KINETIC MODELING OF CHROMIUM(III) EXTRACTION WITH ALIQUAT 336 FROM ALKALINE AQUEOUS SOLUTIONS CONTAINING CHLORIDES

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Abstract: The effects of time, composition and history of preparation of the aqueous phase on the liquid-liquid extraction of chromium(III) with Aliquat 336 from the aqueous alkaline solutions containing chlorides were studied. At time far from the equilibrium the yield and initial rate of the chromium(III) extraction depend on NaOH concentration, ionic strength of the aqueous phase and the way of its preparation. At the constant composition of the feed solution, rate of the Cr(III) extraction in approach to the equilibrium is higher when chromium(III) is extracted from the alkaline aqueous phase freshly prepared by direct dissolution of a weighted sample of $CrCl_3$ than from that obtained by dilution of aged stock solution of $CrCl_3$. Kinetic analysis by the mathematical models showed that within the whole period of time needed to reach the equilibrium, the rate of the Cr(III) extraction is limited by the second-, and third-order chemical reaction towards Cr(III), irrespective of composition and preparation history of the aqueous phase. The three-dimensional diffusion and chemical reaction at phase boundary substrate-product (the contracting volume) models have a significant effect on the chromium(III) extraction within the initial extent of the process.

Introduction

Different industrial processes apply chromium compounds as dyes, paint pigments, for metal plating and in the leather processing as a tanning agent. In such industrial processes, besides the final products, various wastes containing chromium compounds are generated. Chromium(III) basic sulfate is the most frequently and widely applied as a tanning agent in the leather industry because it allows to produce leathers of very high quality. However, many chemical and mechanical operations (chromium tanning, splitting and shaving of chromium-tanned leathers), which are made during processing of raw animal hides/skins into finished leathers, generate large quantities of liquid and solid wastes containing chromium(III).

   Total quantities of these wastes depend on applied technology and on type of leathers produced. Generally, solid tannery wastes containing chromium(III) can constitute from 18 to 57% of the total amount of all solid wastes produced by tanneries. About 40% of Cr(III) compounds, which were not uptaken by hides during tanning operation, remain in spent tanning liquors and these baths are the main source of chromium(III) in tannery effluents. Such wastes create an environmental hazard and moreover, a risk for the human health when they are inadequately treated and/or discharged without purification into the landfill or rivers. It is known that the trace quantities of chromium(III) are needed for the proper functioning of the human organism (Senczuk, 1999; Indulski, 1992). However, oxidation of chromium(III) to carcinogenic chromium(VI) in surface water and soils under favourable conditions (acid rains and the presence of some oxidants like MnO_2) should be taken into account (Kabata-Pendias and Pendias, 1993; Ciszewski and Baraniak, 2006; Apte et al., 2005). Besides, in the natural environment interconversion $Cr(III) \Leftrightarrow Cr(VI)$ is observed and controlled by different factors, e.g. concentration and kind of chromium species, presence of oxidizing or reducing agents, electrochemical potentials of oxidation and reduction reactions, pH, ambient temperature, light, presence of complexing agents (Kimbrough et al., 1999).

   A worldwide legislation exists on chromium limits for discharge of tannery effluents into water bodies and sewers (Bosnic et al., 2000). Many of these regulations distinguish between the limit of chromium(III) and chromium(VI) compounds. However, generally, the typical limit for total chromium concentration in tannery effluents is within the range 2–4 mg/dm^3 (Gauglhofer, 1991; Bosnic et al., 2000).

   The recovery of chromium(III) from the tannery effluents and wastes is justifiable both ecologically and economically. First of all, it reduces a risk of contamination of environment by compounds of chromium. Second, such activities may prevent loses of chromium compounds which could be reused in other industrial processes.

   From literature data it comes that various methods have been examined for removing and recovering of chromium(III) compounds from aqueous solutions and tannery floats/wastewaters. These methods are based on adsorption (Liu et al., 2010; Papandreou et al., 2011), biosorption (Karaoglu et al., 2010; Sundar et al., 2011), ion exchange (Gode and Pehlivan, 2006), and various membrane techniques such as ultrafiltration (Korus and Loska, 2009; Labanda et al., 2009), micellar enhanced ultrafiltration (Auodia et al., 2003), nanofiltration (Religa et al., 2011), reverse osmosis (Hintermeyer et al., 2008) and transport through the bulk, supported, emulsion and polymer inclusion liquid membranes with application of various carriers (Gawronski and Religa, 2007; Buonomenna, 2006; Ochromowicz and Apostoluk, 2010; Alguacil et al., 2009; Konczyk et al., 2010).

   One of the most efficient methods for concentration and separation of different metal species including chromium is the liquid-liquid extraction which is economically feasible when flow rates are high and concentrations of contaminants are greater than 0.5 g/dm^3 (Kentish and Stevens, 2001).

Studies described earlier in literature, concerning the liquid-liquid extraction of Cr(III), indicate that both cationic and anionic species of chromium(III) (formed with ethylenediaminetetraacetic acid (EDTA)) are extracted mainly from acidic and neutral aqueous solutions with acidic extractants (Apostoluk and Bartecki, 1985; Islam and Biswas, 1979; Pandey et al., 1996) and with trioctylmethylammonium chloride (Aliquat 336) (Irving and Al-Jarrah, 1973). Wionczyk and Apostoluk (2004a; b) have showed for the first time that quaternary ammonium compounds effectively extract anionic hydroxocomplexes of chromium(III) which can be formed in the model alkaline solutions prepared from an aged stock solution of $KCr(SO_4)_2$ and NaOH. Wionczyk and co-workers (Wionczyk and Apostoluk, 2005; Wionczyk, 2009) have determined the effects of various parameters and electrolytes on the chromium(III) extraction. This method was examined for the removal of chromium(III) from some industrial spent tanning liquors (Wionczyk et al., 2006) and from protein hydrolyzate obtained by alkaline hydrolysis of wastes of chromium-tanned leathers (Wionczyk et al., 2011a; 2011b).

