Dissolution Kinetics of Ulexite in Phosphoric Acid

MEHMET TUNÇ

Department of Chemistry, Faculty of Sciences, Yüzüncüyil University, Van, Turkey
Fax: (90)(432)2251114; Tel: (90)(432)2145135
E-mail: mtunc@yyu.edu.tr

In present study, the dissolution kinetics of ulexite in phosphoric acid was studied. The effects on the dissolution rate of particle size, temperature, acid concentration, solid-to-liquid ratio and stirring speed were experimentally investigated. It was determined that the dissolution rate increased with decreasing particle size and solid-to-liquid ratio and increasing reaction temperature. For acid concentrations up to 1 mol L^{-1}, dissolution rate increased with increasing acid concentration. For higher acid concentrations, the dissolution rate was decreased as acid concentration increased. No effect of stirring speed on the dissolution rate was observed. The dissolution kinetics of ulexite was examined taking into consideration the heterogeneous and homogeneous reaction models. The tests carried out by graphical and statistical methods were showed that the following models with chemical reaction control for two different concentration levels was best fitted to the experimental data.

$$1-(1-X)^{1/3} = [0.164.D^{-1.44}C^{0.92} (S/L)^{-1.41}e^{-34,196/RT}].t + 0.166 \text{ for } C \leq 1.M$$
$$1-(1-X)^{1/3} = [0.152.D^{-1.48}C^{-1.32} (S/L)^{-1.42}e^{-34,196/RT}].t + 0.176 \text{ for } 1.0 \text{ M} \leq C$$

Key Words: Ulexite, Dissolution kinetics, Phosphoric acid.

INTRODUCTION

Turkey has *ca.* 72 % of the world boron reserves. Boron is found as borates of metals, especially of calcium and/or sodium, in nature. Ulexite, one of the most common boron minerals, has a chemical formula of $Na_2O.2CaO.5B_2O_3 \cdot 16H_2O$[1]. It has a triclinic crystal system, usually in rounded masses of fine, transparent, white fibrous crystals (cotton balls) and in parallel fibrous aggregates. Commercially, the most commonly used compounds of boron are boric acid, boron oxide, sodium borates and perborates. Ulexite and colemanite are used as raw materials for the production of these compounds[2].

Boron compounds are widely employed in many branches of economy, for example in medicine fort the preparation of disinfectants and drugs, in the glass industry for the production of optic and chemically stable glass,

as components of enamels to increase hardness, for the protection of metals against oxidation during soldering, as additives to electrolytes in electro-chemical plating. Boron compounds are also used in the cosmetic, leather, textile, rubber and paint industries. They also find application in the wood-processing industry as a protection against molds.

In recent years the production of boron and its compounds has greatly increased, since it can be used in nuclear engineering, as fuel for rocket motors, in hard and refractory alloys, in high-quality steels, in boron-containing benzines, in the production of heat resistant polymers and also as catalysts[3].

There are many studies that have been performed on the dissolution of ulexite in the acidic aqueous solutions. Imamutdinova[4] studied the dissolution of ulexite in H_2SO_4, H_3PO_4, HNO_3 and HCl solutions. The dissolution process in these acidic solutions was determined to be diffusion controlled. Zdanovskii and Biktagirova[5] carried out a study of the dissolution of ulexite in H_3PO_4 solutions and found that acid mass fraction of 5 %, a solid film of H_3BO_3, formed on the ulexite crystals and the dissolution rate of this product restricted the dissolution rate of mineral. In the works on the dissolution of ulexite in aqueous SO_2 and CO_2 solutions, the dissolution process was found to be diffusion controlled in the case of CO_2 while it is chemical reaction-controlled in SO_2 solutions[6-9]. Imamutdinova *et al.*[10] investigated the disso-lution of ulexite in acetic acid solutions and found that the dissolution rate was maximum at relatively low acid concentrations (10-20 %) and over these concentrations the dissolution rate decreased with increasing acid concentration. Imamutdinova *et al.*[11] also investigated the dissolution of ulexite in perchloric acid solutions and determined that the dissolution was faster than that of HNO_3 solutions. Künkül *et al.*[12] studied the dissolution of ulexite in NH_3 solutions saturated with CO_2 and found that the dissolution kinetics could be expressed with a pseudo-homogenous first order reaction rate model. Tunç *et al.*[13] reported that the dissolution of ulexite in H_2SO_4 was controlled by the diffusion of H_3O^+ through the H_3BO_3 product layer and the by-product layer of $CaSO_4$ and/or $CaSO_4 \cdot 2H_2O$. Shevyakov *et al.*[14] proposed a kinetic mechanism for the dissolution of hydroboracite, colema-nite, ulexite and inderite in hydrochloric acid. Imamutdinova *et al.*[15] studied the dissolution kinetics of ulexite and sodium and potassium borates in nitric, sulfuric and phosphoric acids. Gülensoy *et al.*[16] investigated the effect of the thermal dehydration of some boron minerals on dissolution in aqueous media. Temur *et al.*[17] studied the kinetics of dissolution of colema-nite in H_3PO_4 solutions and observed that the dissolution rate increased with decreasing particle size and solid-to-liquid ratio and with increasing temperature, but stirring speed had no effect on it. The dissolution rate increased up to an acid concentration of 19.52 % (by wt) and then

