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Kinetics of Nickel Extraction with 8-Hydroxyquinoline in Carbon Tetrachloride

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Abstract: In this study we have investigated the kinetics of nickel extraction with oxine in carbon tetrachloride. The extraction rate depends on the oxine concentration, pH and temperature. It was considered that in the extraction process of nickel oxinate in carbon tetrachloride a transition state is formed which is in equilibrium with the reactant substances. On the basis of this hypothesis, the variation of activation energy and entropy was determined.

Keywords: Nickel; Extraction; Kinetics, 8-hydroxyquinoline.

Introduction

Extraction of metals as oxinates in various organic solvents has been the subject of many studies.[1-5] The studies regarding the oxinates extraction generally follow to establish the experimental condition in which various

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metal ions can be separated, or to determine the stability constants in presence of masking agents.[6-8]

The partition equilibrium of oxine chelates is generally reached quickly, and in some experimental conditions high values of extraction percents are obtained.[3, 8] The extraction rate depends on the partition constant of the reagent in various organic solvents. It can be observed that the extraction rate is smaller when the partition constant of oxine in various organic solvents is lower. For this reason, the solvents which solve less this reagent are indicated for the kinetic study of extraction processes.

The low rate to attain the equilibrium is due, in most of cases, to the low rate of the formation of chelate, being characteristic for metals from VI_B, VII_B and $VIII_B$ groups.[9] When the extraction rate depends on the pH of aqueous phase, this is one argument more that the extraction process is determined by the rate of complex formation in aqueous phase.[10]

The complex transfer from aqueous phase in organic phase is generally independent on the pH of aqueous phase, and depends only on the stirring rate of the phases. When studying the mechanism of chelates formation, the experiment is indicated to be performed at high stirring rate of phases and to select thus the extraction rate not depending on the stirring rate of phases.

Experimental

For extraction experiments a solution of nickel perchlorate was used, obtained by dissolving nickel metal in perchloric acid. The excess of acid was evaporated, and the nickel perchlorate solution was prepared by successive evaporation and dilution with double distilled water, until the solution pH is weakly acid. The nickel content in obtained solution was 5.87 mg Ni(II) /mL.

For extraction were used samples of 20 mL aqueous solutions, which contains 117.42 μg Ni(II) /mL, and a certain value of pH, with a constant ionic strength (~ 0.1), corrected with 1N perchloric acid, 1N sodium hydroxide and 0.5 N sodium perchlorate. These samples were mixed with 50 mL of 0.01 mol/L oxine solution in carbon tetrachloride. Before extraction, the aqueous solution pH, was measured using a Radelkis OK-281 pH/ion-meter, equipped with a combined glass electrode.

The contact of phases was done using a thermostat bath with possibility of rotating, which permits the variation of stirring rate.[11]

The samples used for analysis were collected from aqueous phase, at different moments, and the nickel content was determined spectrophotometrically (Digital Spectrophotometer S 104-D) with dimethyl-glyoxime.[12]

The values of extraction parameters were obtained using the following relation:

$$E = \frac{100 \cdot D}{D + {}^{v_a}\!/_{v_o}} \qquad (1)$$

where: E is extraction percent, D is distribution coefficient, v_a and v_o are the volume of aqueous and organic phase respectively, during of extraction process.

Results and discussions

The study of extraction process at different stirring rates of the two phases, maintaining constant the other parameters, indicate that at stirring rate higher that 40 rot/min, the extraction process is independent by stirring rate. In consequence, all further experiments were performed at a stirring rate of 60 rot/min.

The experimental results have shown that the extraction rate of nickel oxinate in carbon tetrachloride is dependent on the aqueous phase pH, the system temperature and the oxine concentration in organic phase.

When all other parameters are maintained constant, is observed that the extraction process of nickel oxinate in function by time of phases stirring is dependent on the aqueous phase pH (Figure 1). The extraction percent increase with the increase of aqueous phase pH. The dependence of extraction rate on the aqueous phase pH, is another argument which sustain that the extraction process is determined by the rate of complex formation in aqueous phase. The transfer of complex from aqueous phase in organic phase is, generally, independent on the aqueous phase pH.

