# STUDIES OF THE INTERFACE BETWEEN MERCURY AND SOLUTIONS OF TETRAALKYLAMMONIUM SALTS IN N,N'-DIMETHYLFORMAMIDE

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The interface Hg/solution of tetraalkylammonium salts in N,N'-DMF was studied by using impedance and chronocoulometric measurements. The $C_d$–$E$ and $R$–$E$ curves were determined and maxima are noted at fairly negative potentials which are attributed to a change in orientation of the cations at the interface. The $Q$–$t$ curves support this assumption revealing the existence of a slow surface process at these potentials.

Studies of the electrochemical behaviour of organic compounds and the organic electrosyntheses are generally carried out in non-aqueous solvents: acetonitrile (AN), dimethylformamide (DMF), etc. Furthermore, to increase the potential range available and to reduce solubility problems, tetraalkylammonium salts are used as a supporting electrolyte.

In our laboratory we are investigating the reduction of various organic compounds (benzophenone, rubrene, etc.) on the DME using DMF and salts of tetraalkylammonium as supporting electrolyte. In this paper we refer. to a previous study carried out with the supporting electrolyte to obtain information on the structure of the double layer in which the electrode reaction is localized. A chronocoulometric study was also carried out with this system which revealed the existence of a non-faradaic surface process, possibly due to the change of orientation of the adsorbed cation, when the electrode reached a fairly negative potential. This process is also manifested on the $C_d$–$E$ curves by the appearance of a shoulder in this potential range.

## EXPERIMENTAL

### Chemicals

DMF (Aldrich Chemical Co. Ltd.) was of 99·99% purity for HPLC with a water content of 0·0037%. It was stored in dark bottles in an argon atmosphere. The DMF was transferred from ₜhe bottles to the working cells in an argon atmosphere in a "dry box" system.

Tetraethylammonium perchlorate (TEAP) was obtained from TEAP "purum" (Fluka AG) dissolved in the minimum quantity of warm methanol. On cooling, a white mass recrystallized. It was filtered off, washed with cold methanol, and allowed to dry for 24 h in a heated vacuum dessicator, the temperature not exceeding 60°C.

Tetrabutylammonium perchlorate (TBAP) was obtained by reacting 40% tetrabutylammonium hydroxide (Fluka AG) with 70% perchloric acid (Carlo Erba). The salt thus precipitated was purified by triple recrystallization from an ethanol–water mixture, active carbon being used in the first recrystallization.

Tetrahexylammonium perchlorate (THAP) was recrystallized from THAP purum (Fluka AG) dissolved in the minimum quantity of warm ethanol. It was precipitated by the addition of doubly distilled water until the water–ethanol ratio was 30 : 70, allowed to cool, filtered off, abundantly washed with ethanol, and dried in vacuum at 60—70°C for at least 12 hours.

Tetraoctylammonium perchlorate (TOAP) was prepared in the same way as THAP from commercial TOAP purum (Fluka AG) except that water was added in the ratio of 20 : 80.

### Electrodes and Apparatus

A$^v$DME was used for the impedance measurements and a hanging mercury drop electrode (HMDE) from Metrohm AG Herisau for the chronocoulometric study.

The Ag/AgCl electrode, prepared by anodizing a silver wire in 0·1M-HCl, was introduced into a mixture of DMF–AN (1 : 3) saturated with tetraethylammonium chloride and AgCl. The junction with the sample was made by means of porous glass GIII and methylcellulose gel. All potential values are referred to SCE. To this end the SCE was introduced into the cell and the potential difference between it and our reference electrode was measured by a digital voltmeter. A Pt ring was used as a counter electrode.

The instrumental equipment used for the impedance measurements (lock-in amplifier Solartron) and for chronocoulometry has already been described[1,2].

## RESULTS AND DISCUSSION

The behaviour of the interface Hg/TXAP(DMF) with X: ethyl (E), butyl (B), hexyl (H), and octyl (O), was studied by using impedance and double-step potential chronocoulometric measurements.

### Impedance Measurements

The measurements were made with an a.c. voltage signal of 5 mV amplitude and 1 000 Hz frequency in 0·1 mol l$^{-1}$ solutions. The potential ranged from 100 to −2 000 mV. The values of the differential capacity obtained from the imaginary component of the impedance at various potential values are shown for the four tetraalkylammonium cations in Fig. 1.

All the curves show a desorption peak at positive potentials; its capacity depends on the frequency. This peak is also observed in AN in the presence of octadecyltriethylammonium perchlorate (OTEAP) and it is assigned to the displacement of OTEA cation by perchlorate ions[3]. THAP and TOAP, at more negative potentials show a shoulder whose localization is displaced to more positive values when the

size of the cation increases. This shoulder is not observed with TEAP. With TBAP a slight tendency is seen to increase the capacity at fairly negative potentials. Likewise the values of the differential capacity decrease with increasing size of the cation, a behaviour which was also noted by Fawcett et al.[4] and Gambert and Baumgartel[5] in other organic solvents.

