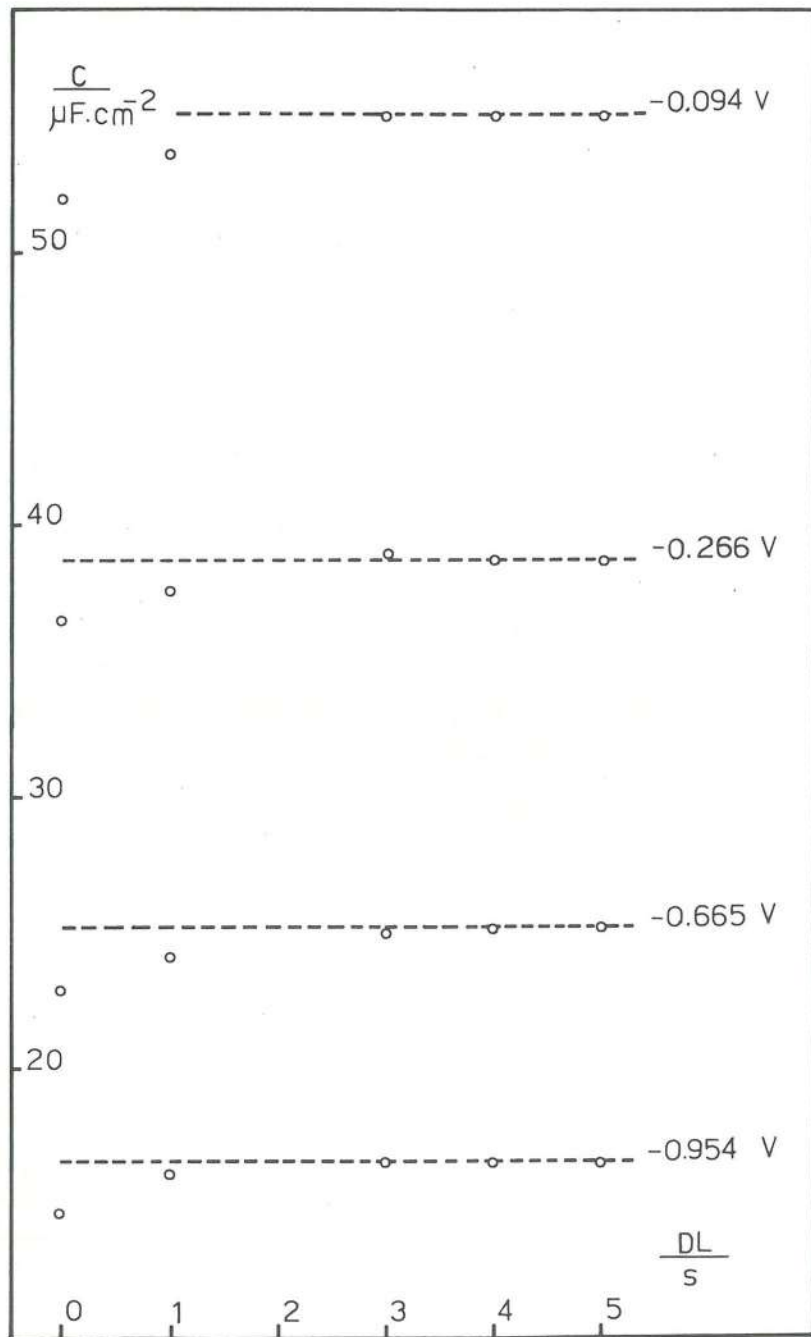
FIGURE 2 - Plot of the dependence of the differential capacity on the value of the delay, DL, at different electrode potentials.
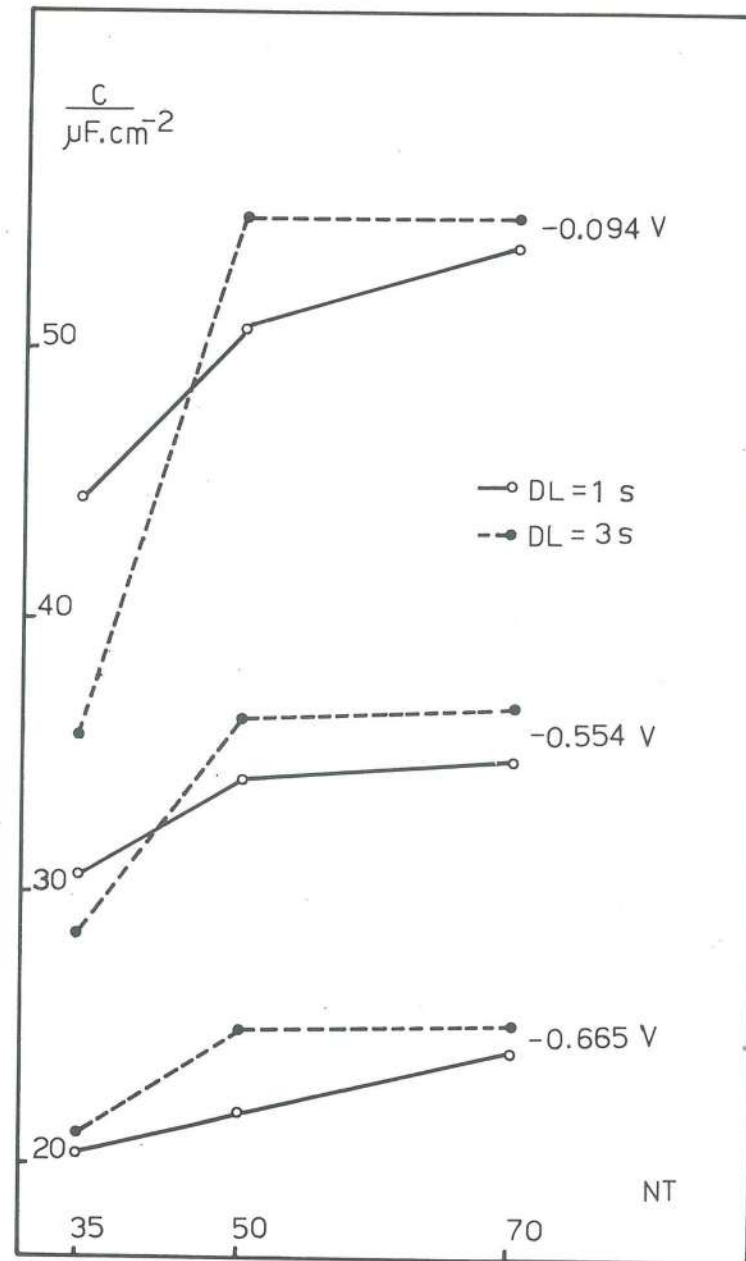

