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Studies on the kinetics and equilibrium of the solvent extraction of chromium(III) from alkaline aqueous solutions of different composition in the system with Aliquat 336

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ABSTRACT

The kinetics and equilibrium of Cr(III) extraction with Aliquat 336 from the alkaline aqueous solutions containing anions of various complexing abilities and solvating properties, as: nitrates, or perchlorates, or sulphates, were studied and interpreted. Stoichiometry of Cr(III) complexes formed in the organic phases was also discussed. It was found that under the same conditions the yield and the rate of Cr(III) extraction as well as values of mass transfer coefficient increase in the following order of anions: perchlorates < nitrates < sulphates. The equilibrium of extraction of Cr(III) in the systems with nitrates and/or perchlorates differs significantly from that one established for the extraction of Cr(III) from the alkaline aqueous solutions of sulphates. Experiments with the modified Lewis cell and analysis of the experimental data by mathematic models appeared that the studied extraction of Cr(III) occurs in the mixed diffusion-kinetic regime, irrespective of the kind of anions present in the aqueous phase.
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1. Introduction

Chromium compounds are applied in many industrial processes, e.g. in metal electroplating, glasses colouring, textile dyeing, in preservation of wood, and in the leather processing as a tanning agent. However, such processes generate liquid and solid wastes containing large quantities of Cr(VI) and Cr(III) compounds. Effluents and solid wastes containing compounds of chromium create an environmental hazard and a risk for the humane health when they are discharged without purification into the landfill or rivers. It is known that compounds of Cr(VI) were determined to exert a carcinogenic action on humans while the trace amounts of chromium(III) are essential to the proper functioning of the human organism [1,2]. However, a strong possibility of oxidation of chromium(III) to toxic chromium(VI) in soils and surface waters should be taken into account under favourable conditions, e.g. acid rains and the presence of some oxidants like MnO_2 [3,4]. Therefore, recovery and removal of chromium(III) from solid and liquid industrial wastes have both ecological and economical aspects. First of all, it reduces a risk of contamination of environment and prevents loses of compounds of chromium which can be reused in other industrial processes.

Different methods have been proposed in literature to recover chromium(III) from aqueous solutions, and also from industrial floats and wastewaters.

Precipitation of chromium(III) with some alkaline compounds, such as sodium carbonate, magnesium oxide, calcium and sodium hydroxide is quite commonly realized process for removing of chromium(III) from spent tanning liquors [5]. Recently, many other methods have been examined to remove and recover chromium(III) from aqueous solutions and tannery effluents/wastewaters, for example:

- adsorption on different adsorbents (activated carbon, zeolites, ion-exchange resin Lewatit S 100) [6,7] and biosorption [8],
- ultrafiltration [9,10], micellar enhanced ultrafiltration [11,12], nanofiltration [13], and reverse osmosis [14]
- electrodialysis [15], electrolysis [16], electrocoagulation [17],
- partial freezing [18],
- transport through bulk, supported liquid, and polymer inclusion membranes with application of various carriers [19–24].

The solvent extraction is one of the most efficient method for concentration and separation of various metal species including chromium(III).

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As it comes from earlier literature data on chromium(III) extraction, both cationic and anionic species of Cr(III) were extracted mainly from acidic or neutral media. Namely, cationic complexes of chromium(III) were extracted with acidic extractants, e.g. with carboxylic acids [25] and organophosphorus acids [26] as well as with partially ammoniated organophosphorus acids [27] while anionic complexes of chromium(III) formed, e.g. with ethylenediaminetetraacetic acid (EDTA) were extracted with trioctylmethylammonium chloride (Aliquat 336) [28].