The appearance of this type of shoulder at very negative potentials was reported by Gambert and Baumgartel[3] using AN as solvent and with asymmetric alkylammonium salts, that is, when one of the alkyl groups is replaced by a chain in which the number of carbon atoms progressively increases. These authors also found a maximum at very negative potentials in the presence of THpAP (Hp-heptyl)[5]. They relate this disturbance[6] of the capacity curves to adsorption of ions; in their opinion, the formation of the maximum can be attributed to a change of orientation from perpendicular to parallel, which the cations undergo when the electrode potential becomes more negative. This enhances the approximation of the positive centres to the surface of the electrode. The authors found a similar effect on the differential capacity in the presence of alkanes[6] although, in this case, the maximum is caused by desorption since the molecules are neutral.

To analyze this behaviour a more complete study was carried out with TOAP at various concentrations, the capacity curves being recorded at different frequencies (Figs 2 and 3). It is noted that both maxima vary with the frequency and concentration. The first maximum increases considerably with the concentration, whereas the second rises only slightly when the concentration passes from 5 to 20 mmol l$^{-1}$ and at concentrations above 40−90 mmol l$^{-1}$ the value is practically the same. We did not find at low concentrations the minimum corresponding to zero charge which, as Gambert and Baumgartel point out[5], appears to be due to adsorption of these cations already at potentials close to $E_{zc}$.

The variation of the two capacity maxima with frequency is shown in Fig. 3. It can be seen that the variation is much greater for the first maximum than for the second.

The resistive component of the impedance also shows a variation as the size of the cation increases, as well as a strong dispersion with the frequency in the potential region corresponding to the shoulder on the $C_d$–$E$ curve, as if a faradaic process were involved (Fig. 4). A slight tendency to increase may be attributed, according to Kojima and Bard[7], to the "border effect" since the electrode used has not a fine capillary termination. Nevertheless, with THAP and TOAP in this potential region the variation of the resistive component is very marked, with a tendency to a common value at high frequencies and very positive potentials. The variation of the resistive component can be attributed only to the border (screening) effect. It is rather a question of a process occurring on the surface of the electrode since it coincides with the potential region of the capacity curves in which the shoulder appears.
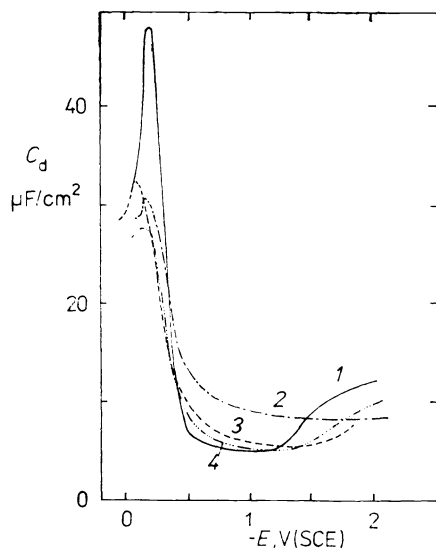
FIG. 1

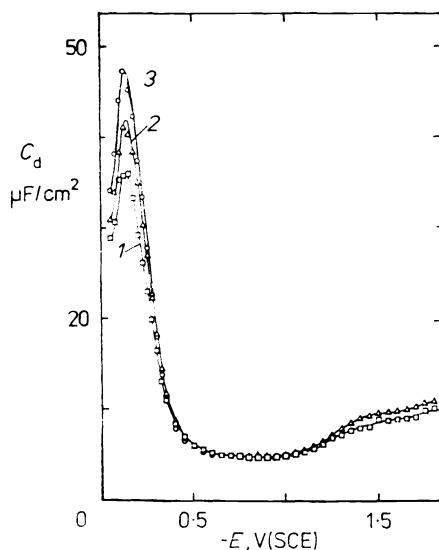$C_d$–$E$ curves of 0·1M-TXAP in DMF. *1* TOAP; *2* TEAP; *3* TBAP; *4* THAP



FIG. 2

$C_d$–$E$ curves of TOAP in DMF. Conc. TOAP (mmol l$^{-1}$): *1* 5; *2* 10; *3* 20