When are maintain constant the aqueous phase pH and the oxine concentration in organic phase, is observed dependence between extraction kinetics and system temperature (Figures 2-4).

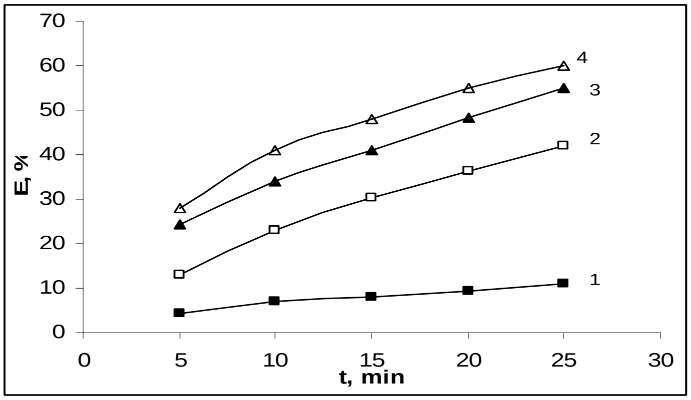

Figure 1. The dependence of nickel oxinate extraction on the aqueous phase pH, at 298 K, $[Ni^{2+}] = 2\ 10^{-3}$ mol/L, $[ox] = 10^{-2}$ mol/L, (1): pH = 2.60, (2): pH = 3.00, (3): pH = 3.35, (4): pH = 4.05.

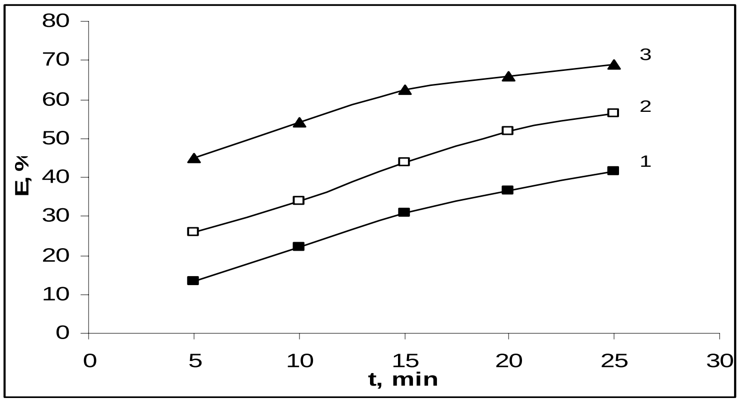

Figure 2. The dependence of nickel oxinate extraction on the system temperature, at pH = 3.00, $[Ni^{2+}] = 2\ 10^{-3}$ mol/L, [ox] = 10^{-2} mol/L, (1): T = 298 K, (2): T = 308 K, (3): T = 318 K.

As it can be seen from Figures 1-4, the extraction percent of nickel with oxine in carbon tetrachloride as function of time, increase with the increases of aqueous phase pH and system temperature.

When are maintained constant the aqueous phase pH and nickel concentration from aqueous phase, the increase of oxine concentration in organic phase has as result the increase of extraction rate (Figure 5).

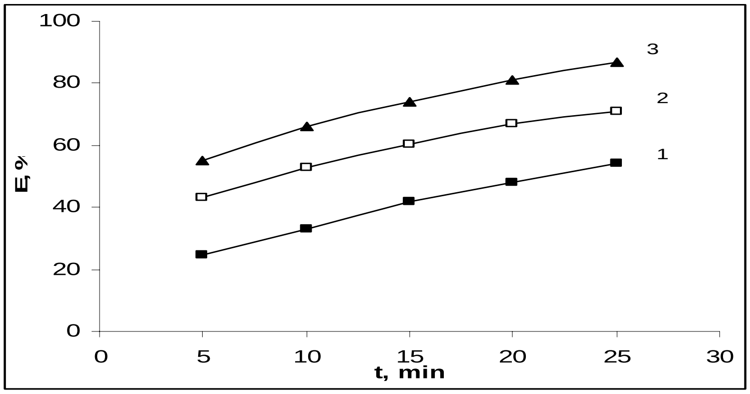

Figure 3. The dependence of nickel oxinate extraction on the system temperature, at pH = 3.35, $[Ni^{2+}] = 2\ 10^{-3}$ mol/L, [ox] = 10^{-2} mol/L, (1): T = 298 K, (2): T = 308 K, (3): T = 318 K.