FIGURE 3 - Plot of the dependence of the differential capacity on the number of measurements, NT, for two values of the delay (1 and 3 seg).

fig 4 and the excellent linear behaviour was observed at any potential and in all solutions, and the correlation coefficients obtained by on line computer fitting were always 0.999. The values of A_0 oscillate around the value estimated, giving a good indication that the procedure followed was acceptable, in opposition to the results reported by Mohilner et al [8], principally because in their work they used a capillary with a very large bore.

A home made potentiostat was employed. The cell was water jackted, water being pumped through from a thermostated bath ($\pm$ 0.2 C); a saturated calomel (NaCl) reference electrode, was introduced in a thermostated compartment terminated by a Luggin capillary.

The solutions were prepared from recrystalized urea and NaCl with "Millipore" water, the compositions of which are given in table 1.

TABLE 1: Composition, values of pzc and γ_{max} for the solutions of urea studied

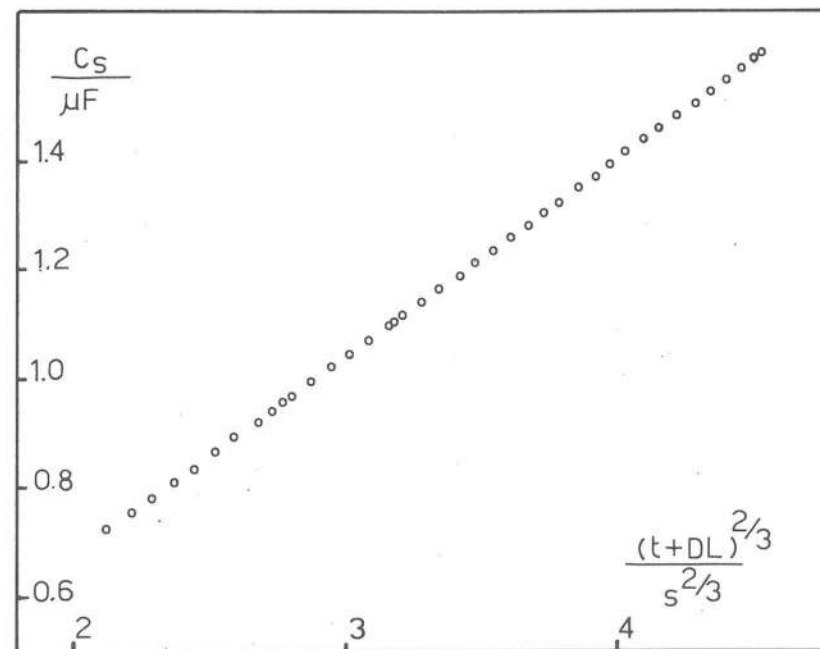| c (urea)	a (urea)	c (NaCl)	a (NaCl)	-pzc	γ_{max}
m	m	M	M	V(sce)	Nm
0	0	1.000	0.657	0.521	424.2
0.4	0.378	1.006	0.657	0.534	420.0
0.7	0.648	1.008	0.657	0.553	418.6
1.0	0.898	1.010	0.657	0.561	417.5
2.0	1.689	1.019	0.657	0.588	414.5
5.0	3.686	1.038	0.657	0.593	409.2
10.0	6.334	1.055	0.657	0.616	404.5

FIGURE 4 - Plot of the dependence of the total capacity, Ct, on $(+DL)^2$ where +DL is the time in drop life, for E = -0.200 V (SCE), DL = 3 seg and NT = 75.

Numerical treatment of the data

Integration of differential capacity - potential and charge - potential data was performed numerically using a cubic adjusted to four experimental points and moving the cubic along the interval of integration.

Differentiation of γ vs ln a_u curves required to obtain the surface excesses, was performed on the smoothed data using either the moving cubic technique referred earlier, with the derivative taken at the middle point of the interval employed, or performed with the coefficients of the smoothing polimonial. The differences on the values of the surface excesses obtained with both procedures were very small and well within with the expected precision of the calculation. The smoothing process was carried out with a second degree polinomium after an analysis of the residues originated by polinomium of degrees 2,3 and 4.