FIG. 3

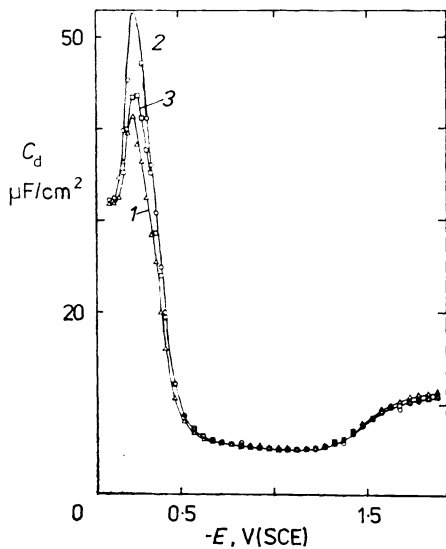$C_d$–$E$ curves of TOAP in DMF. Frequency (Hz): *1* 420; *2* 620; *3* 1 000

With TEAP and TBAP the equivalent circuit corresponds to a resistance $R_{ohm}$ in series with a capacity $C_{d1}$. Nevertheless, in the case of THAP and TOAP, to take account of the possible change of orientation mechanism, an impedance must be introduced. Therefore, the equivalent circuit without a faradaic reaction could be that, shown in Fig. 5.

The real and imaginary components of the impedance of this network are given, respectively, as

$$Z'_{tot} = R_{ohm} + \frac{1/R_1}{(1/R_1)^2 + \omega^2(C_1 + C)} \tag{1}$$

$$Z''_{tot} = \frac{\omega(C_1 + C)}{(1/R_1)^2 + \omega^2(C_1 + C)^2} . \tag{2}$$

By combining both expressions we obtain

$$R_1 = \frac{(Z'_{tot} - R_{ohm})^2 + Z''^2_{tot}}{Z'_{tot} - R_{ohm}} . \tag{3}$$

$\omega(C_1 + C)$ can be determined from the value of $R_{ohm}$ in accordance with

$$\omega(C_1 + C) = \frac{Z''_{tot}}{(Z'_{tot} - R_{ohm})^2 + Z''^2_{tot}} . \tag{4}$$

As can be seen, Eqs (3) and (4) involve measured quantities. The $R_{ohm}$ is taken as the common value to which the values of resistance at very positive potentials tend and it coincides with the values measured at high frequencies.
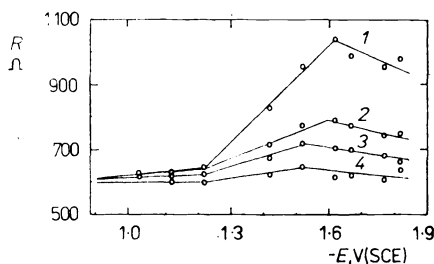


FIG. 4

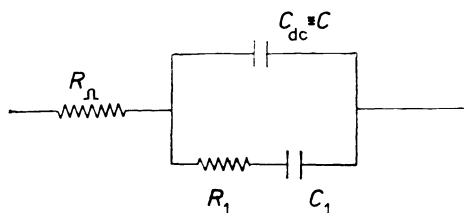$R_{ohm}-E$ curves of TOAP in DMF at different frequencies (Hz): 1 320; 2 800; 3 1 500; 4 4 000

FIG. 5

Equivalent circuit

Therefore, the values of $R_1$ and $\omega(C_1 + C)$ at each potential and frequency can be determined.

*Chronocoulometry*

The analysis of the chronocoulograms obtained with the solutions of quaternary salts (TXAP) in DMF make clear important facts which confirm what was set out in the previous section.

Fig. 6 represents the charge stored in the electrode in terms of $t^{1/2}$ for the direct pulse, and of $\Theta$ for the inverse. It is seen that instead of lines parallel to the time axis, as corresponds to a process of charge and discharge of the double layer when the potential is varied, straight lines are obtained for the direct pulse whose slopes increase when $E_f$ becomes more negative for the same cation. This effect becomes more marked with the change from X = ethyl to X = octyl. Moreover, if the slopes of the straight lines at the same potential for the different cations TXA$^+$ are compared, an increase is also found with the change from X = ethyl to X = octyl.

The parameters of the straight lines represented in Fig. 6 are set out in Table I. The slopes corresponding to the inverse pulse are practically equal to zero for all the cations.

The morphology of these graphs is similar to what a faradaic process would be. Since at the potentials used this is impossible, it can only be assumed that a slow surface process occurs which modifies the charge of the electrode. At the initial potential $E_i = -1\,200$ mV, as was pointed out in previous studies, there is adsorption of the cations, which is very weak in TEAP and increases with the size of the cation. At the final potentials indicated in Fig. 6, the adsorption will be stronger because the charge of the electrode becomes more negative. Therefore, in the direct pulse the
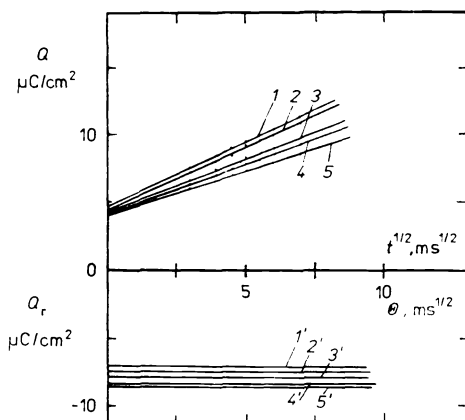


