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Voltammetric reduction of polyprotic acids at the platinum microelectrode: dependence on supporting electrolyte ☆

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Abstract

The voltammetric behavior of weak and strong polyprotic acids was studied at platinum microelectrodes under steady-state conditions in solutions of very low ionic strength, including those without added supporting electrolyte. Three diprotic acids (sulfuric, oxalic, and malonic), one triprotic acid (phosphoric acid), and one tetraprotic acid (pyrophosphoric acid) were chosen for the investigation. The reduction of hydrogen ion in solutions of strong diprotic acid (sulfuric acid) with no supporting electrolyte results in a voltammetric wave 1.5 times higher than the diffusional wave obtained with excess electrolyte. This agrees well with the theoretical prediction for one-electron reduction of monovalent cation accompanied by divalent anion. The voltammetric reduction waves of oxalic, malonic, and phosphoric acids in solutions without supporting electrolyte were twice as high as the diffusion-controlled waves with excess electrolyte. This is what theory predicts for a monoprotic strong acid. The strong (H^+) and weak (HA^- for oxalic and malonic, H_2A^- for phosphoric, and H_2A^{2-} for pyrophosphoric acid) forms of acids are reduced in one (oxalic and malonic) or two (phosphoric and pyrophosphoric) voltammetric waves. The influence of the concentration of supporting electrolyte on the height of reduction waves of acids was examined for two kinds of supporting electrolyte, with mono- and divalent cations, over a wide range of their concentrations. The experimental results are compared with theoretical predictions. The diffusion coefficients of $H(COO)_2^-$ and $HCH_2(COO)_2^-$ ions were calculated from the steady-state diffusion-controlled currents.

Keywords: Voltammetric reduction; Polyprotic acids

1. Introduction

The voltammetric reduction of hydrogen ion at the platinum microelectrode results in a well-defined, transport-controlled wave [1]. The height of the steady-state wave is proportional to the acid concentration over a very wide range, and to the transport rate of hydrogen ion. Additionally, the use of microelectrodes allows voltammetric measurements in solutions of very low ionic strength, including solutions without supporting electrolyte. These features have been employed in voltammetric examination of the transport of hydrogen counterion in colloid suspensions and in polyelectrolyte solutions [2–4], and for monitoring the changes in the concentration of hydrogen ion during the oxidation of a polyaniline film [5]. Also, reduction of hydrogen ion in solutions of strong acids appears to be a good test system for determination of the size and the surface quality of Pt and Au microelectrodes [1].

Strong acids are dissociated completely, and in solutions containing no deliberately added supporting electrolyte there is only one kind of cation, the hydrogen cation. The reduction current in these solutions is controlled by diffusional and migrational transport of H^+. In agreement with the theory for acids of the HA type, the ratio of the steady-state currents obtained in the absence and the presence of sufficient excess (factor of 20) of supporting electrolyte should be two [6–10]. This ratio has been confirmed experimentally for the reduction of hydrogen ion in $HClO_4$ solutions [1]. The theory predicts that the ratio of the steady-state currents obtained without and with excess supporting electrolyte should depend on the charge of the anion associated with the hydrogen cation [9,10]. Consequently, strong acids of the type H_2A, H_3A and H_4A should behave differently from a monoprotic

☆ Dedicated to Professor Hiroaki Matsuda on the occasion of his 70th birthday.

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