III - RESULTS AND DISCUSSION

Fig. 5 shows a set of drop time - potential curves obtained with a blunt capillary. The observed decrease in the drop time with increase in concentration of urea in solution is primary indication of adsorption of urea at the interface, almost over the entire range of concentrations studied. There is no evidence of desorption of urea even at the most negative polarizations. By polinomial fitting, values of the potential of zero charge were determined and are given in table 1.
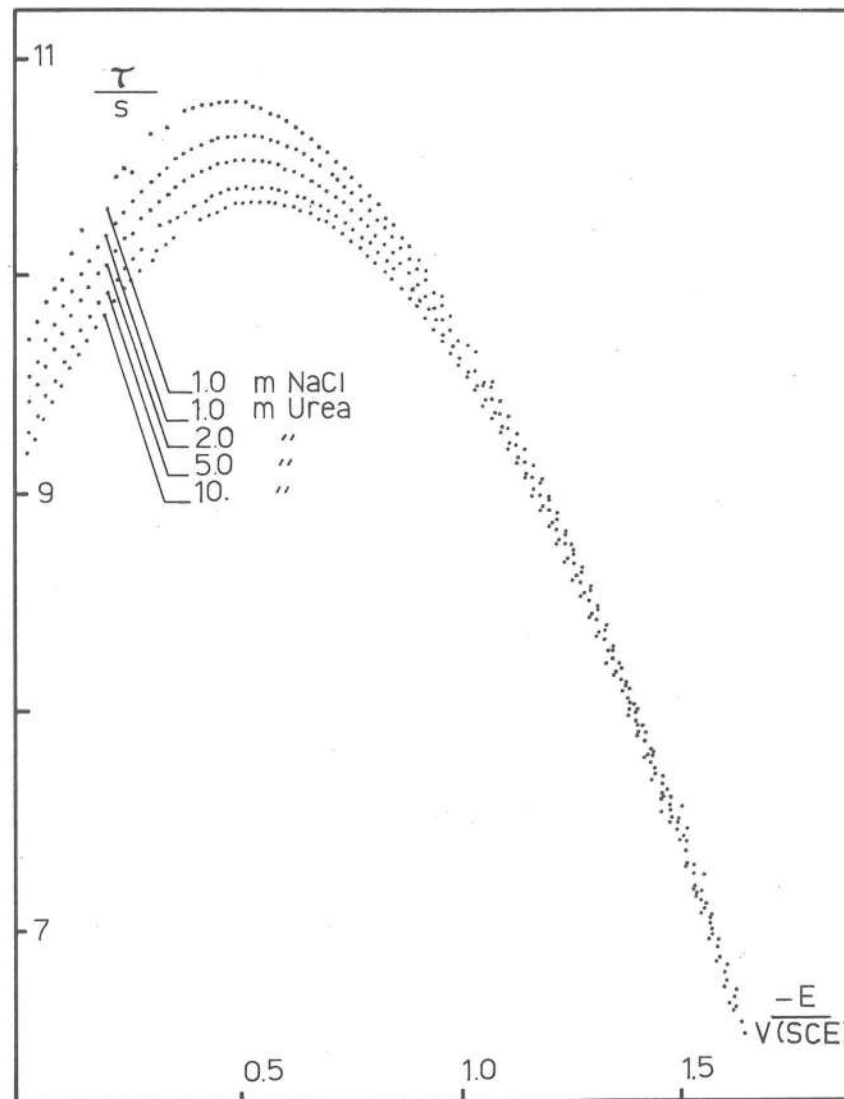
FIGURE 5 - Drop time - potential curves for urea solutions with the indicated concentrations.

The values of γ_{max} obtained from the same data and using as calibration the value of γ_{max} = 424.2 Nm for the base electrolyte, at 298 K, are also given in table 1.

The experimental differential capacity - potential curves, for seven concentrations of urea are displayed in fig. 6. The first aspect to notice is that adsorption of urea decreases the value of the differential capacity for potentials less negative than -0.700V(SCE) without changing the existence of the "hump" characteristic of the base electrolyte 0.700V the capacity increases with increase in the concentration of urea in solution. This behaviour contrasts with that of a similar molecule, thiourea, which, upon adsorption, changes significantly the values and the shape of the differential capacity of the base electrolyte. However, the study of adsorption of urea from KNO_3 solutions also indicated that the shape of the differential capacity potential curve for the base electrolyte was not significantly affected by the presence of adsorption of urea.

Analysis of the differential capacity potential data was performed as indicated earlier using as integration constants the values in table 1. The values of the relative surface excess of urea Γ_u, are the true thermodynamic quantities because differentiation was performed using the known activity of urea at constant chemical potential of the base electrolyte.

