

FORMAL REDOX POTENTIALS OF FERRICYANIDE FERROCYANIDE COUPLE IN CERTAIN NON-AQUEOUSWATER MIXTURES

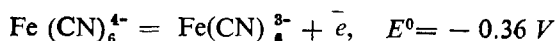
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Formal oxidation-reduction potential of ferri-ferrocyanide couple has been determined in dioxane, acetone, acetonitrile, DMF and DMSO with water mixtures. As the weight percentage of these non-aqueous solvents increased, the formal oxidation-reduction potential of the system decreased. The decrease of potential has been found to be in the order—Dioxane, acetone, acetonitrile, DMF and DMSO.

INTRODUCTION

THE ferrocyanide-ferricyanide couple reaches a rapid reversible equilibrium. Several concordant values have been obtained for cells employing this couple in the form of potassium salts. However, the potential is a function of the potassium ion concentration and the correction to give an accurate E° value is rather large. With equal concentrations of the two negative ions, the observed potential is around $-0.48 V$. Kolthoff and Tomsick (1935) have made a calculation of the E° value as follows:—



The formal potential of the ferro-ferricyanide system varies from strongly acidic to strongly alkaline media. These potentials are also dependent on the concentration of the acid as well as on the nature of anion (Swift 1939).

Papp and Mohai (1962) measured the redox potential of ferro-ferricyanide couple in presence of potassium compounds. They observed that the potential was the highest (495 mV) in a 1.0 M KOH solution and the lowest (405 mV) in K_2PO_4 solution in the concentration range 0.001 — 1.0 M. The potentials varied with the concentration of potassium ion as well as with the nature and concentration of the anions present (Farsang & Tomesanyi 1966).

Farsang and Tomesanyi (1966) studied the polarographic redox waves of 10^{-3} to 10^{-6} M $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ in 1M KCl recording by cyclic voltage sweep chromopotentiometry at the carbon-paste and saturated electrode.

Rock (1966) redetermined the standard potential of ferrocyanide-ferricyanide system in a cell free from salt bridge in which the liquid junction potential was minimized by an appropriate choice of an electrode. The value obtained at 25°C is $E^\circ = -0.3704 \pm 0.005$ Volt.

Mohai *et al.* (1964) studied the system by taking the hydrogen [{hexacyano ferrate (III)}—{hexacyanoferrate(II)}] and observed the effect of $p\text{H}$ presence of various cations. Recently, Boguslavskii (1965) used an electrode made from a film of

poly-(tetracyanoethylene) deposited on a quartz rod for the determination of redox potential of $K_3Fe(CN)_6$ - $K_4Fe(CN)_6$ system.

In the present investigation the effect of non-aqueous solvents on the redox potential of ferricyanide-ferrocyanide couple is reported. An attempt has been made to determine the formal redox potential of the couple in dioxane, acetone, acetonitrile, DMF and DMSO with water mixtures upto 50%.

EXPERIMENTAL

Reagents — Potassium ferrocyanide and potassium ferricyanide used were of analytical reagent grade supplied B.D.H.

Acetone (A.R.) and Dioxane (A.R.) were supplied by B.D.H. DMF, DMSO and acetonitrile were "Baker analyzed" reagents (J. T. Baker Chemical Co., Phillipsburg, N. J.) were used. The non-aqueous solvents were purified before use.

Apparatus — A Leeds and Northrap student potentiometer was used to measure all potentials to ± 0.2 mV.

A bright platinum foil which was thoroughly cleaned was used as an indicator and an aqueous saturated calomel electrode as a reference electrode in all the measurements.

Procedure — The solutions have been prepared in the required non-aqueous-water mixtures in presence of sulphuric acid, and a constant total acid concentration of 0.01 M was maintained in all the solutions in various solvents. The potentials were measured in the inert atmosphere of nitrogen using saturated calomel electrode as reference electrode. The ionic strength was maintained constant (0.02 M) using sodium sulphate in all the measurements. All the measurements were made by keeping the cell in thermostat maintained at $25^\circ \pm 0.1^\circ C$. The redox potentials vs. the reference electrode were calculated using the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{[OX]}{[Red]}, \quad (1)$$

where "E" is the observed potential and E^0 is the formal redox potential.

RESULTS AND DISCUSSIONS

The ferri-ferrocyanide system constitutes a redox system. The results obtained for the ferrocyanide-ferricyanide system in the various non-aqueous solvent-water mixtures have been summarised in Table I. The results indicate that there is a large decrease in potential even in the presence of 10% of the non-aqueous solvent in water media. The decrease in potential is in the following order : Dioxane, acetone, acetonitrile, dimethyl formamide and dimethyl sulphoxide.

The plots of redox potentials, E against $\log \frac{[Fe(CN)_6]^{-3}}{[Fe(CN)_6]^{-4}}$ gave a straight line in each solvent. The slopes of these lines are found to be 0.059 volts which indicated that the value of "n" in the expression (1) is one in each solvent mixture.

The value of E^0 is dependent on the hydrogen ion concentration and the nature of anion due to formation of hydroxy polyacids. The results indicate that in these media, the hydrated species are not very much effected upto 40% of the solvent studied.

TABLE I

Formal redox potentials of ferri-ferrocyanide couple in the non-aqueous-water mixtures(Temperature $25^{\circ} \pm 0.5^{\circ}\text{C}$)

Wt. % of solvent	E° Volts				
	Dioxane	Acetone	Acetonitrile	DMF	DMSO
0.0	0.370	0.370	0.370	0.370	0.370
10.0	0.146	0.142	0.139	0.134	0.134
20.0	0.117	0.116	0.101	0.087	0.087
30.0	0.093	0.087	0.081	0.044	0.038
40.0	0.068	0.066	0.062	—	—0.022
50.0	0.053	0.050	—	—	—0.082

The results also show that the potentials decrease with the decrease in the dielectric constant of the medium. The results obtained 50% of the non-aqueous solvent indicate that the ferro-ferricyanide system is not a useful redox system for either quantitative oxidations or in the preparative organic chemistry using ferricyanide as an oxidant. For this system, a general observation can be that the dielectric constant of the pure non-aqueous solvent increases from dioxane to dimethyl sulphoxide. In the presence of DMSO, the potential becomes even negative as the weight percent of dimethyl sulphoxide is increased upto 40%.

Under these experimental conditions, it has been established that the ferricyanide solution does not react with any of the five non-aqueous solvents used.

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