From the other side, taking into account available literature data, it can be found out that the extraction of chromium(III) from alkaline media is a problem still recognized very scarcely and it is also interesting and important issue with an environmental studies approach.

Recently, Wionczyk et al. (2011c) have reported studies on the kinetics and equilibria of the liquid-liquid extraction of chromium(III) with Aliquat 336 from alkaline aqueous solutions, containing anions of various complexing abilities and hydration properties, which were freshly prepared by dilution of the aged stock aqueous solutions of various chromium(III) salts (nitrates, perchlorates, or sulfates).

Consequently, as a development of the all investigations mentioned above, in this paper the studies are reported on the liquid-liquid extraction of chromium(III) with Aliquat 336 from alkaline solutions containing chloride ions. The effects of extraction time, composition and history of preparation of the aqueous phases (directly from weighted sample of $CrCl_3$ or by dilution of aged solution of $CrCl_3$) are presented. The kinetic models with application of mathematical rate equations and a discussion on the estimation of factors limiting the chromium(III) extraction under examined conditions are given. Moreover, results described in this paper are compared with those reported recently by Wionczyk et al. (2011c).

Experimental

Reagents

The initial aqueous phases were freshly prepared alkaline solutions of composition: chromium(III) – 0.005 mol/dm^3, sodium hydroxide – 0.3 mol/dm^3 or 0.5 mol/dm^3, chloride ions – 0.015 mol/dm^3. These aqueous phases were prepared immediately before the extraction in the following two different ways: (WS) – by direct dissolution of a weighted sample of $CrCl_3 \cdot 6H_2O$ and appropriate alkalization with

NaOH; (AQ) – by direct dilution and alkalization of the aged (for several months) stock aqueous solution of chromium(III) chloride. All compounds with high purity were obtained from POCh (Poland). Distilled water was used in the studies.

Solution of Aliquat 336 (90% of trioctylmethylammonium chloride, for synthesis Merck-Schuchardt) in heptane (p.a., Chempur, Poland) at concentration 0.05 mol/dm^3 modified with 1% (v/v) of 1-decanol (>99% for synthesis, Merck-Schuchardt) was used as the initial organic phase.

Extraction of chromium(III)

The equal volumes of the aqueous and organic phases were shaken mechanically in thermostatic water bath shaker type Elpin 357 (Poland) with constant speed (140 rpm) at constant temperature (25 ± 0.5 ºC) for appropriate period of time varying within the range from 0.5 to 360 minutes. Then, the phases were transferred to separation funnels and were left to clarify and separate for 3 h.

The distribution of chromium(III) in both phases was determined spectro-photometrically with 1,5-diphenylcarbazide after oxidation of Cr(III) to Cr(VI). The concentration of chlorides in the aqueous phase was estimated by Volhard's method.

Kinetic models and calculations

The studies on the kinetics of heterogeneous processes can be carried out using the isothermal method in which observations of an extent of process/reaction (α) within a period of time (t), are made at constant temperature. In general, this method is more appropriate for kinetic analysis of the slowest processes and is based on the determination of a rate equation according to the mathematical model which the most precisely explains the systematic changes of α with time and describes mechanism of process/reaction. Values of α vary from 0 at the beginning of process to 1 when it is over.

An extent/progress of the chromium(III) extraction in the presented system was measured by dimensionless fraction (α) of Cr(III) extracted to the organic phase after any period of the extraction time and it was as follows:

$$\alpha = \frac{c_o^t}{c_a^0} \tag{1}$$

where c_a^0 stands for initial concentration of chromium(III) in the aqueous phase at the beginning of process and c_o^t denotes concentration of chromium(III) extracted to the organic phase at time t of the process duration. The yield of chromium(III) extraction (%E) from the aqueous to the organic phase was calculated as follows:

$$\%E = \alpha \cdot 100. \tag{2}$$

The rate of heterogeneous process under conditions far from the equilibrium can be kinetically described by the following general equation in the differential form (Perez-Maqueda et al., 2005):

$$\frac{d\alpha}{dt} = k_T \cdot f(\alpha) \tag{3}$$

where k_T is temperature-dependent rate constant, f(α)a term describing the relation between the rate of process/reaction and its mechanism.

After introduction to Eq. (3) of the following designation

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) \tag{4}$$

the total integral form of Eq. (3) is:

$$g(\alpha) = k_T \cdot t. \tag{5}$$

The various rate equations (kinetic models) describing the mechanism of a heterogeneous process are proposed in literature (Galwey and Brown, 1998). Some of the integral forms of the rate equations, which were selected for the kinetic analysis of the experimental results received in the examined extraction system, are specified in Table 1.

Table 1. Some of the most important rate equations (models) proposed for kinetic analysis of heterogeneous processes (Galwey and Brown, 1998)

Kind of kinetic model	Symbol	Mechanism	Integral form $g(\alpha) = k_T \cdot t$
Geometrical models	R2	phase boundary controlled reaction (contracting area)	$1 - \sqrt{(1-\alpha)}$
	R3	phase boundary controlled reaction (contracting volume)	$1 - \sqrt[3]{(1-\alpha)}$
Diffusion models	D1	one-dimensional diffusion	α^2
	D2	two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha) + \alpha$
	D3	three-dimensional diffusion (Jander equation)	$[1 - (1-\alpha)^{1/3}]^2$
	D4	three-dimensional diffusion (Ginstling-Brounshtein equation)	$[1 - (2\alpha \cdot 3^{-1})] - (1-\alpha)^{2/3}$
'Order of reaction' models	F1/ A1	first order /Avrami-Erofeev equation, n = 1	$-\ln(1-\alpha)$
	F2	second order	$(1-\alpha)^{-1} - 1$
	F3	third order	$(1-\alpha)^{-2} - 1$

