A Rotating Disc Study on Silver Dissolution in Concentrate HNO_3 Solutions

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In this study, a semi-empirical model was derived for dissolution process of metallic silver in nitric acid solutions. Rotating disc technique was used to study silver dissolution in nitric acid solution as a function of rotating disc speed, reaction temperature, nitric acid concentration and rotating disc surface area. It was determined that the dissolution of silver increased with increasing rotating speed, temperature and disc surface area while it decreased with increasing nitric acid concentration. The activation energy for the dissolution process was found to be 25.552 kJ mol^{-1}. The following semi-empirical model for the process controlled by diffusion was developed by statistical methods:

$$x = 1.7739 \cdot 10^{-2} \cdot \omega^{0.52} \cdot c^{-2.4079} \cdot A^{0.95} \cdot e^{-25552/RT} \cdot t$$

Keywords:
Rotating disc technique, silver dissolution, nitric acid

Introduction

Silver nitrate, which is an important chemical in industry, is used especially in photography, in silver plating, in the production of glass, indelible ink, mirrors and in the other silver salts. It is colorless, transparent tabular, and rhombic crystalls. This salt is produced by solving metallic silver in dilute nitric acid solutions, and then evaporating the solution.[1] Silver nitrate used in photography must have a very high purity expect.[2] Some investigations were performed to determine kinetics and mechanism of silver dissolution in nitric acid solutions; Stansbie expressed that in the reactions of metals and alloys with nitric acid; the physical and chemical states of metal, its purity, reaction temperature and products formed in the solution should be considered, and reactions of metallic silver and nitric acid takes place by a complex mechanism.[3] Urmanczy studied the reaction between rotating silver discs and nitric acid solutions and claimed that the discs didn't dissolve in 2.59–3.95 mol dm^{-3} nitric acid, but did dissolve in 4.49–5.17 mol dm^{-3} nitric acid[4]. In another study performed by Batten at 25 ^{o}C with 2.72 mol dm^{-3} nitric acid, it was found that the reaction was significantly depending on the metal if it was on the base of reactor, dispersed in the acid or immersed vertically into the acid. It was stated that this effect might depend on whether the reaction was very complex and autocatalytic and could be due to the intense interface at the base of the reactor.[5] Ozmetin et al. studied the kinetics of reaction between metallic silver and nitric acid solutions from 7.22 to 14.44 mol dm^{-3} and found that the dissolution rate was controlled by film diffusion with an activation energy of 18.81 kJ mol^{-1}.[6] In their another studies, for the reaction between metallic silver and nitric acid from 4.04 to 7.22 mol dm^{-3}, they found that the dissolution rate was controlled by chemical reaction with an activation energy of 57.66 kJ mol^{-1}.[7] A lot of studies have been carried out on the dissolution kinetics of silver in nitric acid with different techniques.[8,9]

Since the hydrodynamics of the liquid medium and the solid/liquid contact surface area remain constant, the rotating disc technique is a powerful tool for the study of chemical reaction mechanisms and has some advantage as compared with other methods, i.e. homogenous model, shrinking core model.[10,11] In the some kinetic investigations, it is possible to see applications of the rotating disc technique. In a study, silver dissolution with thiourea in the presence of ferric sulphate was investigated with rotating disc technique,[12] and in other studies, dissolution kinetics of Mazýdağý phosphate ore in nitric acid solutions was studied with same technique,[13] and a kinetic study of the cementation of copper from sulphate solutions onto a rotating aluminum disc was carried out.[14]

In this study, the rotating disc method was employed therefore the changing of surface area of metal particle and forming of dense interface at the reactor bottom.[5,6] For the condition of high nitric acid concentrations, dissolution characteristics of silver rods were investigated and a semi-empirical model was derived. It was aimed to use the dissolution conditions obtained from this method in the preparation of silver nitrate solutions for crystallization process.[15]

Material and methods

The cylindrical silver rods used in the experiments had a silver content of 99.87 % Ag, 0.07 % Cu, and 0.06 % others in mass. The silver rods were cut as discs having thickness of 3 cm and radius of 0.9, 1.8 and 3.0 cm. Their surfaces were smoothed with silicon carbide paper. The disc was incorporated in a holder made of teflon and attached horizontally to the stirrer shaft. Only one face of disc was exposed to the solution, the other faces were covered with acid resistant varnish. During the experiments the stirring speed was kept constant within +/– 1 rpm and temperature within +/– 0.1 °C. The dissolution process was carried out in a 500 cm^3-glass reactor with three necks and flat base. The reactor was equipped with three baffle for homogenous mixture. The silver disc was polished and rinsed with deionized water before each experiment. During the experiments, the disc surface was controlled with a mirror against the occurance of bubles. In all the experiments, the distance of disc from reactor base was kept as 3 cm. Choosen quantities and their range used in the experiments are given in Table 1. For each experimental condition the experiment was repeated twice, and analysed with volumetric and A.A.S. Methods[16] and the arithmetic average of the results of the two experiments was used for the theoretical dissolution analyses.