decreased with increasing acid concentration and it was found that the dissolution rate was controlled by surface chemical reaction. Yesilyurt et al.[18] investigated determination of the optimum conditions for the dissolution of colemanite in H_3PO_4 solutions and found that the most significant parameters affecting the dissolution were the reaction time and particle size, whereas the acid concentration and stirring speed had a lesser effect. Tunç et al.[19] investigated the dissolution kinetics of ulexite in sulphuric acid solutions and determined that the dissolution rate increased with increasing reaction temperature and decreasing particle diameter, solid-liquid ratio and acid concentration, while no important effect of stirring speed was observed. It was found that the dissolution process was controlled by the diffusion of H_3O^+ ions to the mineral surface through the product and by-product layer. Alkan et al.[2] investigated the dissolution kinetics and mechanism of ulexite in oxalic acid solutions and found that the reaction rate was controlled by product-layer diffusion. In addition to these, there are many studies in different aqueous media containing various acids[20,21]. Küçük et al.[22,23] studied the optimization and dissolution kinetics of ulexite containing clay minerals in sulfur dioxide-saturated water and found that the dissolution rate was controlled by chemical reaction and the activation energy for the process was 49.87 kJ mol^{-1}.

Investigation of the dissolution conditions and the dissolution kinetics of ulexite in H_3PO_4 solutions will be beneficial to the solution of some problems encountered in the production of boric acid, such as decreasing reaction yield and filtration. For this reason, the aim of the present work is to study the reaction kinetics by taking into parameters such as particle size, solid to liquid ratio and stirring speed in addition to reaction temperature and acid concentration on the dissolution process.

EXPERIMENTAL

The ulexite mineral used in the study was obtained from the region of Bigadiç, Balikesir, Turkey. After the mineral had been manually cleaned of visible impurities, it was crushed, ground and sieved by ASTM standard sieves to obtain particle size fractions of 1.500 ± 0.850, 0.850 ± 0.600 and 0.600 ± 0.425 mm in diameter. The chemical analysis of ulexite showed that it contained 40.51 % B_2O_3, 13.94 % CaO, 7.36 % Na_2O, 35.55 % H_2O and 2.64 % others. X-Ray diffractogram of the sample is given Fig. 1.

The dissolution process was carried out in a 250 mL spherical glass vessel at atmospheric pressure. A mechanical stirrer was used for stirring the reactor contents and a thermostat for keeping the reaction medium at a desired constant temperature within ± 0.5 ºC. A back cooler for preventing liquid loss of the reactor content by evaporation was attached to the reactor. The parameters and their ranges used in the experiment are given in Table-1.
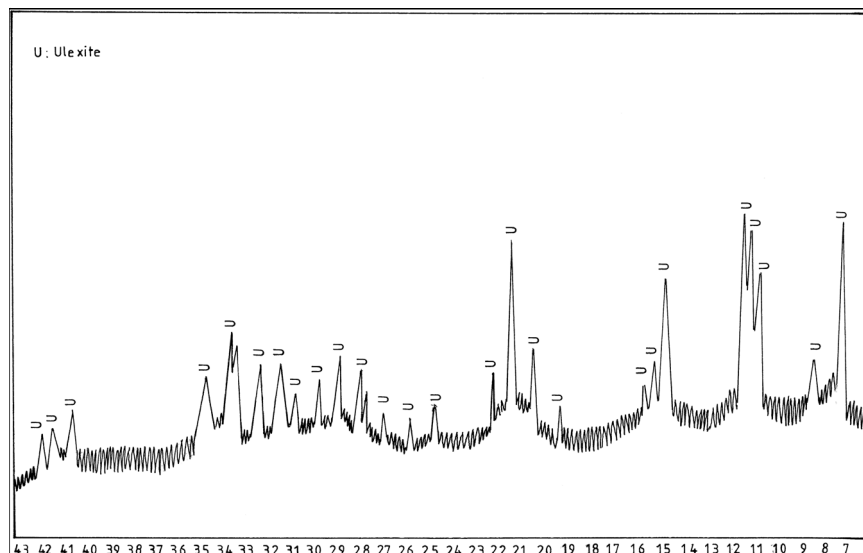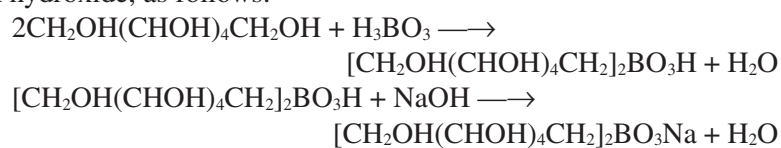
Fig. 1. X-ray diffractogram of the original ulexite mineral