Results and discussion

The effect of extraction time, composition and history of preparation of the aqueous phase

The relationships between the yield of chromium(III) extraction and the contact time of phases (aqueous and organic) for various composition and history of preparation of the initial aqueous phase (WS or AQ methods given in 2.1.) in the tested system are showed in Fig. 1. They indicate that an elongation of extraction time and reduction of NaOH concentration in the initial aqueous phase from 0.5 mol/dm^3 to 0.3 mol/dm^3 affect positively the extraction of chromium(III) from the alkaline aqueous solutions of chlorides, irrespective of the mode of preparation of the feed aqueous solutions. Namely, at 0.3 mol/dm^3 of NaOH in the aqueous phase, chromium(III) is extracted almost completely with the high yield equal to 98-99% after 2 hours, while at 0.5 mol/dm^3 of sodium hydroxide, the extraction of chromium(III) attains the maximum 89–90% only after 5 hours of the phase contact. The lower concentration of NaOH in the aqueous phase the shorter time is needed to achieve the equilibrium of the chromium(III) extraction under examined conditions. The negative effect of the increasing concentration of NaOH on the efficiency of Cr(III) extraction from the alkaline chloride solutions is attributed to the negative influence of the ionic strength of the aqueous phase as it can be expected according to the findings of our previous studies (Wionczyk and Apostoluk, 2005; Wionczyk, 2009).
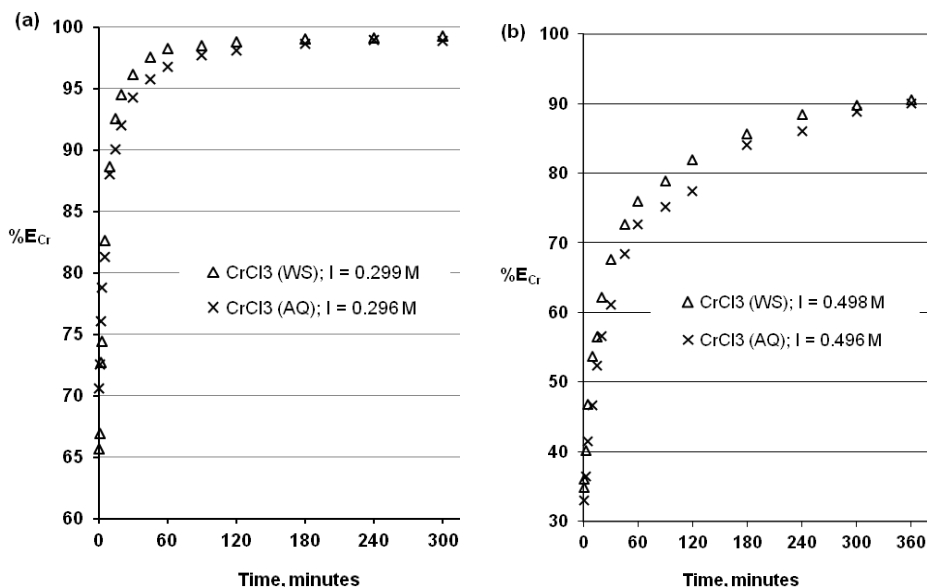

Fig. 1. Effect of time and preparation history (WS and AQ) of the initial aqueous phases on the extraction of Cr(III) (%E) from the aqueous solutions of chlorides in: (a) 0.3 M; (b) 0.5 M NaOH. I – denotes the initial ionic strength of the aqueous phase

The results given in Fig. 1 shows that extraction of chromium(III) in the studied system depends also on the history of preparation of the initial aqueous phases (WS or AQ). Namely, at constant contact time of phases and at constant initial composition of the aqueous phase, the yield of extraction of Cr(III) from the fresh aqueous alkaline solution prepared from sample of CrCl$_3$·6H$_2$O (WS) is slightly higher than this from the diluted aged stock solution of chromium(III) chloride (AQ). However, these differences between Cr(III) extraction are observed only at the time far from the equilibrium of extraction. It means that yield of chromium(III) extraction depends on the way of preparation of the feed alkaline aqueous solution (WS or AQ). It may be discussed in terms of different Cr(III) complex species which can be present in the fresh and/or aged aqueous solutions of chromium(III) chlorides. The percent of Cr(III) extraction at the equilibrium is constant and its value does not depend on the history of preparation of the initial aqueous phase.

The rate of chromium(III) extraction in an approach to the equilibrium state

Depending on the possibilities of hydrodynamic control of an examined extraction system, different techniques used for determination of the rate of the extraction of an individual component can be divided as follows:

- methods in which measurements are made at constant interfacial area of the organic and aqueous phases, e.g. the method using a modified Lewis cell,
- methods in which there is a lack of the constant interfacial area because both organic and aqueous phases are vigorously mixed which leads to their mutual dispersion.

In the present work all experiments concerning the effect of time on the chromium(III) extraction were made under constant processing conditions (temperature, volume ratio of phases, shaking speed of phases, time of phase separation). Then, the results of those experiments were treated in accordance with the one of the methods for determination of the rate of liquid-liquid extraction in which interfacial area of aqueous and organic phases is not constant.

The liquid-liquid extraction is a complex process consisting of various chemical reactions and several processes, e.g. diffusion, mass transfer and distribution. Its total rate is limited by the rate of its slowest stage. A total equilibrium of the extraction can be described by one general equation at the assumption that side reactions do not proceed in the aqueous and organic phases. Then, like the velocity of an elementary chemical reaction, the rate of the extraction of component can be determined by the measurements of changes of its concentration in a unit of time at constant temperature.