Fig 7 shows the dependence of Γ_u on which is very similar to that reported by Parsons *et al* [4], although higher values of Γ_u were obtained in the present work, possibly due to the fact that the analysis was made using activities.
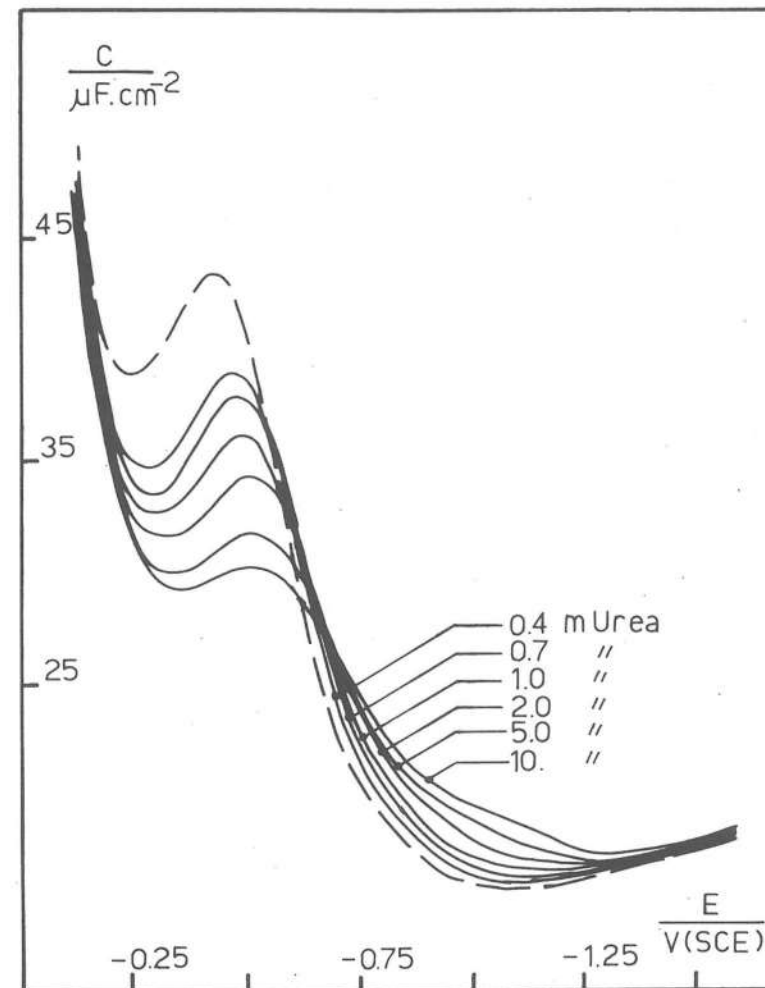
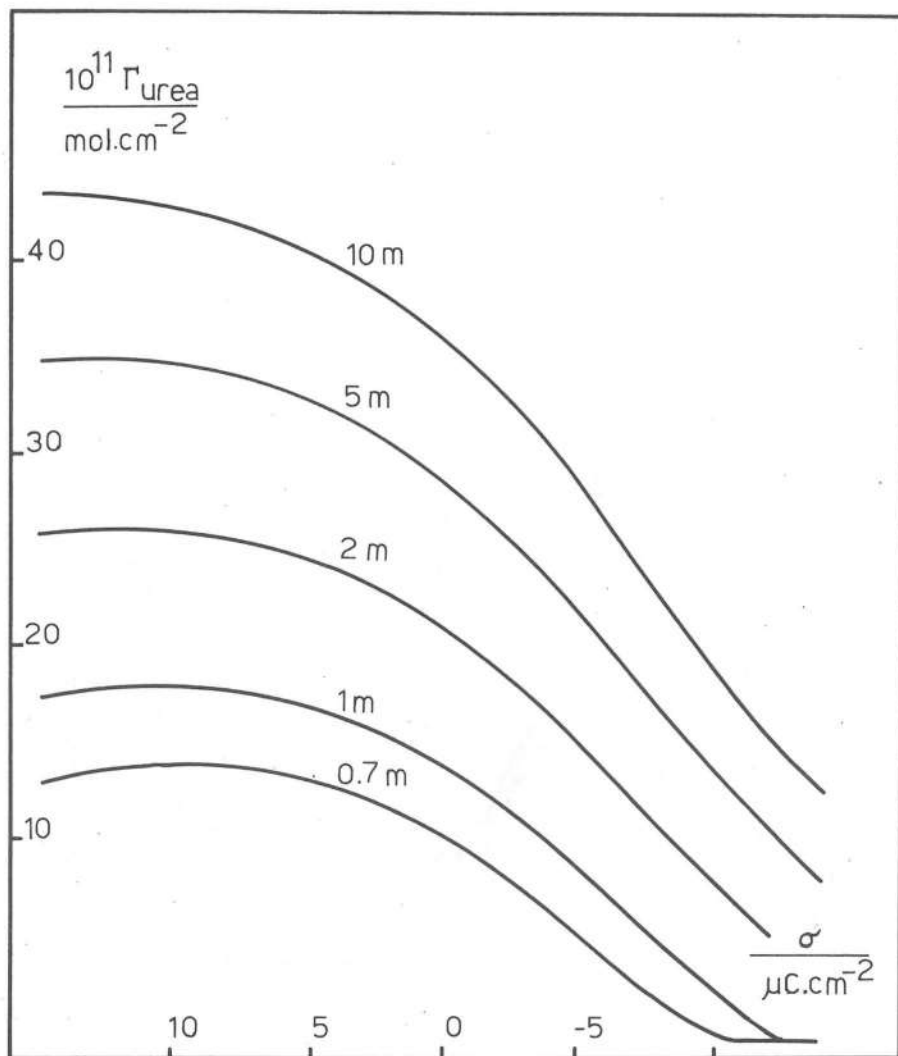FIGURE 6 - Capacity-potential curves for solutions of urea in 1.0M NaCl.