Wionczyk and Apostoluk [29–31] have demonstrated for the first time that quaternary ammonium compounds effectively extract chromium(III) from the alkaline model solutions of $KCr(SO_4)_2$. In these studies the effects of different parameters on the equilibrium of chromium(III) extraction were examined [29–31]. The thermodynamic functions (the changes of enthalpy, entropy, and free energy) for the extraction of chromium(III) in this system with Aliquat 336 at temperatures from 273 to 298 K were also estimated [32]. Moreover, Wionczyk et al. examined this method for the removal of chromium(III) from some industrial spent tanning liquors [33] and from the protein hydrolyzate obtained by alkaline hydrolysis of wastes of chromium tanned leathers [34,35]. These studies shown that the extraction of chromium(III) both from appropriately prepared (diluted and alkalized) spent tanning baths and from alkaline protein hydrolyzate with trioctylmethylammonium compounds was very effective and its yields were equal to about 99% at the aqueous/organic phase volume ratio equal to 5/1 [33,35]. It was also demonstrated that chromium(III) was efficiently stripped from the loaded organic phase with 0.5 M sulphuric acid [30,33,35]. Then, as a consequence of our earlier studies and on the base of available literature data concerning the recovery, removal, and separation of chromium(III) from different industrial effluents and/or wastewaters, we can conclude that the extraction of chromium(III) from alkaline media is interesting and important question from point of view of environmental studies. However, this problem is still recognized weakly. Namely, there is a lack of the kinetic and equilibrium studies on the extraction of anionic chromium(III) species from the alkaline aqueous solutions of different composition.

Therefore, the goal of our present studies is a comparison of the rate of chromium(III) extraction with Aliquat 336 from alkaline solutions of different compositions, prepared from the following chromium(III) compounds: $Cr(ClO_4)_3$, or $Cr(NO_3)_3$, and/or $KCr(SO_4)_2$. We also show in this paper the effects of contact time of phases, concentration of NaOH in the aqueous phase, and concentration of Aliquat 336 in the organic phase on the kinetics and equilibrium of chromium(III) extraction from the alkaline aqueous solutions containing anions of various complexing abilities and solvating properties (nitrates, or perchlorates, or sulphates). The stoichiometry of chromium(III) complexes formed in the organic phase, especially in the systems with $Cr(NO_3)_3$ and $Cr(ClO_4)_3$, is also discussed. Moreover, we present our considerations concerning the application of the kinetic models, used usually in the kinetic analysis of heterogeneous processes or reactions, for determination of some factors limiting the extraction of Cr(III) in the studied systems.

2. Experimental

2.1. Reagents

Solutions of Aliquat 336 (90% of trioctylmethylammonium chloride, for synthesis Merck-Schuchardt) in heptane (p.a., Chempur, Poland) modified with 1% (v/v) of 1-decanol (>99% for synthesis, Merc-Schuchardt) of concentration varying from 0.010 to 0.10 M were used as the initial organic phases in both kinetic and equilibrium studies.

The initial aqueous phases were 0.005 M solutions of Cr(III) at concentration of NaOH varying from 0.3 M to 0.7 M. They were freshly prepared from concentrated NaOH solution and from 0.1 M stock aged solutions of $Cr(ClO_4)_3$, or $Cr(NO_3)_3$, or $KCr(SO_4)_2$. All compounds were received from POCh (Poland) and were of reagent grade purity. Distilled water was used in the all kinetic and equilibrium studies.

2.2. Equilibrium studies

Equal volumes of the aqueous and organic phases were shaken mechanically in a thermostatic water bath shaker type Elpin 357 (Poland) with constant speed (140 c.p.m.) at constant temperature ($25 \pm 0.5\,^{\circ}C$) for established experimentally time needed to reach the extraction equilibrium. Excepting experiments in which the effect of time on the extraction was tested. Then, the phases were transferred to separatory funnels and were left to clarify and separate for 3 h. The distribution of chromium(III) in both phases was determined spectrophotometrically 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 while the concentration of free quaternary ammonium salt in the organic phase was calculated from material balance.