Table 1 – *Quantities used in this study and their values*

Quantities	Values
Reaction temperature, K	293, 303, 308*, 318
HNO_3 concentration, mol cm^{-3}	7.7×10^{-3}*, 8.67×10^{-3}, 9.63×10^{-3}, 11.55×10^{-3}, 14.44×10^{-3}
Rotating speed, rad s^{-1}	20.94, 41.89*, 62.83, 83.78, 104.72
Disc surface area, cm^2	0.636*, 2.545, 7.069

* The values kept constant

Experimental

In the rotating disc experiments, the effect of rotating speed, acid concentration, temperature and disc surface area on dissolved metallic silver amount, were investigated. The parameter values for each experiment were choosen as seen Table 1. The results of these dissolution experiments were given in Figure 1–4.

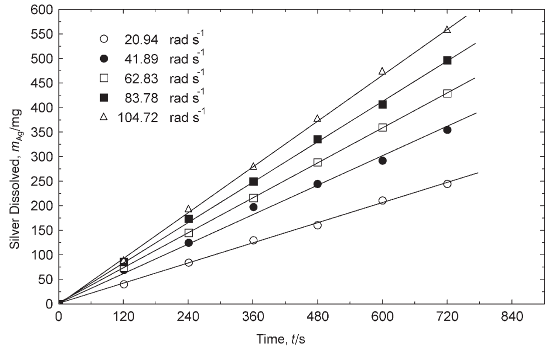

Fig. 1 – *The effect of rotating speed on silver disc dissolution at 308 K, 7.7×10^{-3} mol cm^{-3}, 0.636 cm^2*

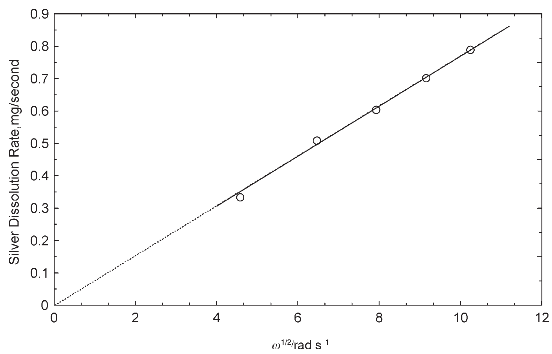

Fig. 2 – *The rates versus $\omega^{1/2}$ plot as the method of Levich Equation, 308 K, 7.7×10^{-3} mol cm^{-3}, 0.636 cm^2*

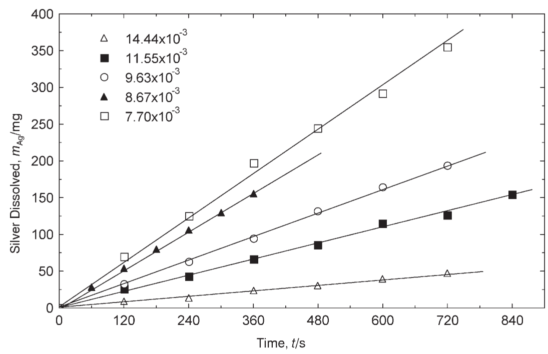

Fig. 3 – *The effect of nitric acid concentration on silver disc dissolution at 308 K, 41.89 rad s^{-1}, 0.636 cm^2*

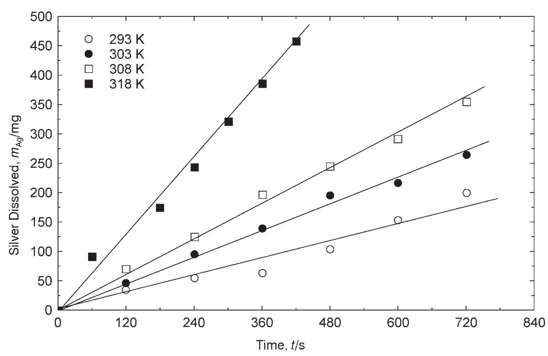

Fig. 4 – *The effect of temperature on silver disc dissolution at 7.7×10^{-3} mol cm^{-3}, 41.89 rad s^{-1}, 0.636 cm^2*