TABLE-1
PARAMETERS AND THEIR RANGES USED IN THE EXPERIMENTS

Parameters	Values
Initial particle diameter (mm)	1.500 ± 0.850*, 0.850 ± 0.600, 0.600 ± 0.425
Initial acid concentration (mol L⁻¹)	0.15, 0.5, 1*, 2, 3
Reaction temperature (°C)	30*, 40, 50, 60
Solid-to-liquid Ratio (g mL⁻¹)	0.02*, 0.05, 0.08
Stirring speed (s⁻¹)	41.87*; 62.80, 83.73

*The constant value used when the effects of other parameters were investigated

After the reactor content containing 100 mL of phosphoric acid solution was heated to the reaction temperature, a known amount of the sample was added to the solution while stirring was maintained. The content of reactor was filtered as soon as the process finished and B_2O_3 in the solution was analyzed titrimetrically using a digital titrator. Since the aqueous solutions of boric acid have a weak acidic character, it can not be determined directly by titration with a basic solution. For this reason, the addition of mannitol into the solution gives a character of mild acid to boric acid, thus giving a facility of direct analysis of boric acid by a basic solution, such as sodium hydroxide, as follows:

$$2CH_2OH(CHOH)_4CH_2OH + H_3BO_3 \longrightarrow$$
$$[CH_2OH(CHOH)_4CH_2]_2BO_3H + H_2O$$
$$[CH_2OH(CHOH)_4CH_2]_2BO_3H + NaOH \longrightarrow$$
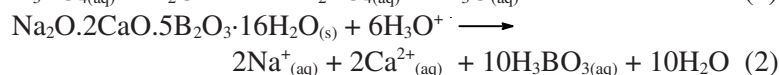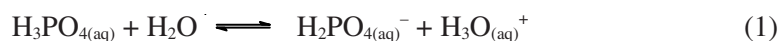$$[CH_2OH(CHOH)_4CH_2]_2BO_3Na + H_2O$$

The effect of each parameter on the dissolution process was investigated using their values given in Table-1. In the experiments, while the effect of a parameter was studied, the values of other parameters were kept constant at the values shown with asterisks in Table-1. The dissolution data obtained were plotted in the form of conversion fraction (X) *vs.* time, described as follows,
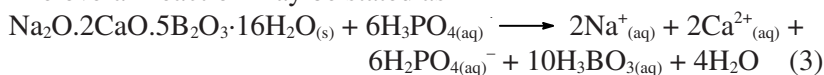
$$X = \frac{\text{the amount of B}_2\text{O}_3 \text{ passing to the solution from the original sample}}{\text{the amount of B}_2\text{O}_3 \text{ in original sample}}$$

RESULTS AND DISCUSSION

Dissolution reaction: It was measured that pH changed from 1.71 to 1.90 in a 20 min experiment with 0.5 M H$_3$PO$_4$ solution and from 1.38 to 1.55 in a 20 min experiment with 2.0 M H$_3$PO$_4$ solution. Only one proton of phosphoric acid dissociates in these pH levels. This means that when ulexite is added to a phosphoric acid solution, the following reactions take place.