2.3. Kinetic studies

Kinetic experiments on Cr(III) extraction were carried out by means of a modified Lewis cell [36] having a constant interfacial area of 18.9 cm^2. The cell consists of a glass tube, two stirrers rotating in different directions and two additional glass tubes controlling the stream direction inside the cell. The same volumes of the aqueous and organic phases (90 cm^3) were poured carefully into the apparatus. The rotation rate of the stirrers was kept within the range of 30–180 rpm to maintain a flat and stable interface. 1.0 cm^3 of the organic and aqueous phases was withdrawn after appropriate periods of time and analyzed for chromium(III) by atomic absorption spectroscopy (Varian SPECTR AA800). The first sample was taken directly after filling the apparatus before the stirrers were switched on. Chromium(III) concentration in the organic phase was determined after stripping the metal with 0.5 M sulphuric acid. Each time after collecting a sample, 1.0 cm^3 of each of samples of the fresh organic and aqueous solution were added to the stirred cell.

3. Results and discussion

3.1. Equilibrium studies

3.1.1. The effect of time and the aqueous phase composition

The influence of shaking time and the concentration of sodium hydroxide on the extraction of chromium(III) from the alkaline aqueous phases containing ClO_4^-, or NO_3^-, or SO_4^{2-} is illustrated in Fig. 1. From these experimental results it comes that an elongation of contact time of phases and an decrease of NaOH concentration affect positively the chromium(III) extraction with Aliquat 336, irrespective of the kind of anions present in the aqueous phase. As it can be seen, chromium(III) is extracted with Aliquat 336 almost completely from solutions of sulphates, nitrates, and perchlorates at low concentration of NaOH equal to 0.3 M. Satisfactorily high yield of the extraction of Cr(III) is also observed for 0.5 M NaOH in the presence of both sulphates (over 90%) and nitrates or perchlorates (over 80%). The results obtained in the system with 0.7 M NaOH indicate that chromium(III) is extracted with higher and maximum yield (60%) only from solution containing sulphates, while from the solutions of perchlorates and nitrates, the extraction of Cr(III) achieves only 20–30% even after long enough contact time