FIGURE 7 - Dependence of the surface excess of urea (Γ_u) on the charge density (σ).

The shift in pzc towards more negative values with increase in urea concentration, not only confirms the adsorption of urea at the uncharged metal surface but also indicates that the orientation of the adsorbed molecules is such, as to point the negative end of the dipole towards the electrode surface. The magnitude of the variations of pzc are smaller than in the case of adsorption from nitrate solutions the difference being possibly due to different degrees of ionic adsorption.

Assignment of an isotherm to describe the adsorption of urea was carried out using the dependence of Γ_u on concentration and . Best fits were obtained for a Frumkin isotherm with parameters indicated in table 3.

The virtual independence of the isotherm on the electrical variable indicates congruence which was also noticed in Parsons *et al*[4] work and the small value of the interaction parameter makes the isotherm very close to a Langmuir isotherm proposed to describe the adsorption behaviour in nitrate solutions. The value of the saturation coverage corresponds to an area occupied by adsorbed urea molecule of 0.24nm^2 which points to an orientation in the adsorbed state with the dipole not perpendicular to the surface. The small value of the interaction parameter indicates the existence of small interactions among adsorbed urea molecules in strong contrast with repulsive caracter of the interaction among thiourea molecules. Very significant is also the difference between the values of ΔG^o_{ads} for urea and thiourea[9] , the former being almost 10% of the latter, and this fact reflects the difference in the chemical affinity of $\supset S = C$ and $\supset O = C$ groups towards mercury, once it is expected that the electrostatic interactions of each of the molecules dipoles with the electrical field

TABLE 2: Values of A_o at different potentials obtained with

DL = 3 seg and NT = 75

-E (SCE)	$A_o * 10^4 cm^2$
0.260	2.94
0.385	2.39
0.445	3.91
0.665	3.57
0.950	3.74
1.529	3.00

TABLE 3: Parameters of the Frumkin Isotherm

$$\Gamma_{sat} = 0.69 \times 10^{-9} \text{ mol cm}^{-2}$$

$$A = -1.1$$

$$\Delta G^o_{ads} = -8.61 \text{ KJ mol}^{-1}$$

are similar. The largest difference in the behaviour of urea and thiourea is indicated by the considerably small value of the interaction parameter in the Frumkin isotherm and on the standard free energy of adsorption, with both values pointing to small interactions among urea molecules in the adsorbed state and between mercury and urea molecules. Further reinforcement of this so different behaviour between urea and thiourea will be shown with the effect of temperature in a forthcoming paper.

Further analysis of the structure of the adsorbed layer was attempted plotting the dependence of inner layer potential drop on the amount of urea adsorbed in fig. 8. Such dependence was found to be linear at all values of the charge density, indicating that the inner layer permittivity is, to a first approximation, independent of the amount of urea adsorbed. The slope of the lines in fig 8 are smaller than in the case of adsorption of thiourea and decrease steadily to zero at $\sigma = +9 \mu Ccm^{-2}$. This suggests that a maximum in the adsorption of urea is attained at that value of charge density which is a proposition supported by the crossing point observed at $\sigma = +9\mu Ccm^{-2}$ of all σ vs E curves in fig. 9.