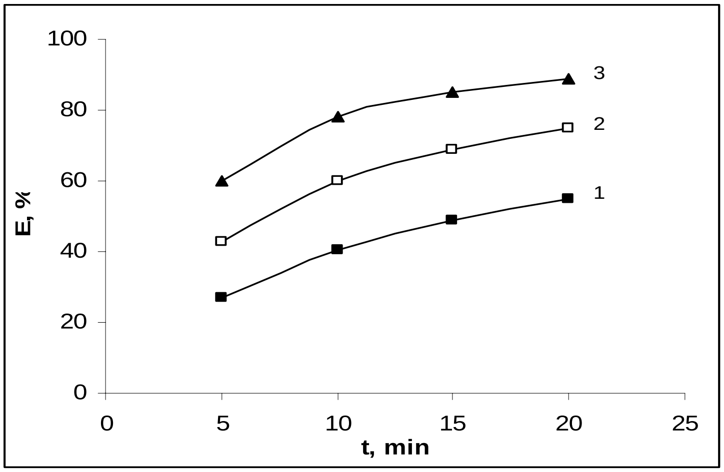

Figure 4. The dependence of nickel oxinate extraction by system temperature, at pH = 4.05, $[Ni^{2+}]$ = 2 10^{-3} mol/L, [ox] = 10^{-2} mol/L, (1): T = 298 K, (2): T = 308 K, (3): T = 318 K.

For the graphical representation of lg $\{[Ni^{2+}]_{t=0}/[Ni^{2+}]_t\}$ noted as lg α, versus time, straight lines are obtained, which indicate a first order reaction towards nickel ($[Ni^{2+}]_{t=0}$ and $[Ni^{2+}]_t$ are the nickel concentration in aqueous phase, at t = 0 and at time t, respectively) (Figure 6). The extraction rate will be determined by the rate of chelate formation between nickel and oxine.

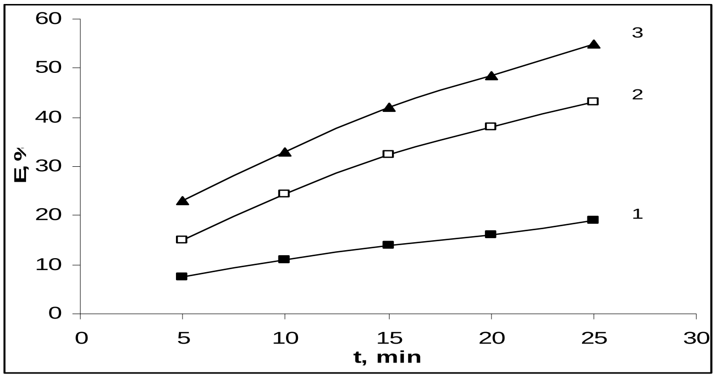

Figure 5. The dependence of nickel oxinate extraction on the oxine concentration from organic phase, at pH = 4.05, $[Ni^{2+}]$ = 2 10^{-3} mol/L, T = 298 K, (1): [ox] = 2 10^{-3} mol/L, (2): [ox] = 5 10^{-3} mol/L, (3): [ox] = 10^{-2} mol/L.