$$\text{H}_3\text{PO}_{4(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_{4(aq)}^- + \text{H}_3\text{O}_{(aq)}^+ \qquad (1)$$

$$\text{Na}_2\text{O.2CaO.5B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}_{(s)} + 6\text{H}_3\text{O}^+ \longrightarrow$$
$$2\text{Na}^+_{(aq)} + 2\text{Ca}^{2+}_{(aq)} + 10\text{H}_3\text{BO}_{3(aq)} + 10\text{H}_2\text{O} \quad (2)$$

The overall reaction may be stated as

$$\text{Na}_2\text{O.2CaO.5B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}_{(s)} + 6\text{H}_3\text{PO}_{4(aq)} \longrightarrow 2\text{Na}^+_{(aq)} + 2\text{Ca}^{2+}_{(aq)} +$$
$$6\text{H}_2\text{PO}_{4(aq)}^- + 10\text{H}_3\text{BO}_{3(aq)} + 4\text{H}_2\text{O} \quad (3)$$

According to the overall equation, it is clear that the products are boric acid, sodium dihydrogen phosphate and calcium dihydrogen phosphate.

Effects of parameters: As seen in Fig. 2, the dissolution rate increased as the particle size decreased. This situation might be attributed to the increasing contact surface of the samples as the particle size decreased. The variation of the dissolution rate for various solid-to-liquid ratios is given in Fig. 3. This figure shows that decreasing solid-to-liquid ratios favour the dissolution process, which can be explained by the decrease in the amount of solid per amount of reagent in the reaction mixture. Fig. 4 shows that increasing reaction temperature has an increasing effect on the dissolution rate, as expected from the exponential dependence of the rate constant in the Arrhenius equation. The experimental results for the effect of stirring speed on the dissolution process are shown in Fig. 5. It is evident that the dissolution rate is practically independent of the stirring speed. The experiments for observing the effect of phosphoric acid concentration on the dissolution process showed that the dissolution rate increased with increasing acid concentration up to an acid concentration of 1 mol L^{-1} and further increase in acid concentration caused a decrease in the dissolution rate as seen in Fig. 6. This situation may be attributed to the fact that more

boric acid forms with increasing acid concentration, but it cannot diffuse to bulk solution through the reaction surface as fast enough. This causes a solid boric acid film to precipitate around the unreacted particle. The boric acid precipitation probably affects a rate-controlling mechanism after 1 mol L^{-1} acid concentration.
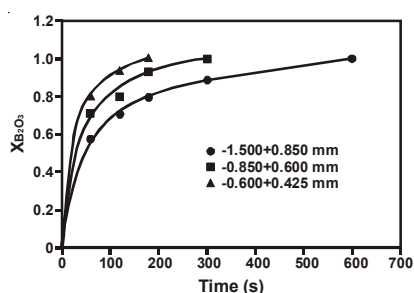

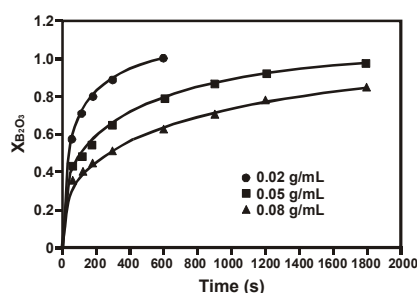Fig. 2. Effect of particle size on the dissolution ulexite (C, 1 mol L^{-1}; T, 30°C; S/L, 0.02 g mL^{-1} and W, 41.87 s^{-1})

Fig. 3. Effect of solid-to-liquid ratio on the dissolution of ulexite (C, 1 mol L^{-1}; T, 30 °C; D, 1.500±0.850 mm and W, 41.87 s^{-1})
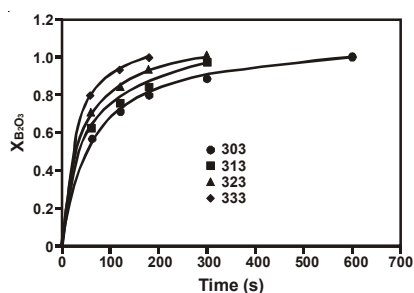

Fig. 4. Effect of temperature on the dissolution of ulexite (C, 1 mol L^{-1}; D, 1.500 ± 0.850 mm; S/L, 0.02 g mL^{-1} and W, 41.87 s^{-1})
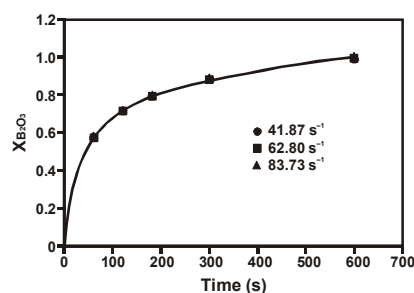