The negative signs of the slopes may be taken as evidence that the average orientation of the urea molecules is with the oxygen atom (negative end of the dipole) pointing towards the electrode. The continuous decrease of the slope of the lines in fig. 8 may be understood in terms of a compensation effect between the adsorbing dipole of urea and that of the replaced water molecules. Such would only be possible if the component of the adsorbed molecule perpendicular
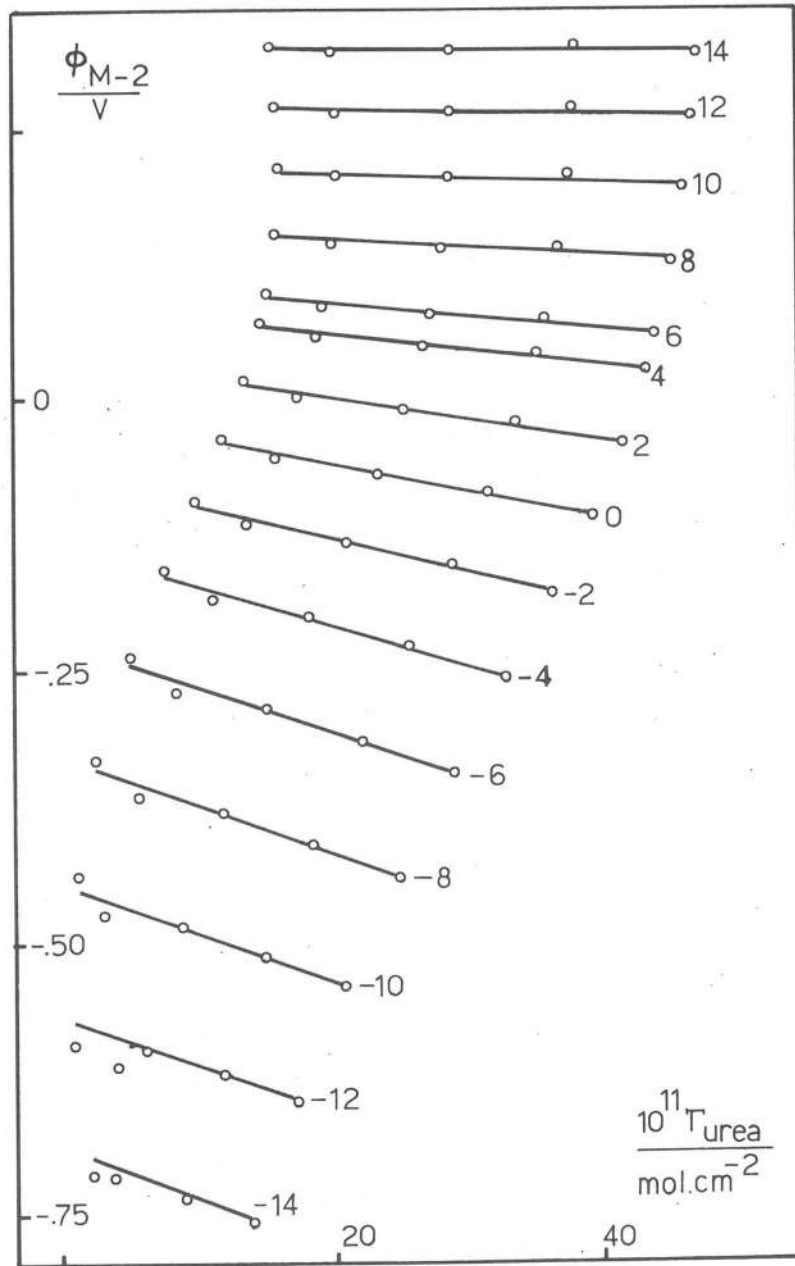
FIGURE 8 - Inner layer potential drop as a function of the amount of urea adsorbed (Γ_u) , at constant charge densities.
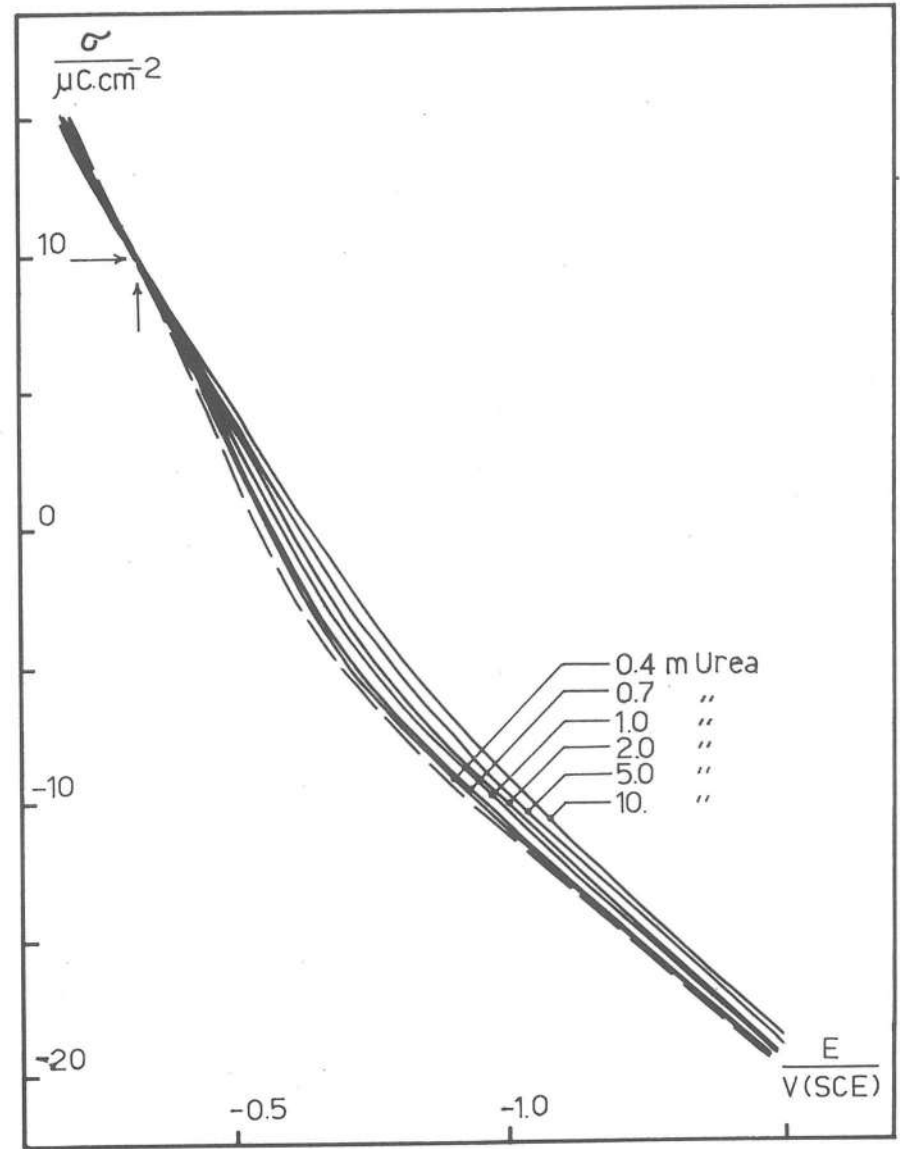

