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EFFECTS OF TETRA-ALKYLAMMONIUM SALTS ON

THE POLAROGRAPHY OF Cd^{2+}, Zn^{2+} AND Mn^{2+} IN WATER

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ABSTRACT

The addition of *tetra*-alkylammonium salts, namely *tetra*-methylammonium, *tetra*-ethylammonium, *tetra*-butylammonium and *tetra*-hexylammonium salts, to the supporting electrolyte, in the presence of different metal ions, does not change the observed cathodic current for shorter carbon chains. However, an important effect is observed when $n \geq 4$ (number of carbon atoms of each chain). This is shown through the polarograms which were recorded for different solutions of cadmium, zinc and manganese ions, in the presence and absence of those ions.

The interpretation based on electrocapillary curves has shown that electron transfer through the double-layer becomes more difficult as the length of the carbon chain increases.

Polarographic and electrocapillary experiments were followed all over.

Keywords: *Tetra*-alkylammonium salts; Polarography; Electrocapillary curves; Cadmium; Zinc; Manganese

INTRODUCTION

The hydrophobic character of *tetra*-alkylammonium (TAA) cations, which is associated to the reduction of these ions at very low negative potentials [1], is well known.

Electrode reactions studies of these salts in protic solvents have rarely been used, especially when they are dissolved together with the supporting electrolyte. These salts have more commonly been employed as background electrolytes though many of them can dissolve easily in both aprotic and protic solvents. TAA cations are strongly adsorbed on mercury from aqueous solutions as it was reported by R. Payne [2] and R. Dietz and M. E. Peover [3]. Such phenomena are not observed in several non-aqueous solvents [4].

Very few studies of the properties of the mercury/*tetra*-alkylammonium salts interface have been presented, although they have permitted a better knowledge of the double layer structure at the level of the electrode/solution interface which is essential to interpret the kinetics of electrode reactions. It would be particularly useful for studies of the kinetics of the simple process of radical anion formation by one electron transfer to the parent molecule to be carried out.

On the other hand, the hydrophobic character of *tetra*-alkylammonium cations which is certainly associated with the evidence of the reduction of these ions occurs at much more negative potentials than those of alkaline ones[1], is well known.

The values of these potentials at which reduction occurs are dependent on the type of the radicals to which the nitrogen atoms are bound. Among these cations those having longer carbon chains are those which suffer reduction at more negative potentials [5].

Emmert [5], McCoy and Moore [6] and Schlubach [7], developed important works concerned with the electrochemistry of these compounds with both saturated

and unsaturated carbon chains and short and long chains. Such studies have shown the high reactivity of these compounds and as a consequence of it several investigations have been developed in three main areas:

- electrochemical reduction of tetra-alkylammonium salts and mechanistic determination of reduction as well as identification of resulting products;
- amalgam and *tetra*-alkylmetals formation and their catalytic capacity on reaction reduction of some organic products;
- influence of those compounds on the polarographic reduction of different organic and inorganic ions.

This paper is concerned with the effect of tetraalkylammoniun salts on the reduction of different heavy metals, namely Cd^{2+}, Zn^{2+} and Mn^{2+} in water, using dropping mercury electrodes in this investigation.

EXPERIMENTAL

Equipment: Polarograph TACUSSEL Type EPL 2 with DME as working electrode. A platinum spiral as counter electrode and a SCE as reference electrode were used.

Scan speed: 285 mV/min; **recorder speed:** 15 mV/min; **sensitivity:** 0.5 μA/cm. All scans started at -0.3 V.

Solutions: 1 ml of electroactive species (Cd^{2+}, Zn^{2+} or Mn^{2+}) solutions 5×10^{-3} M and/or 1 ml of *tetra*-alkylammonium salts solution of different concentration were added to 25 ml of supporting electrolyte sollution (potassium chloride, sodium chloride, potassium perchlorate and sodium sulphate). All the solutions are aqueous solutions except those of *tetra*-hexylammonium salt which were prepared with water:ethanol 1:1 for solubility purposes. *p.a.*reagents were used all over. Solutions were prepared from tridestilled water, the last destillation being obtained from permanganate. All the experiments were performed at 25º C.

RESULTS AND DISCUSSION

The polarograms of Cd^{2+} in presence of *tetra*-alkylammonium salts with carbon chains over 4 carbon atoms present two polarographic waves, being the first one due to cation reduction and the second one due to the capacity effects (fig. 1d) and 1e)).
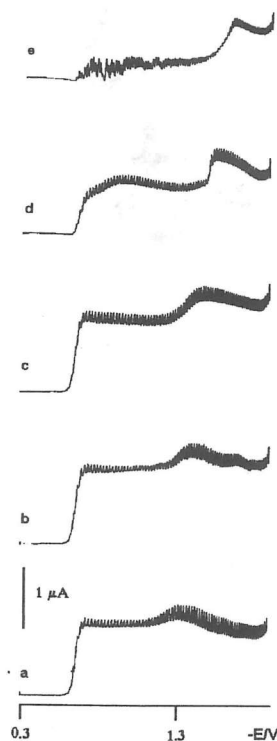

Fig. 1 - Polarograms of Cd^{2+} $1.85X10^{-4}$ M, in potassium chloride 1M solution, in the absence (a) and in the presence of *tetra*-alkylammonium ions: (b) *tetra*-methylammonium $3.70X10^{-4}$ M; (c) *tetra*-ethylammonium $3.70X10^{-4}$ M; (d) *tetra*-butylammonium $3.70X10^{-4}$; (e) *tetra*-hexylammonium $1.85X10^{-4}$ M.

