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Fig. 1. Dependence of the emf of galvanic cell (I) on the concentration of ferricinium fluoroborate cation. 1, 2, 3, 4 –solvent: 1 N KCl + 0.01 N HCl; 1 N $NaClO_4$ + 0.01 N $HClO_4$; 1.01 N HCl; 1.11 N $HClO_4$, respectively.

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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# AN ELECTRODE REVERSIBLE TO THE FERRICINIUM CATION

Ferrocene is practically insoluble in water and aqueous salt solutions, which leads to the fact that a smooth platinum electrode in the system suspension of ferrocene–aqueous acid solution of a ferricinium-cation salt, in the absence of another reversible oxidation-reduction system, does not have a stable and reproducible potential value. In such solutions, small additions of rapid oxidation-reduction systems determine the value of the potential of a smooth platinum electrode.

A suspension of crystalline ferrocene in aqueous acid solutions is oxidized very slowly by ferric chloride, whereas oxidation of amorphous ferrocene proceeds rapidly and quantitatively. As was shown ([1,2]), the rate of electron exchange in the homogeneous liquid system ferrocene–ferricinium-cation salt–solvent considerably exceeds the exchange rate of such rapid systems as $FeCl_3$—$FeCl_2$, $K_3Fe(CN)_6$—$K_4Fe(CN)_6$ under the same conditions. The above-listed properties of the system ferrocene–ferricinium-cation salt determined the method for preparing electrodes reversible to the ferricinium cation.

**Fig. 1.** Dependence of the emf of galvanic cell (I) on the concentration of ferricinium fluoroborate cation. 1, 2, 3, 4 –solvent: 1 N KCl + 0.01 N HCl; 1 N $NaClO_4$ + 0.01 N $HClO_4$; 1.01 N HCl; 1.11 N $HClO_4$, respectively.

A mixture of finely crystalline ferrocene, obtained by sublimation, and amorphous ferrocene is mechanically applied to a smooth platinum plate.

Amorphous ferrocene is obtained by precipitation with water from a solution of ferrocene in acetic acid. Electrodes prepared in this way, in an aqueous acid solution of a ferricinium-cation salt, within 1-2 min acquire a stable potential value reproducible to within ±0.5 mV. When transferred from one solution of a ferricinium-cation salt to another, differing in ferricinium-cation concentration, and back again, the electrodes within 1-2 min assume the previous potential value.

In studying the electrode properties of the ferrocene-ferricinium electrode we used the following galvanic cells:

$$\mathrm{Pt} \mid \mathrm{Fe(C_5H_5)_2},\ \mathrm{Fe(C_5H_5)_2^+BF_4^-} \mid \mathrm{KCl},\ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}. \tag{1}$$

Temperature 25°. The total molality of salt and acid was kept constant and equal to 1.01 g-equiv/kg of solvent. In Fig. 1 are given

dependence of the emf of galvanic cell (I) on the logarithm of the volume concentration of ferricinium borofluoride in solutions of 1 N KCl + 0.01 N HCl, 1.01 N HCl, 1 N $NaClO_4$ + 0.01 N $HClO_4$, and 1.11 N $HClO_4$.

Since in each series of experiments the ionic strength was kept constant, this ensured constancy of the ionic activity coefficients and of the diffusion potential; therefore, under conditions of complete dissociation of ferricinium borofluoride, one should expect a linear dependence of the emf of the cell on $\lg C_{\mathrm{Fe(C_5H_5)_2^+BF_4^-}}$, with a slope coefficient of 59 mV. As can be seen from the graph, the above statement was fully confirmed and made it possible to calculate the standard potential of the ferrocene-ferricinium electrode in the salt solutions listed above.

| Solvent | 1 N KCl + 0.01 N HCl | 1 N $NaClO_4$ + 0.01 N $HClO_4$ | 1.01 N HCl | 1.11 N $HClO_4$ |
|---|---|---|---|---|
| *E*, mV | 637 | 618 | 605 | 560 |

The ferrocene-ferricinium electrode can be used for determining the activity coefficients of ferricinium cation salts, its concentration, and for studying complex formation of the ferricinium cation.

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## REFERENCES

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*Note: Figure translations are in progress. See original paper for figures.*