Consequently, by analogy to the elementary chemical reaction, the integral forms of the first-order ($\ln c_{Cr_a} = k_1 t$) and the second-order ($1/c_{Cr_a} = k_2 t$) kinetic equations, usually used to define the order of a chemical reaction (Jones and Atkins, 2009), were applied to examine which of the kinetic relations precisely describes the changes of chromium(III) concentration in the aqueous phase (c_{Cr_a}) with time (t) during progress of the Cr(III) extraction. The fits of the experimental data obtained from the studies on

the extraction of chromium(III) with Aliquat 336 under the all tested conditions to these first-order and second-order kinetic equations are graphically demonstrated in Fig. 2a, b.
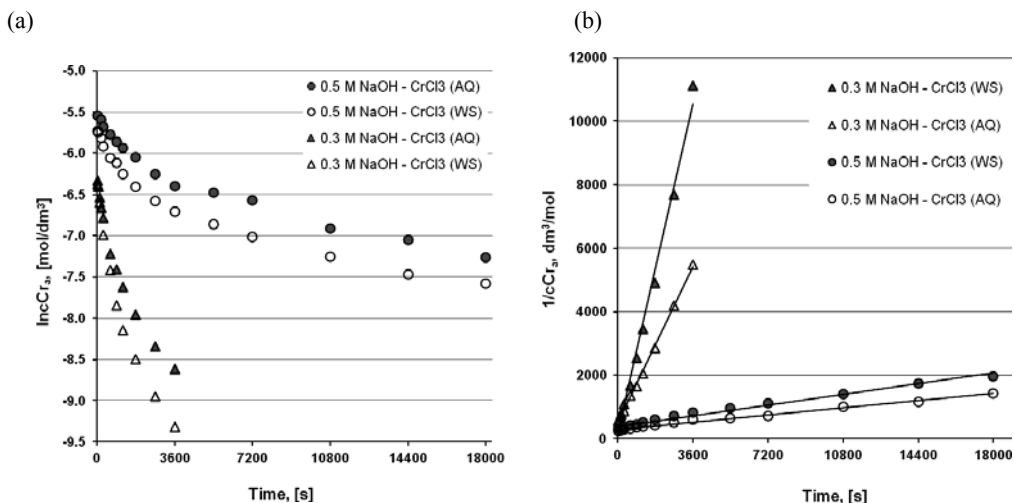
(a)   (b)

Fig. 2. The fits of experimental data to (a) the first-order, (b) the second-order kinetic equations determined in the systems $CrCl_3$-NaOH-0.05 M Aliquat 336 with the aqueous phases of various compositions and history of preparation (WS and AQ)

From Fig. 2a, it is evident that under each studied conditions the experimental points deviate from straight lines of the kinetic relation $\ln c_{Cr_a} = k_1 t$ within the whole periods of time needed to attain the equilibrium of chromium(III) extraction. Then, it may be supposed that at time far from the equilibrium, the rate of the extraction of chromium(III) in the tested system cannot be expressed by the first-order kinetic equation. However, for the extraction of Cr(III) from the aqueous phases at 0.5 mol/dm³ of NaOH, it is possible to find such range of the extraction time, 0.5-30 minutes, within which more than three experimental points will be well fitted to this kinetic equation giving the linear dependence. At concentration of NaOH equal to 0.3 mol/dm³, it is difficult to select such range of the initial extraction time within which more than three experimental points will be precisely fitted to the dependence $\ln c_{Cr_a} = k_1 \cdot t$. Moreover, it should be noted that after 30 seconds of the phase contact, which corresponds to the first experimental points in Fig. 1, the yield of extraction of chromium(III) from the feed chloride solution at 0.3 mol/dm³ of NaOH exceeds 65%, irrespective of the way of preparation of the aqueous phases. Then, to test of linearity of the relation $\ln c_{Cr_a} = k_1 \cdot t$ in the system with lower concentration of NaOH, several experimental points should be obtained at the initial extraction time shorter than 30 seconds. However, this is practically impossible under the applied experimental conditions.

From Fig. 2b it comes that within the periods of time (60 and 300 minutes) which are necessary to reach the equilibrium of extraction, the changes of reciprocal of Cr(III) concentration in the aqueous phases with time of the extraction create precisely the linear dependences typical for the second-order kinetic equation ($1/c_{Cr_a} = k_2 t$). These straight lines are characterized by various slopes (k_2) which depend on the concentration of NaOH and on the preparation history of the alkaline Cr(III) feed solutions. Equations of the straight lines plotted in Fig. 2b, and consequently, the values of their slopes (k_2) were determined using the method of regression analysis. Moreover, the quality of mathematical fit of the experimental data to the second-order kinetic relationship ($1/c_{Cr_a} = k_2 \cdot t$) was evaluated applying the statistical criteria (determination coefficient R^2; standard deviation of estimate and of the slope of regression line S.D.; Fisher-Snedecor test function F). Those parameters and values of slopes (k_2) of the straight lines (in Fig. 2b), which correspond to the rate constants of the chromium(III) extraction under each examined conditions, are given in Table 2. The number of experimental points, N, and the ranges of the extraction time, within which the kinetic equation was tested, are also specified in this Table.