The polarographic reduction of cadmium in the presence of TAA salts, with carbon chains $n \geq 4$, occurs at the same potential as in the absence of TAA salts but the current intensity is smaller. This current was kept smaller than one registered for the same concentration of cadmium ion in solution where tetrabutylammonium were absent within the potential interval -0.64V, -1.45V (Fig. 1 (d)). At this potential the intensity of current quickly jumps to the observed values for solutions without TAA salts. After this point the polarograms are always coincident. According to Hayter and Hunter[8] TAA cation adsorption on the electrode surface is simultaneous with the anionic halides, which Frumkin[9] and Devanathan and Fernando[10] consider it as an exception. When anion desorption occurs a reorientation of TAA cations is observed[8]. So, starting by a charged head orientation to the electrode surface and the hydrophobic chains to the solution, it inverts to the charged head orientated to the solutions and the hydrophobic chains to the electrode surface. This new orientation of the TAA cations favours the approximation of the solvated metallic ions and electron transfer from the electrode[9].

The value of potential where the jump occurs is dependent on the TAA solution concentration (fig.2) and on the number of carbon atoms of each chain (fig.1) of the TAA salts.
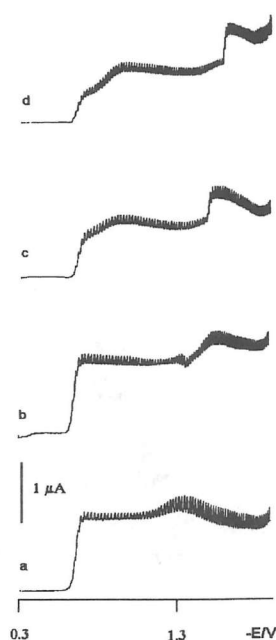
Fig. 2 - Effect of concentration of the *tetra*-butylammonium ion on the redution of Cd^{2+} in KCl 1M solution ; (b) 3.70×10^{-5} M; (c) 3.70×10^{-4} M; (d) 3.70×10^{-3} M

So the potential increases with concentration and number of chain carbon atoms.

A good interpretation of this phenomenon is obtained through electrocapillary curves (EC) for different solutions of supporting electrolyte and TAA salts and these results were compared with EC resulting from pure supporting electrolyte solutions (fig.3).
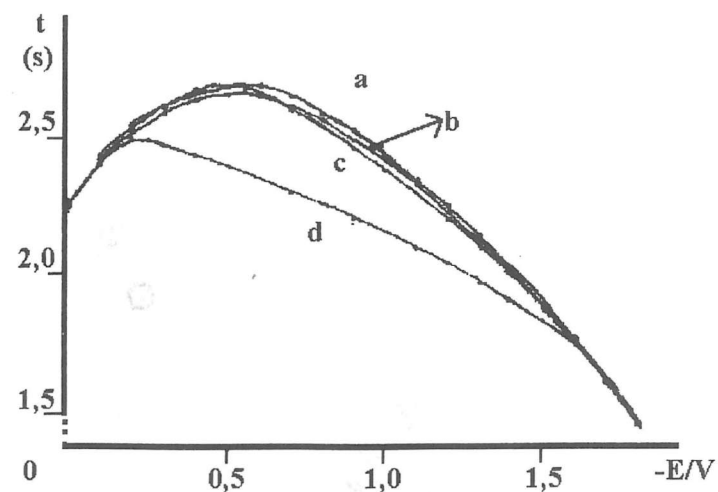
Fig. 3 - EC curves of KCl 1 M (a) and of tetra-alkylammonium ions in KCl 1 M: (b) *Tetra*-methylammonium 3.85×10^{-4} M; (c) *Tetra*-ethylammonium 3.85×10^{-4} M; (d) *Tetra*-butylammonium 3.85×10^{-4} M

It can be seen that only *tetra*-butylammonium ion (Fig. 3 (d)) originate a flat region under the EC maximum. The potential at which the electrocapillary curve acquires the normal curvature coincides with that at which the second polarographic wave is observed in the polarograms (Fig. 1 (d)).

