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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 NaClO₄ + 0.01 N HClO₄; 1.01 N HCl; 1.11 N HClO₄, 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 FeCl₃—FeCl₂, K₃Fe(CN)₆—K₄Fe(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.

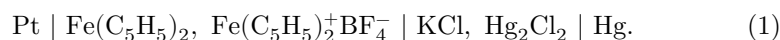
Fig. 1. Dependence of the emf of galvanic cell (I) on the concentration of ferricinium fluoroborate cation. 1, 2, 3, 4 —solvent: 1 N KCl + 0.01 N HCl; 1 N NaClO₄ + 0.01 N HClO₄; 1.01 N HCl; 1.11 N HClO₄, respectively.

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:



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 NaClO₄ + 0.01 N HClO₄, and 1.11 N HClO₄.

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 $\lg C_{\text{Fe}(\text{C}_5\text{H}_5)_2^+\text{BF}_4^-}$, 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
<i>E</i> , 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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Note: Figure translations are in progress. See original paper for figures.

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