Results and discussion

At the laminar flow condition in which heterogeneous reaction rate is faster than mass transfer rate, the mathematical model for mass transfer to the rotating disc was derived by *Levich*:[11]

$$\frac{1}{A}\frac{\mathrm{d}n}{\mathrm{d}t} = J = 0.62\, D^{2/3} \nu^{-1/6} \omega^{1/2} c \qquad (1)$$

where $\frac{\mathrm{d}n}{\mathrm{d}t}$ is the rate of reaction, (mol s^{-1}), A the surface area of the rotating disc, (cm^2), J flux, (mol cm^{-2} s^{-1}), D diffusion coefficient, (cm^2 s^{-1}), ν kinematic viscosity, (cm^2 s^{-1}), ω angular speed, (rad s^{-1}) and c concentration of chemical active species in the solution, (mol cm^{-3}). According to this equation, the rate of silver dissolution should be a linear function of the square root of angular speed and linear function of first order of surface area. In the experiments, in order to keep laminar flow condition on the disc surface, the upper limit of the stirring speed was choosen as 10.47 rad s^{-1} to satisfy the restriction

$$r^2\, \omega/\nu \le 2 \times 10^5 \qquad (2)$$

where r is the disc radius (cm), ω disc angular speed (rad s^{-1}), ν kinematic viscosity (cm^2 s^{-1}). On the other hand, Eq. 1 is valid under the assumption that the mass transfer occurs, both, by convection and molecular diffusion. At zero or very low stirring speeds, only molecular diffusion may be significant. In the light of this consideration, the lower limit of the stirring speed was taken as 20.94 rad s^{-1}.

The effect of rotating speed on the dissolution is given in Figure 1. It can clearly be seen from this figure that the dissolved silver amount increased with increasing stirring speed. Because of effective remove of dissolved silver on surface with increasing rotating speed, this result has been expected. Also, the plot of the silver dissolution rate versus the square roots of the angular speed, is presented in Figure 2. As seen from this figure, a very good linear relationship between silver dissolution rate and $\omega^{1/2}$ is achieved. This linear relationship confirms to laminar condition on disc surface as required in Levich Equation.

The plot of the silver dissolved amount versus the reaction time for the various acid concentration, is present in Figure 3. It can be seen that the dissolved silver amount decreases with increasing nitric acid concentration. It is thought that the dissolution reaction of metallic silver in nitric acid solutions, having different concentrations, take place through two different mechanisms. In relatively low and high nitric acid concentrations, the following reactions occur, respectively[6,7,17]

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O \qquad (3)$$

$$Ag + 2HNO_3 \rightarrow AgNO_3 + NO_2 + H_2O \qquad (4)$$

There is a catalytic effect of HNO_2 on the dissolution reaction of metallic silver in nitric acid solutions.[8,9]

$$HNO_2 + HNO_3 \Leftrightarrow 2NO_2 + H_2O \qquad (5)$$

According to this equation, HNO_2 decreases with increasing HNO_3 concentration. It has been thought that the concentration of the common ion of $AgNO_3$ and HNO_3 increases with increasing acid concentration and a saturated liquid film is formed on the surface. Both, the decrease of HNO_2 and the saturated liquid film cause a decrease in the dissolution rate with increasing acid concentration[6].

The effect of the temperature on the dissolution was studied in the range of 293–308 K. The experiments showed that increasing temperature had an increasing effect on the dissolution process as seen in Figure 4. This increase was expected due to the exponential dependence of the rate constant in the Arrhenius form.

The effect of rotating disc surface area on dissolved silver amount was studied for the surface area of 0.636, 2.545 and 7.069 cm^2, and given in Figure 5- 6. It can be seen from Figure 5 and 6 that the dissolved amount and dissolution rate of silver in nitric acid increase with increasing surface area. This result was expected due to increasing solid to liquid contact surface area. Also, as seen in Figure 6, increase of dissolution rate of silver with disc surface area is linear and of first order. This result confirms the Levich equation in which dissolution rate is linear with surface area of disc.

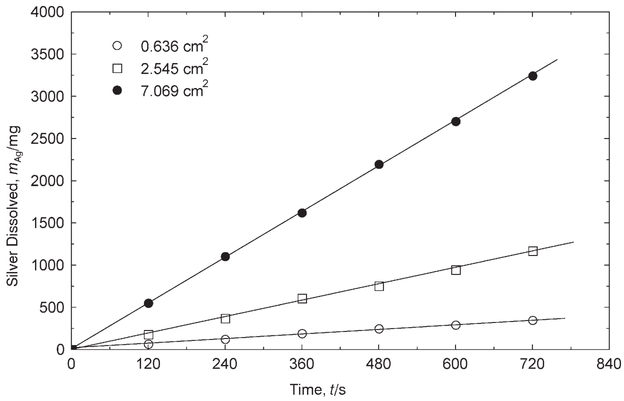

Fig. 5. – *The effect of rotating disc surface area on silver disc dissolution at 308 K, 41.89 rad s^{-1}, 7.7 × 10^{-3} mol cm^{-3}*