The values of statistical criteria (Table 2) reveal that the all relations ($1/c_{Cr_a} = k_2 t$) presented in Fig. 2b are of very good statistical quality. Then, it can be accepted that the rate of the extraction of chromium(III) with Aliquat 336 from the alkaline aqueous solution containing chlorides may be described by the second-order kinetic equation towards Cr(III), irrespective of the initial concentration of NaOH and on the way of preparation of the aqueous phases. Values of the rate constants (k_2) prove that chromium(III) is extracted with the highest rate from the feed aqueous solution prepared directly from the sample of $CrCl_3 \cdot 6H_2O$ (WS) at 0.3 mol/dm^3 of NaOH. Moreover, the rate constant (2.96 dm^{3}mol^{-1}s^{-1}) determined under these conditions is about twice higher than that (1.37 dm^{3}mol^{-1}s^{-1}) established for the aqueous phase prepared by dilution of the aged stock solution of $CrCl_3$ (AQ). From Table 2 it also comes that the effect of the way of preparation of the feed aqueous solution (WS or AQ) on the rate of chromium(III) extraction at higher concentration of NaOH is already lower though the velocity of the Cr(III) extraction in the system with the aqueous phase obtained directly from the sample of $CrCl_3 \cdot 6H_2O$ (WS) is still higher.

Taking these findings into account it can be accepted that the observed differences (Table 2) between the rate of the extraction of chromium(III) from the aqueous alkaline solutions containing chlorides may be attributed to the various kind of complexes of chromium(III) which are probably present in the aqueous phases of different concentration of NaOH and history of their preparation (WS or AQ).

Table 2. The rate constants (k_2) and their statistical assessment determined from the second-order kinetic equation, $1/c_{Cr_a} = k_2 t$, (Jones and Atkins, 2009) for the extraction of chromium(III) in the studied system CrCl$_3$ – NaOH – Aliquat 336 with the aqueous phases of different composition and history of preparation (WS or AQ). The statistical symbols are explained in text

c_{NaOH}^0, mol/dm^3	History of preparation of the aqueous phase	($k_2 \pm$ S.D.), dm^{3}mol^{-1}s^{-1}	R^2	S.D.	F	N	Range of the extraction time, min
0.3	CrCl$_3$ (WS)	2.958 ± 0.067	0.9948	345	1933	11	0.5–60
0.3	CrCl$_3$ (AQ)	1.369 ± 0.017	0.9984	65	6325	11	0.5–60
0.5	CrCl$_3$ (WS)	0.093 ± 0.003	0.9845	67	889	15	0.5–300
0.5	CrCl$_3$ (AQ)	0.063 ± 0.002	0.9888	39	1151	14	0.5–300

The results received in our previous typical extraction studies (Wionczyk et al., 2011c) were taken to compare the effect of different kind of anions (sulphates, nitrates, perchlorates, and chlorides) on the rate of the extraction of chromium(III) in the systems with Aliquat 336 from the alkaline aqueous phases freshly prepared by dilution of the aged stock solutions of different chromium(III) salts (KCr(SO$_4$)$_2$, Cr(NO$_3$)$_3$, Cr(ClO$_4$)$_3$, and CrCl$_3$). The experiments relating to the effect of time on the Cr(III) extraction were carried out in our previous (Wionczyk et al., 2011c) and present studies under the same conditions. Consequently, the quality of fitting of the results obtained previously in work Wionczyk et al. (2011c) to the relation $1/c_{Cr_a} = k_2 t$ and the rate constants (k_2) for those earlier examined systems were determined. The all values of the rate constant (k_2) established from the second-order kinetic equations ($1/c_{Cr_a} = k_2 t$) in the extraction systems with sulphates, nitrates, perchlorates, and chlorides as well as their statistical criteria are presented in Table 3.

From Table 3 it is evident that at concentration of NaOH equal to 0.5 mol/dm^3, the rate of the chromium(III) extraction in the examined systems depends on the type of anions present in the aqueous phases and increases according to the increasing negative values of free energy of hydration of tested anions. However, at 0.3 mol/dm^3 of NaOH, the rate of chromium(III) extraction increases in the other sequence of anions. Namely, under these conditions, the extraction of Cr(III) in the system with chlorides ($\Delta G_{hydr} = -346$ kJ/mol, Marcus, 2004) reached the equilibrium faster than in the system with sulfates, i.e. anions of higher free energy of hydration ($\Delta G_{hydr} = -1090$ kJ/mol, Marcus, 2004).

That effect of anions (Table 3) may be discussed in term of the different kind of Cr(III) complexes which could form in the alkaline aqueous phases in the presence of examined anions. On the other hand, the aggregation of Aliquat 336 (Vandegrift et al., 1980; Wionczyk and Apostoluk, 2005; Oliveira and Bertazzoli, 2007), and consequently, the formation of emulsion in the studied extraction system may be taken into account. As it is known, quaternary ammonium salts aggregate and interact with molecules of solvent in aqueous and non-aqueous solution to form association colloid

such as micelles and microemulsions (Jakubowska, 2012a). Moreover, from literature data it follows that anions of the lyotropic (Hofmeister) series, dependently on their position in that sequence, affect strongly micellization, micellar structure, micellar transitions, and micellar growth of the surfactants (Abezgauz et al., 2010; Muller et al., 2013; Jakubowska, 2012b).

Table 3. The rate constants (k_2) determined from the second-order kinetic equation ($1/c_{Cr_a} = k_2 t$) for the extraction of chromium(III) with Aliquat 336 from the alkaline aqueous phases prepared by dilution of the aged solutions of different Cr(III) salts. Values of k_2 for the Cr(III) extraction in the systems with sulfates, nitrates, and perchlorates were established on the base of results obtained by Wionczyk et al. (2011c)