Fig. 5. Effect of stirring speed on the dissolution of ulexite (D, 1.500 ± 0.850 mm; T 30 °C; S/L, 0.02 g mL^{-1} and C, 1 mol L^{-1})

Kinetics: The rate of a non-catalytic solid-fluid reaction as $A_{(f)} + bB_{(s)}$ → product may be controlled by one of five successive resistances[24]: (I) Resistance to the passage of reactant through fluid film (Fluid film diffusion control) (II) Resistance to the passage of reactant through solid product film (Product film diffusion control) (III) Resistance to chemical reaction of reactant with solid on the surface of particle (Reaction control) (IV) Resistance to the passage of fluid product through solid product film (V) Resistance to the passage of fluid product through fluid film.

First three resistances are especially important and there is an integrated rate equation corresponding to each case, concerning also the particle geometry as follows:

$t/t^* = X$ for fluid film diffusion control (constant size flat plate, cylindrical and spherical particles)   (4)

$t/t^* = X^2$ for product film diffusion control (constant size flat plate particles)   (5)

$t/t^* = X$ for reaction control (constant size flat plate particles)   (6)

$t/t^* = X+(1-X)\ln(1-X)$ for product film diffusion control (constant size cylindrical particles)   (7)

$t/t^* = 1-3(1-X)^{2/3} + 2(1-X)$ for product film diffusion control (constant size spherical particles)   (8)

$t/t^* = 1-(1-X)^{1/2}$ for reaction control (constant size cylindrical particle)   (9)

$t/t^* = 1-(1-X)^{1/3}$ for reaction control (shrinking or constant size spherical particle)   (10)

$t/t^* = 1-(1-X)^{2/3}$ for fluid film diffusion control (shrinking small spherical particle)   (11)

The following pseudo homogenous models may also be applied to non-catalytic fluid-solid reactions:

$$-\ln(1-X) = kt \qquad (12)$$
$$X/1-X = kt \qquad (13)$$

All the above models were applied to experimental data for each temperature using a PC and R^2 values were determined for each model as seen in Table-2.

TABLE-2
INTEGRATED RATE EQUATIONS USED IN THE PROCESS, R^2 VALUES
FOR VARIOUS TEMPERATURES AND THEIR ESTIMATED
ACTIVATION ENERGIES

Eqn. No.	Models	R^2 for various temperatures				Activation energy (E) (KJ mol^{-1})
		303 K	313 K	323 K	333 K	
4, 6	$t/t^* = X$	0.9264	0.9855	0.9471	0.9832	21.21
5	$t/t^* = X^2$	0.9540	0.9951	0.9607	0.9880	24.25
7	$t/t^* = X+(1-X)\ln(1-X)$	0.9908	0.9995	0.9914	0.9997	28.63
8	$t/t^* = 1-3(1-X)^{2/3}+2(1-X)$	0.9992	0.9956	0.9998	0.9961	72.64
9	$t/t^* = 1-(1-X)^{1/2}$	0.9951	0.9994	0.9995	0.9964	31.08
10	$t/t^* = 1-(1-X)^{1/3}$	0.9968	0.9964	0.9953	0.9809	34.20
11	$t/t^* = 1-(1-X)^{2/3}$	0.9793	0.9985	0.9890	0.9998	25.98
12	$-\ln(1-X) = kt$	0.9589	0.9803	0.9439	0.9241	**
13	$X/1-X = kt$	0.9100	0.9140	0.8787	0.8664	**

**Because correlation coefficients were low, corresponding activation energies were not calculated; t = Reaction time (s); t* = Time for complete conversion (s); X = Fractional conversion.