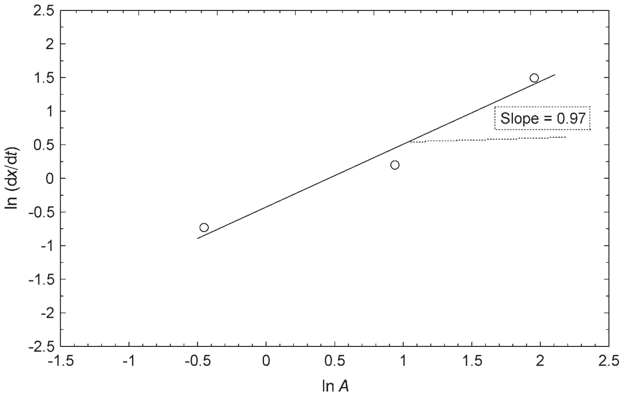

Fig. 6 – *The rates versus A plot as the method of Levich Equation, 308 K, 7.7 × 10^{-3} mol cm^{-3}, 0.636 cm^2*

To derive from the data, a mathematical semi--empirical equation for the this dissolution process, the parameters used to describe the dissolved silver amount were related in the form of using Levich Equation,

$$x = f(\omega, A, c, t, \exp(-E/RT)), \quad (6)$$

and depends on the parameters as follows

$$x = k\,\omega^a c^b A^c \mathrm{e}^{-E/RT} t \quad (7)$$

where x is the dissolved silver amount, (mg), ω disc rotating speed, (rad s^{-1}), c concentration of nitric acid, (mol dm^{-3}), A disc surface area, (cm^2), R universal gas constant, (J mol^{-1} K^{-1}), E activation energy, (J mol^{-1}), T reaction temperature, (K) and t reaction time, (s) and k, a, b, c constants. Constant k involves in some conversion factors and other quantities in Levich equation which are constant for this dissolution process.

The statistical calculation by simultaneous regression gave the results as $k = 1.77 \times 10^{-2}$, $a = 0.52$, $b = -2.41$, $c = 0.95$, $E = 25.552$ kJ mol^{-1}. When this constant values were inserted in Eq. (7), the following semi-empirical model was obtained:

$$x = 1.77 \cdot 10^{-2} \cdot \omega^{0.52} \cdot c^{-2.41} \cdot A^{0.95} \cdot \mathrm{e}^{-25.552/RT} \cdot t \quad (8)$$

As seen from Eq.8, for this dissolution process, the calculated activation energy was found to be 25552 J mol^{-1}. This activation energy value confirms that process is controlled by diffusion through fluid layer.[6,18] Also, dissolved amount of silver was found as a function of $A^{0.95}$ by Eq.(8). This result confirms the Levich equation in which dissolution rate increases with linear first order increasing surface area of disc.[11]

To test the agreement between the experimental dissolved amount and the calculated amount from semi-empric model (Eq. 8), relative mean squares of errors were calculated,[6,7,15] by using Eq. (9), and the agreement between the experimental and calculated values was very good, with a relative mean squares of errors $R = 0.9999$

$$\mathrm{ER} = \left[\frac{1}{N} \sum_{i=1}^{N} \frac{(X_{\mathrm{cal}} - X_{\mathrm{exp}})^2}{(X_{\mathrm{cal}})^2} \right]^{1/2} \quad (9)$$

Where X_{cal} is the calculated value, mg, X_{exp} the experimental value, mg, N the number of experimental data, which is 73 for the present case.

Conclusions

The rotating disc method was used to investigate the dissolution of metallic silver in nitric acid solution. The dissolution rate increased with increasing rotating speed, but reaction temperature and disc surface area decreased with increasing nitric acid concentration. From the Lewich Equation and experimental data, semi-empirical model was derived. The dissolution was found to be controlled by diffusion through fluid layer and the activation energy, E, was calculated as 25552 J mol^{-1}.

Nomenclature

$\frac{dn}{dt}$ – Rate of reaction, mol s^{-1}
$\frac{dx}{dt}$ – Rate of reaction, mg s^{-1}
A – The surface area of the rotating disc, cm^2
J – Flux, mol cm^{-2} s^{-1}
D – Diffusion coefficient, cm^2 s^{-1}
ν – Kinematic viscosity, cm^2 s^{-1}
ω – Angular speed, rad s^{-1}
c – Acid concentration, mol cm^{-3}
E – Activation energy J mol^{-1}
t – Reaction time, s
T – Reaction temperature, K
X – mass of silver, mg
m_{Ag} – mass of silver, mg
X_{cal} – Calculated value, mg
X_{exp} – Experimental value, mg
N – Number of experimental data

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