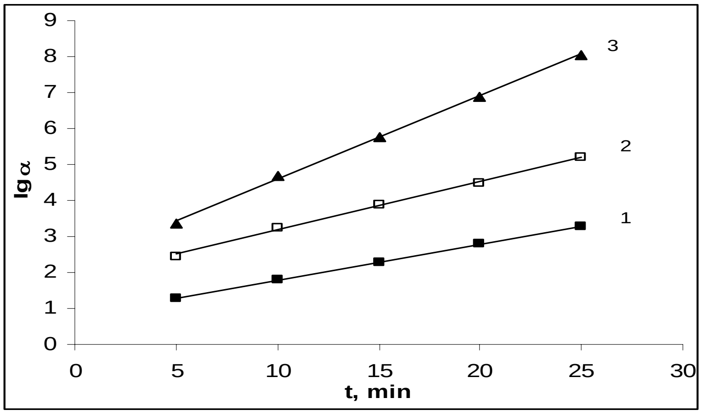

Figure 6. Plot of lgα versus time, at pH = 4.05, $[Ni^{2+}] = 2\ 10^{-3}$ mol/L, [ox] $= 10^{-2}$ mol/L, (1): T = 298 K, (2): T = 308 K, (3): 318 K.

The rate constant is calculated with the following equation:

$$k = \frac{0.693}{t_{1/2}} \qquad (2)$$

where: 0.693 is experimental constant, $t_{1/2}$ represents the time necessary to extract in organic phase 50% of nickel present in aqueous phase, and the experimental values of rate constant are summarized in Table 1.

Table 1. The values of rate constant for nickel extraction with oxine

No.	$[Ni^{2+}]$ (mol/L)	[ox] (mol/L)	pH	T (K)	$t_{1/2}$ (min)	k (1/min)
1.	0.002	0.01	3.00	288	21	0.0223
2.	0.002	0.01	3.00	298	20	0.0346
3.	0.002	0.01	3.00	308	7.5	0.0924
4.	0.002	0.01	3.36	288	21	0.0330
5.	0.02	0.01	3.36	298	7.5	0.0924
6.	0.02	0.01	3.36	308	3.0	0.2310
7.	0.02	0.01	4.05	288	15.6	0.0444
8.	0.02	0.01	4.05	298	6.0	0.1155
9.	0.02	0.01	4.05	308	2.2	0.3150

Considering that the substances which react are, at certain moment, as activated complex, the reaction rate is determined by crossing of activated complex from the point with maximum energy. In given conditions, can be also admitted that exist a concentration determined by activated complex which is in equilibrium with the initial reactant substances.

On the basis of these observations, the rate constant can be described using the following expression:

$$k = \frac{KT}{h}\exp\left(\frac{\Delta S^{\#}}{R}\right)\exp\left(-\frac{\Delta E^{\#}}{RT}\right);\ 1/\mathrm{min} \qquad (4)$$

where: K is Boltzmann constant, h is Planck constant, R is gas constant, $\Delta S^{\#}$ is the entropy of activated complex and $\Delta E^{\#}$ is the energy excess of activated complex, in comparison with the energy of reactant substances.

To establish a correlation between eq. (4) and Arhenius equation (eq. (5)):

$$k = A\exp\left(-\frac{\Delta E^{\#}_{ex}}{RT}\right);\ 1/\mathrm{min} \qquad (5)$$

is necessary that for the studied temperature range to exist a correspondence between those two equations.

Using equations (4) and (5) can be calculated the activation energy and activation entropy. The obtained values are presented in Table 2.

Table 2. The activation energy and entropy at different aqueous phase pH

pH	$\Delta E^{\#}_{ex}$ (cal/mol)	Dependence relation	$\Delta S_{20\ °C}^{\#}$ (cal/mol)
3.00	10132	$\Delta S^{\#} = -19.411 - 4.566 \lg T$	- 30.670
3.36	13908	$\Delta S^{\#} = -5.219 - 4.566 \lg T$	- 16.478
4.05	13981	$\Delta S^{\#} = -4.429 - 4.566 \lg T$	- 15.688

Conclusions

In this study the kinetics of nickel extraction with oxine in carbon tetrachloride have been investigated. The influence of several experimental parameters (pH, oxine concentration and temperature) on the nickel extraction rate was studied. The experimental results show that the extraction percent of nickel with oxine in carbon tetrachloride increases when the aqueous phase pH and system temperature increase. If considering that in the extraction process of nickel oxinate in carbon tetrachloride a transition state is formed which is in equilibrium with the reactant substances, on the basis of this hypothesis, the variation of activation energy and entropy was determined.

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