Models 4, 5, 6, 12 and 13 were eliminated due to low R^2 values. Models 7, 8 and 11 were discarded because of the ineffectiveness of stirring speed and high activation energies. Models 9 and 10 had high R^2 and enough activation energy values. Model 10 was accepted to be the best fitted model although R^2 values reduced gradually as temperature increased. This case may be explained by the fact that increasing in temperature causes to increase in the reaction rate and the formation of a thicker boric acid film around the solid particle. For this model, $1-(1-X)^{1/3}$ *vs.* time (t) was given in Fig. 7.
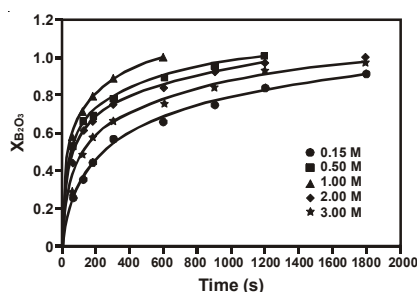

Fig. 6. Effect of acid concentration on the dissolution of ulexite (D, 1.500 ± 0.850 mm; T, 30 °C; S/L, 0.02 g mL^{-1} and W, 41.87 s^{-1})
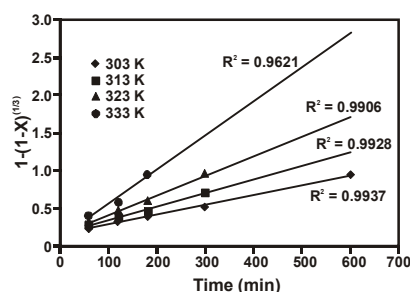
Fig. 7. Graph of $1-(1-X)^{1/3}$ *vs.* t for various temperatures

On the other hand, because dissolution of ulexite increased with acid concentration up to 1.0 M and decreased with higher acid concentrations, two models were derived for these concentration ranges, also containing effects of other parameters statistically using a PC, as follows:

$$1-(1-X)^{1/3} = [0.164 \cdot D^{-1.44} C^{0.92} (S/L)^{-1.41} e^{-34.20/RT}] \cdot t + 0.166 \text{ for } C \leq 1.M \quad (13)$$

$$1-(1-X)^{1/3} = [0.152 \cdot D^{-1.48} C^{-1.32} (S/L)^{-1.42} e^{-34.20/RT}] \cdot t + 0.176 \text{ for } 1.0 \text{ M} \leq C \quad (14)$$

where X = Fractional conversion; D = Mean particle size (mm); S = Amount of solid (g); L = Amount of liquid (mL).

In addition to effectiveness of stirring speed and the value of activation energy, two plots in Figs. 8 and 9 drawn using X values from the models *vs.* experimental X showed that chosen models were suitable.

Conclusion

In this study, the dissolution of ulexite in phosphoric acid solutions was investigated using the parameters such as particle size, acid concentration, solid to liquid ratio, stirring speed and temperature. As the result, decreasing the particle size and solid to liquid ratio, increasing temperature increased the dissolution rate. Stirring speed was not effective on the dissolution. The dissolution rate increased up to 1.0 M of acid concentrations
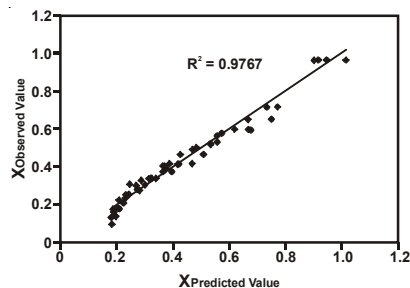
Fig. 8.   Graph of $X_{Observed\ Value}$ vs. $X_{Predicted\ Value}$ for eqn. 13
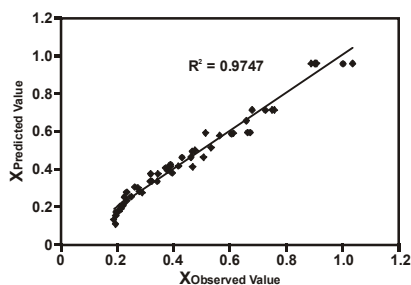
Fig. 9.   Graph of $X_{Observed\ Value}$ vs. $X_{Predicted\ Value}$ for eqn. 14

but decreased in higher concentrations than 1.0 M. This process was determined to be chemical reaction controlled and a model with activation energy of 34.20 kJ mol^{-1} was derived for each concentration range.

This process is more advantageous than well known processes in which boric acid was produced from ulexite. In the present industrially applied process, ulexite reacts with sulphuric acid and by-products are sodium sulphate and gypsum which are not valuable. By-products of this process are primary calcium and sodium phosphates. Primary calcium phosphate is used as fertilizer, stabilizer for plastics, in glass manufacture and food industry and primary sodium phosphate in water treatment, electroplating, dyeing, food industry. For this reason, it may be expressed that this process has also the advantage of protecting the environment and is preferable to present boric acid process from ulexite.

ACKNOWLEDGEMENT

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