c_{NaOH}^0, mol/dm^3	Anions present in the aqueous phase	($k_2 \pm$ S.D.), dm^{3}mol^{-1}s^{-1}	R^2	S.D.	F	N	Range of extraction time, min	ΔG_{hydr}, kJ/mol (Marcus, 2004)
0.3	ClO_4^-	0.571 ± 0.022	0.9911	65	672	7	5–60	–214
0.3	NO_3^-	0.811 ± 0.041	0.9852	119	401	7	5–60	–306
0.3	SO_4^{2-}	1.037 ± 0.059	0.9906	121	634	7	5–60	–1090
0.3	Cl^-	1.369 ± 0.017	0.9984	65	6325	11	0.5–60	–347
0.5	ClO_4^-	0.040 ± 0.001	0.9915	23	1165	11	5–300	–214
0.5	NO_3^-	0.044 ± 0.001	0.9897	27	1056	12	5–300	–306
0.5	Cl^-	0.063 ± 0.002	0.9888	39	1151	14	0.5–300	–347
0.5	SO_4^{2-}	0.118 ± 0.002	0.9964	44	2770	11	5–300	–1090
0.5	ClO_4^-	0.043 ± 0.003	0.9728	9	215	7	5–60	–214
0.5	NO_3^-	0.053 ± 0.002	0.9880	7	494	7	5–60	–306
0.5	Cl^-	0.095 ± 0.002	0.9971	6	2707	9	0.5–60	–347
0.5	SO_4^{2-}	0.142 ± 0.005	0.9922	15	768	7	5–60	–1090

Kinetic modeling of the extraction of chromium(III) from the aqueous alkaline phases containing chlorides

In order to examine the correctness of the findings in Section 3.2. (the rate of the extraction of chromium(III) under studied conditions can be expressed by the kinetic equation of the second-order chemical reaction and also to estimate some factors limiting the extraction rate) the kinetic models (Table 1) used usually for the kinetic analysis of heterogeneous processes were applied to these aims.

The quality of mathematical fit of the experimental data received in the studied extraction system with CrCl$_3$, NaOH and Aliquat 336 to the integral forms, g(α), of the each geometrical (R2, R3), diffusion (D1-D4) and the order of chemical reaction (F1-F3) kinetic models was examined using the method of multiple regression

analysis. Values of statistical parameters (R^2, S.D., F) were used as a measure of precision of the fitting of the obtained results to the each of kinetic models given in Table 1.

Table 4. Fittings of α-time experimental data to the selected kinetic models (given in Table 1)
for the extraction system 0.005 M $CrCl_3$ – 0.3 M NaOH – 0.05 M Aliquat 336,
with the aqueous phases of different history of preparation

Model	Alkaline aqueous phase from							
	Sample of $CrCl_3$ (WS) $\alpha = 0.657–0.983$ $t = 0.5–60$ minutes				Aged solution of $CrCl_3$ (AQ) $\alpha = 0.706–0.968$ $t = 0.5–60$ minutes			
	$(k_T \pm$ S.D.$)10^{-3}$ [s^{-1}]	R^2	F	N	$(k_T \pm$ S.D.$)10^{-3}$ [s^{-1}]	R^2	F	N
R2	0.127 ± 0.022	0.7540	32	11	0.099 ± 0.016	0.8002	41	11
R3	0.125 ± 0.019	0.8037	42	11	0.096 ± 0.013	0.8364	52	11
D1	0.144 ± 0.032	0.6515	20	11	0.117 ± 0.022	0.7215	27	11
D2	0.175 ± 0.032	0.7371	29	11	0.141 ± 0.022	0.7919	39	11
D3	0.134 ± 0.016	0.8797	74	11	0.100 ± 0.011	0.8962	87	11
D4	0.059 ± 0.010	0.7900	39	11	0.046 ± 0.007	0.8314	50	11
F1	0.861 ± 0.092	0.8965	88	11	0.620 ± 0.064	0.9026	94	11
F2	15.23 ± 0.31	0.9959	2446	11	7.622 ± 0.007	0.9992	13061	11
F3	715.8 ± 85.0	0.8764	71	11	219.9 ± 15.4	0.9535	205	11

The rate constants (k_T) and statistical criteria determined for the studied extraction system with the aqueous phases prepared in the different ways (WS or AQ) from $CrCl_3$ and NaOH at concentration equal to 0.3 mol/dm^3 and to 0.5 mol/dm^3 are given in Tables 4 and 5, respectively. The ranges of α and periods of the extraction time within which the kinetic models were tested are also given in Tables 4 and 5.

Parameters of the statistical assessment shown in Table 4, determined in the system with 0.3 M NaOH, reveal that the best fitting of α-time data was obtained to the kinetic model F2. Therefore, within the examined period of extraction time (0.5–60 minutes), far from the equilibrium, which corresponds to the range of α equal to 0.66–0.98, the rate of chromium(III) extraction from the alkaline aqueous solution containing chlorides is limited mainly by the second-order chemical reaction (F2), irrespective of the way of preparation of the aqueous phase (WS or AQ). What is more, under these conditions, the quality of fitting of the changes of α with time to the geometrical (R2, R3) and to the diffusion rate equations (D1-D4) is rather poor. However, the contracting volume (R3) from among the geometrical models and the three-dimensional diffusion rate equation (D3) from among the diffusion models may be taken also into account as models describing the behaviour of chromium(III) during the extraction.

Table 5. Fittings of α-time experimental data to the selected kinetic models (given in Table 1) determined for the extraction system 0.005 M CrCl$_3$ – 0.5 M NaOH – 0.05 M Aliquat 336, with the aqueous phases of various history of preparation