Fig. 6

$Q$–$t^{1/2}$ and $Q_r$–$\Theta$ curves for 0·09M-TOAP at different potentials. $\Theta = \tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}$.  $E_i$(V) $= -1\cdot137$ V; $E_f$(V) $= 1 \; -1\cdot987;$ $2 \; -1\cdot962;$ $3 \; -1\cdot937;$ $4 \; -1\cdot912;$ $5 \; -1\cdot887.$ $1' \; -1\cdot887;$ $2' \; -1\cdot912;$ $3' \; -1\cdot937;$ $4' \; -1\cdot962;$ $5' \; -1\cdot987$

change from $E_i$ to $E_f$ causes an increase in the adsorption. A large part of the results could be explained if in the adsorption process a change of orientation of the adsorbed cation occurs from a position in which the adsorption is due to one of the carbon chains to another in which one of the tetrahedral faces with the remaining three chains is placed parallel to the electrode, with the positive cation charge closer to it. Thus, the differential capacity would increase and the shoulder would be explained. The resistive component of the impedance would also increase since the adsorption process is controlled by diffusion. The change in orientation should be slow due to steric effects which the adsorbed cations produce, and this would explain the dispersion of both $Z'_{tot}$ and $C_{dl}$ with the frequency. The charge of the electrode would increase with increasing $C_{dl}$, although slowly, and produce slopes in the chronocoulometric representation corresponding to the direct pulse.

In the inverse step from $E_f$ to $E_i$, some of the $TXA^+$ cations previously adsorbed in the direct pulse are desorbed. Therefore, the state of the electrode at the initial

TABLE I

Chronocoulometric analysis of tetraalkylammonium perchlorates in DMF. ($E_i$, $E_f$: initial and final potentials vs SCE; $Q°$: forward intercept and $S_f$: forward slope)

| $TXAP^a$ | $-E_i$, V | $-E_f$, V | $Q°$, $\mu C$ cm$^{-2}$ | $S_f$, $\mu C$ cm$^{-2}$ s$^{-1/2}$ |
|---|---|---|---|---|
| TEAP | 1·240 | 1·954 | 6·5 | 0·24 |
|  | 1·340 | 1·954 | 5·5 | 0·12 |
|  | 1·440 | 1·954 | 4·5 | 0·12 |
| TBAP | 1·143 | 1·843 | 4·0 | 0·12 |
|  | 1·143 | 1·893 | 4·5 | 0·22 |
|  | 1·143 | 1·943 | 4·6 | 0·30 |
|  | 1·143 | 1·993 | 4·8 | 0·57 |
|  | 1·143 | 2·043 | 5·1 | 0·86 |
| THAP | 1·141 | 1·841 | 4·7 | 0·31 |
|  | 1·141 | 1·861 | 4·8 | 0·37 |
|  | 1·141 | 1·881 | 5·0 | 0·40 |
|  | 1·141 | 1·891 | 5·1 | 0·44 |
|  | 1·141 | 1·921 | 5·2 | 0·50 |
| TOAP | 1·137 | 1·887 | 4·0 | 0·65 |
|  | 1·137 | 1·912 | 4·3 | 0·72 |
|  | 1·137 | 1·937 | 4·4 | 0·75 |
|  | 1·137 | 1·962 | 4·5 | 0·92 |
|  | 1·137 | 1·987 | 4·7 | 0·94 |

$^a$ 0·1 mol l$^{-1}$.

potential is not reestablished during the 50 ms which are shown in the graph. Much more time is needed for equilibrium to be reached at the potential $E_i$. Therefore, in the chronocoulogram (Fig. 6) the charge corresponding to $E_i$ after the pulse has been applied never reaches the same value as before. So the slopes of the inverse pulse are practically equal to zero and the intercepts higher than those corresponding to the direct pulse.

## REFERENCES

1. Hernández Creus A., González S., Arévalo A.: An. Quim. *84*, 281 (1981).
2. Souto R. M., González S., Arévalo A.: J. Electroanal. Chem. *216*, 283 (1987).
3. Gambert R., Baumgartel H.: J. Electroanal. Chem. *190*, 283 (1985).
4. Fawcett W. R., Ikeda B. M., Sellan J. B.: Can. J. Chem. *57*, 2269 (1979).
5. Gambert R., Baumgartel H.: J. Electroanal. Chem. *183*, 315 (1985).
6. Gambert R., Baumgartel H.: J. Electroanal. Chem. *185*, 147 (1985).
7. Kojima H., Bard A.: J. Electroanal. Chem. *63*, 117 (1975).

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