FIGURE 9 - Charge-potential relationships for different solutions of urea in 1.0M NaCl.

to the surface were comparable to that of the water molecules adsorbed. Variations in the thickness of the inner layer with increase adsorption of urea may also contribute to the observed decrease of the slopes in fig. 8. The contribution of the water molecules to the potential drop across the inner layer is of opposite signs at anodic and cathodic charges, adding, in the latter case, to the contribution of urea dipoles, decreasing the values of the slopes in the former case.

BIBLIOGRAPHY:

1. J.H. Stern, J.D. Kulluk, J. Phys.Chem., 2795, 73, (1969)

2. V.E. Bower, R. Robinson, J. Phys. Chem., 1524, 67 (1963)

3. K.D. Asim, K.K. Kunden, J. Phys. Chem., 2604, 79 (1975)

4. S. Subramanian, D. Balasubramanian, J.C. Ahuwaila, J. Phys. Chem., 226, 73 (1969)

5. R. Parsons, R. Peat, R.M. Reeves, J. Electroanal Chem., 151, 62 (1975)

6. G. Hills, A.F. Silva, Can. J. Chem., 1953, 59 (1981)

7. A.F. Silva, Ph.D. Thesis, Southampton, 1981.

8. D.M. Mohilner, J.C. Kreuser, H. Nakadomary and P.R. Mohilner, J. Electrochem. Soc., 122, 359 (1976)

9. R. Parsons, Proc. Royal Soc. A261, 79 (1961)

PORTUGALIÆ ELECTROCHIMICA ACTA

vol. 4, 1986

ANNUAL INDEX

SUBJECTS

AUTHORS