| Model | Alkaline aqueous phase from | | | | | | | |
| | Sample of CrCl$_3$ (WS) $\alpha = 0.349$–0.897 $t = 0.5$–300 minutes | | | | Aged solution of CrCl$_3$ (AQ) $\alpha = 0.330$–0.888 $t = 0.5$–300 minutes | | | |
	$(k_T \pm$ S.D.$)10^{-3}$, s^{-1}	R^2	F	N	$(k_T \pm$ S.D.$)10^{-3}$, s^{-1}	R^2	F	N
R2	0.026 ± 0.004	0.7538	44	15	0.025 ± 0.003	0.8057	55	14
R3	0.021 ± 0.003	0.7890	53	15	0.021 ± 0.002	0.8369	68	14
D1	0.037 ± 0.006	0.7442	42	15	0.036 ± 0.005	0.8040	54	14
D2	0.033 ± 0.004	0.8197	65	15	0.032 ± 0.003	0.8706	88	14
D3	0.015 ± 0.001	0.9050	134	15	0.014 ± 0.001	0.9396	203	14
D4	0.009 ± 0.001	0.8521	82	15	0.009 ± 0.001	0.8976	115	14
F1	0.101 ± 0.011	0.8550	84	15	0.096 ± 0.009	0.8935	110	14
F2	0.459 ± 0.016	0.9825	786	15	0.398 ± 0.012	0.9886	1130	14
F3	4.915 ± 0.113	0.9927	1892	15	3.789 ± 0.155	0.9787	599	14
	$\alpha = 0.349$–0.676 $t = 0.5$–30 minutes				$\alpha = 0.330$–0.684 $t = 0.5$–45 minutes			
	$(k_T \pm$ S.D.$)10^{-3}$ [s^{-1}]	R^2	F	N	$(k_T \pm$ S.D.$)10^{-3}$ [s^{-1}]	R^2	F	N
R2	0.136 ± 0.013	0.9394	109	8	0.095 ± 0.008	0.9477	128	8
R3	0.103 ± 0.009	0.9471	109	8	0.072 ± 0.006	0.9560	153	8
D1	0.193 ± 0.015	0.9572	157	8	0.134 ± 0.009	0.9670	206	8
D2	0.138 ± 0.009	0.9725	248	8	0.097 ± 0.005	0.9821	386	8
D3	0.046 ± 0.002	0.9854	473	8	0.032 ± 0.001	0.9932	1026	8
D4	0.035 ± 0.002	0.9777	308	8	0.025 ± 0.001	0.9869	528	8
F1	0.398 ± 0.030	0.9610	174	8	0.279 ± 0.018	0.9706	232	8
F2	0.877 ± 0.036	0.9885	604	8	0.620 ± 0.017	0.9950	1386	8
F3	3.989 ± 0.134	0.9922	890	8	2.863 ± 0.115	0.9887	616	8

The results obtained for the system with 0.5 M NaOH (Table 5) indicate that within the whole period of time (0.5–300 minutes) needed to reach the extraction equilibrium, for which $\alpha = 0.33$–0.90, the best linearity fittings of α-time experimental data to the kinetic rate equations were obtained for the F2 and F3 models, irrespective of the history preparation of the aqueous phases. Therefore, the rate of chromium(III) extraction under these conditions is limited both by the second-order and third-order chemical reactions. The assessment of the results in Table 5 indicates that within the period of 0.5–300 minutes, the fittings of experimental data to the geometrical (R2, R3) and to the diffusion models (D1–D4) are of lower importance and statistical quality. However, the model D3 with the determination coefficient R^2 higher than 0.90 may be taken into account as a factor limiting the Cr(III) extraction under these conditions. Moreover, data obtained (Table 5) across the similar extent of the

chromium(III) extraction (α = 0.33–0.68), which corresponds to the shorter initial periods of time (0.5–30 minutes and 0.5–45 minutes) reveal that the all tested geometrical (R2, R3), diffusion (D1-D4) and the reaction order models (F1–F3) give acceptable fittings to the changes of α-time. However, the best linear relations of the α-time data are obtained by the fittings to the F2, F3, and D3 kinetic models.

Then, it can be concluded that within the whole period of time necessary to attain the equilibrium, the extraction of chromium(III) with Aliquat 336 from the fresh alkaline aqueous solutions containing chlorides is limited by the second-order chemical reaction towards Cr(III), irrespective of the NaOH concentration and of the history of preparation of the aqueous phase. However, at NaOH concentration equal to 0.5 mol/dm^3, the rate of the Cr(III) extraction is also limited by the third-order chemical reaction. Moreover, within the shorter initial period of the extraction time the effect of the three-dimensional diffusion (D3) and the chemical reaction at phase boundary (R2) on the rate of chromium(III) extraction is visible.

From Tables 4 and 5 it also comes that values of the rate constants determined from the best fitted kinetic models (F2 and/or F3) for the extraction of chromium(III) in the tested system depend on the NaOH concentration and on the history of preparation of the aqueous phases (WS or AQ) as it was found from the relation $1/c_{Cr_a} = k_2 \cdot t$ in Section 3.2. At constant concentration of NaOH, the extraction equilibrium is reached faster when chromium(III) is extracted from the alkaline aqueous phase freshly prepared by direct dissolution of a weighted sample of CrCl$_3$ than from that obtained from the aged stock solution of CrCl$_3$.

