Electrochemical Metallization at the Liquid–Liquid Interfaces of Non-miscible Electrolytic Solutions

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Summary A direct current applied across the liquid-liquid interphase of a heterogeneous, unreactive Cu^{2+}–$[V(CO)_6]^-$ redox system, causes deposition of a copper layer at the interface.

A NEW redox reaction which occurs between two non-miscible electrolytic solutions, when a current is applied across their interface has been studied. Under suitable conditions the current causes the growth of a metal layer at the interface. The redox couple consists of $[V(CO)_6]^-$ and a noble metal cation, each confined in one phase of a heterogeneous system made up of two non-miscible solvents.

The most significant results have been obtained with $[Bu_4N][V(CO)_6]$,[1] and $CuSO_4$. The electrolyte $[Bu_4N]$-$[V(CO)_6]$ is soluble in organic solvents, but very insoluble in water, so that $CuSO_4$ and $[Bu_4N][V(CO)_6]$ are separated quantitatively in H_2O–$ClCH_2CH_2Cl$ or H_2O–CH_2Cl_2 mixtures.

These heterogeneous electrolytes are unreactive at room temperature. Although decomposition of $[V(CO)_6]^-$ occurs at b.p., the reaction does not involve the reduction of Cu^{2+} to the metal. If current is passed through a symmetrical electrolyte system, with a $ClCH_2CH_2Cl$ phase containing $[Bu_4N][V(CO)_6]$ between two aqueous phases containing $CuSO_4$ in a U-tube, a film of copper is formed at the interface facing the anolyte, and CO is evolved (expt. 1).

Copper film formation is independent of the electrode processes at the ends of the chain; a two-layer electrolyte, with an inert electrode in each layer, and the aqueous layer as anolyte, can also be employed.

The efficiency of the reduction of Cu^{2+} depends rather

TABLE

Electrochemical metallization of liquid–liquid interfaces[a]

Expt	Aqueous phase solutes (conc./M)	Current density mA/cm^2	Time/ min	Recovered metal layer weight/mg cm^{-2}
1	$CuSO_4$(0·35)	3	15	Traces
2[b]	$CuSO_4$(sat.) + $Al_2(SO_4)_3$ (sat.) + H_2SO_4 (1) ..	10	30	0,9
3	$CuSO_4$ (0·35) + H_2SO_4 (1)[c] + Agar	6	45	3
4	$CuSO_4$ (0·35) + NH_3 (1)	4	45	—
5[d]	$AgNO_3$ (0·1) + NH_4SCN (sat.)	10	20	e
		E.m.f./mV	Time/h[f]	
6	$CuSO_4$ (0·35)	680—650	3—10	
7	$CuSO_4$ (0·35) + Agar	380	7	

[a] Temp. 25 °C; $[Bu_4N][V(CO)_6]$ (0·1M) in $ClCH_2CH_2Cl$ except for expts. 2 and 5; voltages in range 10—80 V for expts. 1—5. [b] 0·46 M $[Bu_4N][V(CO)_6]$ in $ClCH_2CH_2Cl–Et_2O$ (78:22 w/w). [c] Gelatinized $CuSO_4$ solution acidified by diffusion of 1 M H_2SO_4 for 100 h. [d] 0·01 M $[Bu_4N][V(CO)_6]$ in $ClCH_2CH_2Cl$. [e] Powdery Ag precipitated at interface; weight not measured. [f] Time after contacting solutions.

randomly on experimental conditions, and is lower than the efficiency of ordinary cathodic deposition of copper. The copper film is usually broken by CO bubbles formed in the underlying $ClCH_2CH_2Cl$ phase, and cannot be recovered as such.

Fragmentation of the copper layer was avoided by superimposing $[Bu_4N][V(CO)_6]$ solution in $ClCH_2Cl–Et_2O$ on the aqueous solution containing increasing concentrations of $CuSO_4$ and an auxiliary electrolyte (expt. 2), or alternatively by supporting the aqueous phase on Agar (expt. 3). Continuous coherent layers have been recovered in this way, with current efficiencies of *ca.* 60% of those of ordinary cathodic deposition. In these cases the layer probably behaves progressively as a bielectrode, but prolonged electrolysis causes deterioration of the metal layer, if the organic solvent is depleted in $[V(CO]_6]^-$.

Non uniformity of current density at the interface affects the thickness of the copper layer; partly covered surfaces and copper films similar in shape to an adjacent cathode can be obtained. Analogous results with poorer yields have been obtained with aqueous $CuNO_3$ while copper(II) amines gave no metal at all (expt. 4).

The redox process at the interface may be represented as in equation (1). The absence of a spontaneous reaction (1)

$$[V(CO)_6]^-_{DCE} + 2Cu^{2+} \rightarrow V^{3+}_{aq} + 6(CO) + 2Cu \qquad (1)$$

can be ascribed to forbidden heterogeneous electron transfer at the liquid–liquid interphase, and homogeneous reaction is probably thermodynamically unfavourable in each phase, owing to the low activity of $[V(CO)_6]^-$ in H_2O and Cu^{2+} in $ClCH_2CH_2Cl$.

If enough MeOH is added to achieve complete miscibility of the two phases, then Cu and CO are produced spontaneously. Also, the electrode system (2) gives an e.m.f., Cu being positive (expts. 6 and 7). Spontaneous current in the short-circuited system (2) as well as higher imposed currents cause deposition of Cu at the Cu electrode, and oxidation of $[V(CO)_6]^-$ at the Pt electrode.

$$Cu\,|\,H_2O,\ CuSO_4\,||\,ClCH_2CH_2Cl,\ [Bu_4N][V(CO)_6]\,|\,Pt \qquad (2)$$

This electrolytic process and the interfacial deposition of copper are equivalent to the homogeneous spontaneous reaction (1) except that the site of oxidation and reduction differ, and the ions are transferred between different phases.

Silver salts behave similarly; although a solution of $[Bu_4N][V(CO)_6]$ in $ClCH_2CH_2Cl$ or CH_2Cl_2 causes spontaneous precipitation of Ag in contact with aqueous $AgNO_3$, in the presence of high concentrations of CN^-, NCS^-, or NH_3, the heterogeneous system does not react spontaneously at room temperature. Current flowing from aqueous to non-aqueous phase causes immediate precipitation of Ag powder at the interface (expt. 5).

Aqueous nickel sulphate leads to carbonylated nickel compounds.

All experiments were performed in an inert atmosphere, with deaerated solvents.

The present examples belong to the still narrow class of heterogeneous redox processes at the interface between solutions which have been reported.[2,3]

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