THE USE OF ROTATING DISK ELECTRODES FOR THE STUDY OF THE KINETICS OF SORPTION PROCESSES. II.*

ION EXCHANGE OF COPPER(II) ON DOWEX 50 WX 8 IN KCL MEDIA

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The voltammetry of the Cu^{2+}—Cu^{+} reduction wave on the glassy carbon rotating disk electrode has been studied in weakly acid solutions of potassium chloride. In the same solutions was also studied the kinetics of the adsorption of copper(I) on Dowex 50 WX 8 cation exchange resin by continuous measurement of the diffusion current of the Cu^{2+}—Cu^{+} reduction wave. The kinetic type was determined and rate constants calculated under various conditions; the activation energy for the film kinetic process was found.

Part I of this series[1], which utilized the voltammetric metal ion concentration monitoring method using a rotating disk electrode[2], dealt with the kinetics of the adsorption of iron(III) from strongly acid media (up to 3·0 molar) on Dowex 50W X 8. This method has now been applied to studying the adsorption of copper(II) from potassium chloride solutions on the same ion exchange material. As a basis of the study, the voltammetric behaviour of copper(II) in this medium has been studied at the glassy carbon rotated disk electrode, which has already proven to be an advantageous indication device[1,3–6]. The adsorption rate and kinetic type were studied with varying pH and temperature, as well as at various concentrations of KCl and varying adsorbent–adsorbate ratios.

EXPERIMENTAL

Reagents and apparatus. The copper solutions used were prepared from "Specpure" copper(II) oxide (Johnson, Matthey, England), and were standardized by EDTA titration. The KCl, KOH and HCl solutions were prepared from the p.a. chemicals. The catex was Dowex 50W X 8, 50/100 mesh, H^{+} cycle (The Dow Chemical Co., U.S.A.) (Grain radius, r^0, centres around $1·1 . 10^{-2}$ cm). The rotating disk electrode and instrumentation used were described in a previous paper[1]. pH measurements were made on the pH Meter 25 (Radiometer, Copenhagen).

Procedure. The copper(II) reduction wave in neutral KCl media is sufficiently well separated

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from the reduction wave of dissolved oxygen that it is not necessary to deaerate the solutions prior the measurement. However, in acid media, the oxygen reduction wave is shifted to positive values and deaeration becomes necessary. The experimental procedure and instrumentation were identical to that described in the preceeding paper[1], where a schematic representation of the experimental curves is given. The pH was adjusted with HCl and KOH in both the copper solution and in Dowex suspension, and measured in both prior to the kinetic measurement. In all cases, the pH and temperature of the Dowex suspension were identical to those of the copper solution.

RESULTS AND DISCUSSION

The Voltammetry of Copper(II) in KCl Solutions

The reduction wave of Cu^{2+} to Cu^{+} in KCl at the glassy carbon rotating disk electrode is well formed and has a clearly defined current plateau. The half-wave potential is dependent on the concentration of KCl, increasing with increasing KCl and is independent of the pH in the range studied (1·0 to 3·5). Resolution from the reduction wave of dissolved oxygen is increasingly marked with increasing pH, due to the shift of the latter to positive potentials with increasing acidity. The dependences of the current, both at an overvoltage of 50 mV and on the diffusion controlled plateau, on the square root of the electrode rotation rate are linear and pass approximately through the origin, in accordance with the Levich equation for reversible systems[6]. The diffusion coefficient, calculated from this equation, has the value $7·2 . 10^{-6}$ cm^{2}/s at pH 3·5 and 0·5M-KCl, as compared to literature value of $6·8 . 10^{-6}$ cm^{2}/s in the same solution[7], found using a gold r.d.e. The diffusion current was found to be independet of both the concentration of KCl and of the pH in the range studied. The decrease in the diffusion current with time on continuous polarization at either 0 or −100 mV (s.c.e.) is small and linear after the first 5—10 s; the current stability is good.