Table 6. The rate constant (k_T) determined from the F2 and F3 kinetic models for the extraction of Cr(III) in the system with Aliquat 336 and with the alkaline aqueous phases prepared by dilution of the aged stock solutions of different Cr(III) salts. Values of k_T for the systems with sulphates, nitrates, and perchlorates were taken from Wionczyk et al. (2011c)
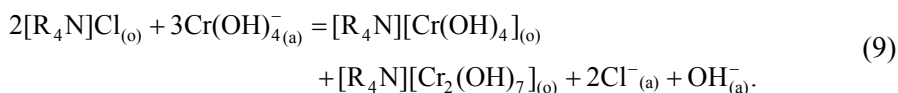
c_{NaOH}^0, [mol/dm^3]	Anions in the aqueous phase	Model F2 $(k_T \pm$ S.D.$)\cdot10^{-3}$ [s^{-1}]	Model F3 $(k_T \pm$ S.D.$)\cdot10^{-3}$ [s^{-1}]	Range of extraction time [min]	Range of α
0.3	ClO$_4^-$	2.95 ± 0.12	44.4 ± 4.5	5–60	0.642–0.949
0.3	NO$_3^-$	4.41 ± 0.12	85.4 ± 11.0	5–60	0.693–0.986
0.3	SO$_4^{2-}$	6.40 ± 0.16	130 ± 16	5–60	0.733–0.959
0.3	Cl$^-$	7.62 ± 0.01	220 ± 15	0.5–60	0.706–0.968
0.5	ClO$_4^-$	0.23 ± 0.01	1.14 ± 0.05	5–300	0.310–0.794
0.5	NO$_3^-$	0.22 ± 0.01	1.42 ± 0.02	5–300	0.325–0.807
0.5	Cl$^-$	0.40 ± 0.01	3.79 ± 0.16	0.5–300	0.330–0.888
0.5	SO$_4^{2-}$	0.68 ± 0.01	10.2 ± 0.6	5–300	0.439–0.928
0.5	ClO$_4^-$	0.23 ± 0.01	1.14 ± 0.05	5–1200	0.310–0.673
0.5	NO$_3^-$	0.30 ± 0.01	1.32 ± 0.07	5–90	0.325–0.670
0.5	Cl$^-$	0.62 ± 0.02	2.86 ± 0.12	0.5–45	0.330–0.684
0.5	SO$_4^{2-}$	0.91 ± 0.08	4.68 ± 0.26	5–30	0.439–0.683

A comparison between the rate constants of the Cr(III) extraction determined in the present and in the earlier studies (Wionczyk et al., 2011c) from the best fitted F2 and F3 kinetic models ($R^2 > 0.90$) in the systems with Aliquat 336 and with the alkaline aqueous phases prepared from the aged aqueous solutions of different Cr(III) salts (CrCl$_3$, or KCr(SO$_4$)$_2$, or Cr(NO$_3$)$_3$, or Cr(ClO$_4$)$_3$) is given in Table 6. These results confirm findings from Section 3.2, that the velocity of the chromium(III) extraction depends on concentration of NaOH and on the kind of anions present in the aqueous phase. On the other hand, values of the rate constant determined from F2 and F3 models varying with hydration properties of anions present in the aqueous phase, i.e. with their free energy of hydration in order like that established from relation $1/c_{Cr_a} = k_2 \cdot t$ (Section 3.2, Table 3). Moreover, Table 6 shows that at constant composition of the aqueous phase, the values of the rate constants determined from the F3 model are considerably higher than those calculated from the second-order kinetic model (F2).

Taking into account the all kinetic considerations presented in this paper, it can be assumed that the extraction of chromium(III) in the studied system with chlorides may be described as follows:

$$[R_4N]Cl_{(o)} + Cr(OH)_{4(a)}^- = [R_4N][Cr(OH)_4]_{(o)} + Cl^-_{(a)} \tag{6}$$

$$2[R_4N][Cr(OH)_4]_{(o)} = [R_4N][Cr_2(OH)_7]_{(o)} + [R_4N]OH_{(o)} \tag{7}$$

$$[R_4N]OH_{(o)} + Cr(OH)_{4(a)}^- = [R_4N][Cr(OH)_4]_{(o)} + OH^-_{(a)} \tag{8}$$

and summing up

$$\begin{aligned} 2[R_4N]Cl_{(o)} + 3Cr(OH)_{4(a)}^- &= [R_4N][Cr(OH)_4]_{(o)} \\ &+ [R_4N][Cr_2(OH)_7]_{(o)} + 2Cl^-_{(a)} + OH^-_{(a)}. \end{aligned} \tag{9}$$

Further studies are planned with the application of some instrumental techniques, for instance spectroscopy UV-VIS, to confirm the above assumptions and to explain the differences in kinetic behavior of chromium(III) during the extraction with Aliquat 336 from the alkaline aqueous solutions of different composition and history of their preparation.

Conclusions

It was demonstrated that within time far from the equilibrium, the extraction of chromium(III) with Aliquat 336 from the aqueous alkaline feed solution containing chlorides depends on composition and history of preparation of the aqueous phase. A reduction in the initial NaOH concentration from 0.5 mol/dm^3 to 0.3 mol/dm^3 and

thus, the ionic strength of the aqueous phase, affect positively the yield and the rate of chromium(III) extraction under studied conditions.

At constant composition of the feed aqueous solution the equilibrium of the chromium(III) extraction is attained faster when chromium(III) is extracted from the aqueous phase freshly prepared by direct dissolution and alkalization of a sample of $CrCl_3 \cdot 6H_2O$ than from that freshly prepared from the aged (several months) stock aqueous solution of $CrCl_3$.

The kinetic analyses of the experimental data by the mathematical models and by the method of multiple regression analysis reveal that within the whole period of time needed to attain the equilibrium, the initial rate of chromium(III) extraction is limited mainly by the second-order and also by the third-order chemical reaction towards chromium(III), irrespective of composition and the preparation history of the aqueous phase. However, within the shorter initial period of time which corresponds to the smaller extent of the extraction, the three-dimensional diffusion and the chemical reaction at phase boundary substrate-product (the contracting volume) models can have a significant effect on the rate of chromium(III) extraction.

It can be also concluded that the extraction of chromium(III) with Aliquat 336 from the alkaline aqueous phases, prepared by dilution of the aged stock solutions of chromium(III) salts, depends on a kind of anions present in the aqueous phase, and exactly, on their hydration properties. Namely, at concentration of NaOH in the feed aqueous solution equal to 0.5 mol/dm^3, the rate constants of Cr(III) extraction increase with the increasing negative values of free energy of hydration of anions present in the aqueous phase according to the following order: perchlorates < nitrates < chlorides < sulfates. At 0.3 mol/dm^3 of NaOH, the effect of these anions on the rate of Cr(III) extraction is varying in the different sequence: perchlorates < nitrates < sulfates < chlorides.

Acknowledgements

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