To interpret the possible influence of the supporting electrolyte in such phenomena different electrolytes besides potassium chloride were utilised. These electrolytes were sodium chloride, potassium perchlorate and sodium sulphate the current jump being at approximately the same potential with a maximum difference in relation to potassium chloride of 20 mV (potassium perchlorate), that is very small (fig. 4). In the presence of none (ClO_4^-) or weakly specifically adsorbed anions (SO_4^{2-})[11], the *tetra*-butylammonium ions shift the potential of polarographic wave of Cd^{2+} to more negative values, next to the potential of the second wave (fig 4c) and 4d)).
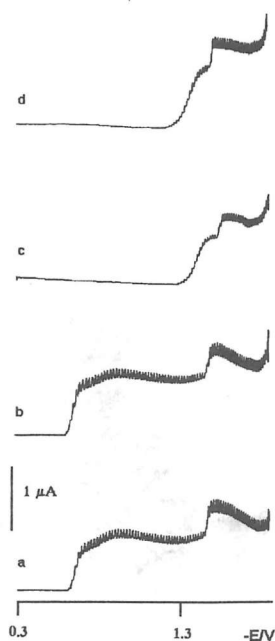
Fig. 4 - Cd^{2+} (1.85X10^{-4} M) polarograms in the presence of *tetra*-butylammonium ions (3.70X10^{-4} M) with different supporting electrolyte: (a) KCl; (b) NaCl; (c) NaClO$_4$; (d) Na$_2$ SO$_4$

pH effects were also studied and the acid zone was excluded because the reduction wave of the hydronium ion is developed at lower potentials than those of the second polarographic wave. Such effects in the alkaline region were studied using the ammonium buffer at concentration 1M (0.5:0.5) (fig. 5b)). No essential difference concerning the influence of *tetra*-alkylammonium salts was observed where cadmium reduction occurs at different pH's and in neutral solutions.
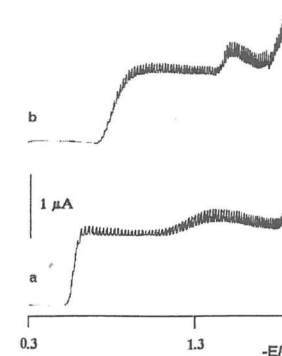
Fig. 5 - pH effects: (a) neutral solution; (b) alkaline solution; of Cd^{2+} (1.85X10^{-4} M).

Other cations besides cadmium were searched namely the zinc ion and manganese ion, having both similar chemical properties to the first ion, and more negative reduction potentials than the one of Cd^{2+} . However, these potentials were higher (Zn^{2+}) or lower (Mn^{2+}) than those corresponding to the current jump .

In relation to Zn^{2+}, the presence of *tetra*-butylammonium and *tetra*-hexylammonium salts shifts the reduction polarographic wave of the zinc ion to the current jump potential (fig. 6). In the case of the manganese ion, the presence of *tetra*-butylammonium ion does not show any effect, though the presence of *tetra*-he-.xylammonium ion, that shifts the current jump to a more negative potencial than the cation reduction potential, the current jump occurs to a higher value than that of the standard cation reduction potential (fig. 7). The diffusion current limit decreases similarly to what was observed in relation to cadmium ion in presence of *tetra*-butylammonium ion.
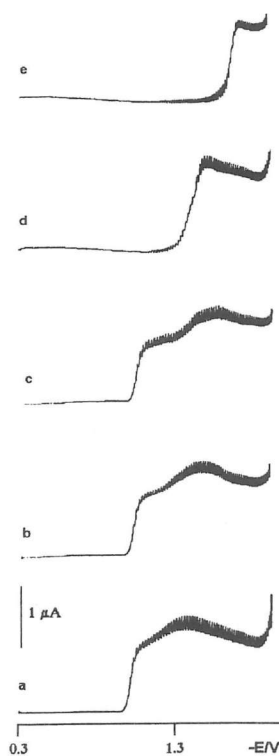
Fig. 6 - Polarograms of Zn^{2+} 1.85×10^{-4}, in potassium chloride 1M solution, in the absence (a) and in the presence of *tetra*--alkylammonium ions: (b) *tetra*-methylammonium 3.70×10^{-4} M; (c) *tetra*-ethylammonium 3.70×10^{-4} M; (d) *tetra*-butylammonium 3.70×10^{-4} M; (e) *tetra*-hexylammonium 1.85×10^{-4} M.
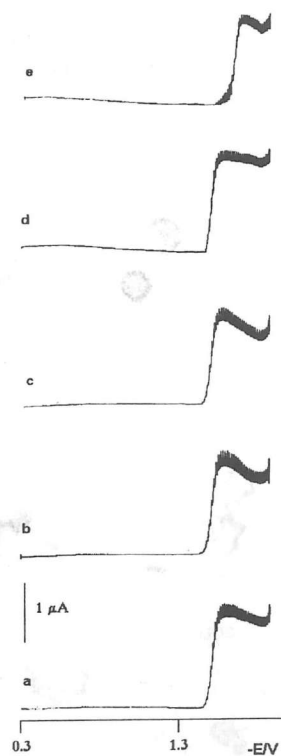
Fig. 7 - Polarograms of Mn^{2+} 1.85×10^{-4}, in potassium chloride 1M solution, in the absence (a) and in the presence of *tetra*--alkylammonium ions: (b) *tetra*-methylammonium 3.70×10^{-4} M; (c) *tetra*-ethylammonium 3.70×10^{-4} M; (d) *tetra*-butylammonium 3.70×10^{-4} M; (e) *tetra*-hexylammonium 1.85×10^{-4} M.

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