The voltammetric wave was studjed in the temperature range, 20—50°C. In all cases, the wave stability remained good and the noise level was low. The decrease in the diffusion current with continuous polarization remained linear after the first few seconds at all temperatures, but was somewhat more marked at higher temperatures. The half-wave potential increased slightly (2 mV/°C), and the diffusion current increased in a manner corresponding to reversible systems (2·3%/°C) (cf[9]). Calculation of the charge transfer rate constant at the standard potential[6] gave $k^0 > 10^{-2}$, i.e. the system behaves "reversibly" under the given conditions.

The Kinetics of the Adsorption Process

The rate of the exchange process was followed at various concentrations of copper(II), and using various volumes of Dowex, from 2 to 8 cm^3 (total electrolyte volume = = 100 ml before addition of Dowex, which was suspended in a total of 10 ml of the appropriate solution). At sufficiently low concentrations of copper(II) and high volumes of Dowex, the reaction rate becomes independent of the concentration of both Dowex and copper, as was similarly found during the study of iron(III) adsorption on the same resin[1]. In this region, i.e. with low concentrations of adsorbate and high concentrations of adsorbent, the rate of the adsorption process should be controlled by film kinetics[8]. The kinetics type was tested using 8 cm^3 of Dowex and with $2 . 10^{-4}$ of Cu^{2+} in a final volume of 110 ml. The reaction rate

was found to be controlled by film kinetics, *i.e.* to conform to the equation[8]

$$\ln (1 - U) = k_F t , \tag{1}$$

where U is the fractional adsorption at time t, and k_F is the film kinetics constant. At pH 3·5 and a temperature of 24°C, a value of $k_F = 4·90 . 10^{-2} s^{-1}$ was found. With lower concentrations of Dowex (2 cm^3) in a final volume of 110 ml) and at higher copper concentrations (above $4 . 10^{-4}$M), gel kinetics becomes the rate controlling process, *i.e.* the process follows the equation[8,9]

$$U = k_G t^{1/2} \quad U \leqq 0·05 , \tag{2}$$

where k_G is the gel kinetic rate constant. This dependence is again in keeping with theoretical predictions for larger concentrations of adsorbate and smaller amounts of adsorbent[8]. With the above mentioned ratios, at 24°C and pH 3·5, a gel kinetic constant of $k_G = 6·96 . 10^{-1} s^{-1/2}$ was found, giving, for the diffusion coefficient in the grain, the value $D_G = 5·0 . 10^{-5} cm^2/s$, where $D_G = k_G^2 \pi^3 (r^0)^2/36$ (*cf.*[8]).

The effect of pH. The kinetic ion exchange curves were studied for the adsorption of $2 . 10^{-4}$M-Cu^{2+} on 8·0 cm^3 Dowex in a final volume of 110 ml in the pH range 1·0 to 3·5. The rate decreases progressively with decreasing pH, and the kinetics is in all cases film controlled. The dependence of k_f on the pH is linear and conforms to the equation $k_f = (1·53 pH - 0·30) . 10^{-2} s^{-1}$ in the range studied.

The effect of temperature, E_{act}. It was found that, at pH 2·5, 1M-KCl, the adsorption of $2 . 10^{-4}$M Cu^{2+} on 8 cm^3 Dowex in a final volume of 110 ml is controlled by film kinetics (Eq. (1)) in the temperature range, 20–50°C. The rate of the process increases continuously; typical values of k_F for various temperatures are as follows:

T, °C	23	32	37	45
$k_F . 10^2$, s^{-1}	4·60	6·20	7·84	11·30

A plot of log k_F vs $1/T$ (where T is in K) is linear, and gives a value of E_{act}, at this pH, of 7·4 kcal/mol. In all cases, the gel kinetic plot is non-linear.

The effect of the concentration of KCl. The rate of the process was found to increase somewhat with increasing concentration of KCl (up to 1·5M). The process was controlled at all concentrations by film kinetics, although conformation to equation (1) was not so satisfactory at higher KCl concentrations. At the same time, the process also did not conform to equation (2). At pH 2·3, the value of k_F was found to increase to 140% of its original value when the KCl concentration was increased from 0·1M to 1·5M. The value of k_F increased linearly with the square of the KCl concentration. Nardin and coworkers[10], in their equilibrium experiments, also

found that the concentration of alkali metal chloride effects the adsorption of cupric ions on Dowex resins.

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