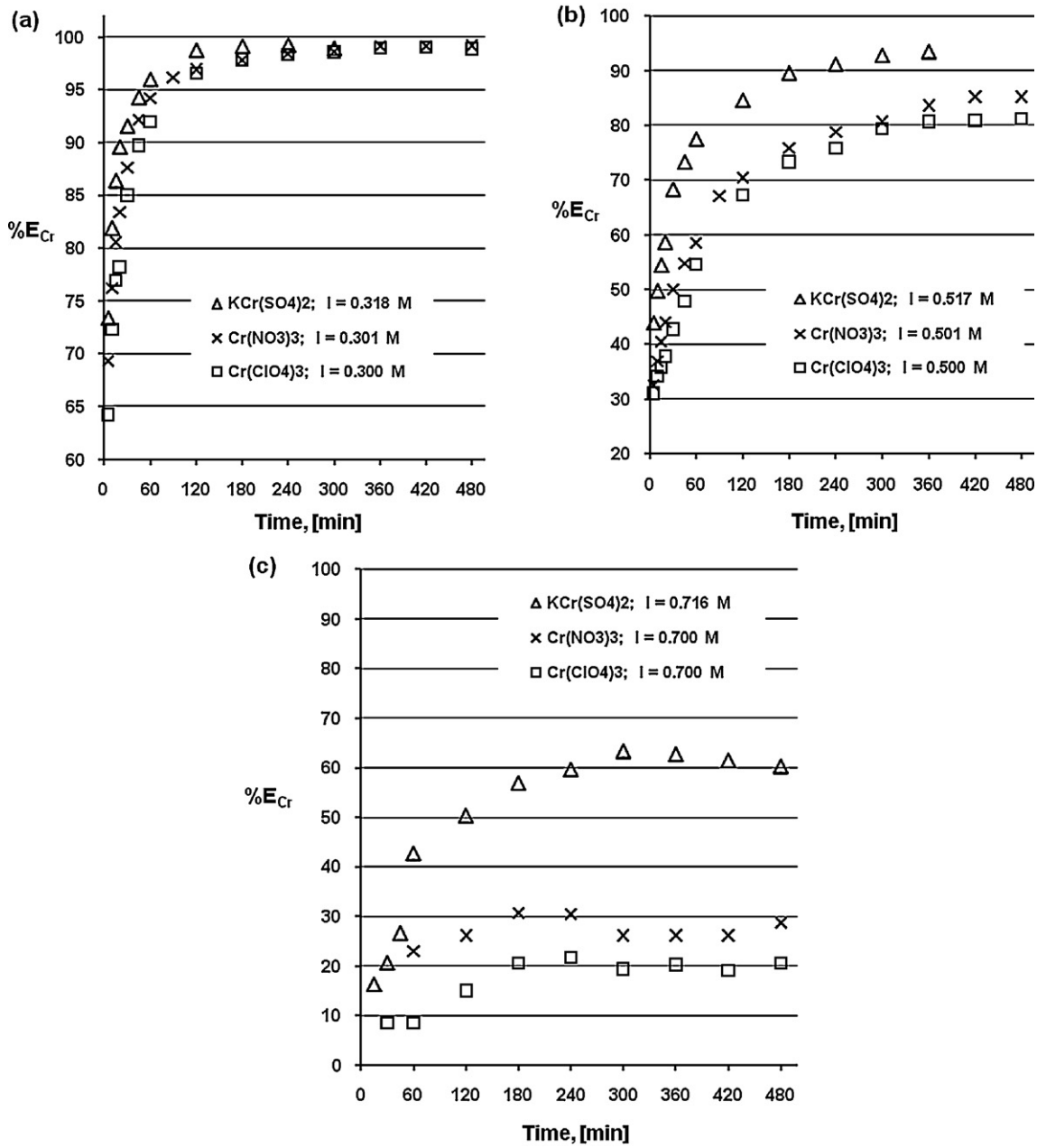

Fig. 1. Effect of time and concentration of NaOH on the extraction of chromium(III) (%*E*) from the aqueous solutions of sulphates, nitrates, and perchlorates in: (a) 0.3 M; (b) 0.5 M; (c) 0.7 M NaOH. *I* – the ionic strength of the aqueous phase. $c^0_{Cr(III)} = 0.005$ M; $c^0_{Alq} = 0.05$ M; temp. 25 ± 0.5 °C.

of the phases exceeding 5 h. So, it can be concluded that the time needed to reach the equilibrium of Cr(III) extraction depends on concentration of NaOH in the aqueous phase. On the other hand, the higher concentration of sodium hydroxide in the aqueous phase the longer time is necessary to reach the equilibrium of Cr(III) extraction. Consequently, the results in Fig. 1 reveal that an increase of the initial NaOH concentration from 0.3 M to 0.7 M reduces extensively percent of chromium(III) extracted from the aqueous phases containing the same kind of anions. This negative effect of increasing concentration of NaOH on the extraction of Cr(III) is attributed to the increasing ionic strength of the aqueous phase. This remark is in a good agreement with the findings of our previous studies [31,32].

From a different side, comparing the results (Fig. 1) obtained for the aqueous phases at constant concentration of NaOH but containing different anions (perchlorates, or nitrates, or sulphates), one can find that chromium(III) is extracted with the highest yield from the alkaline aqueous solutions of sulphates whereas with the lowest yield from the aqueous phases containing perchlorates. So that, a decrease of the yield of Cr(III) extraction cannot originate only from the negative effect of the ionic strength because at constant NaOH concentration the ionic strength of the alkaline solutions of sulphates is slightly higher than the solutions containing other anions (Fig. 1(a)–(c)). Taking this into account, the reduction of percent of the Cr(III) extraction can be also discussed in terms of certain properties of anions present in the aqueous phases as well as of their competitions with hydroxochromates(III) within the extraction system. Namely, the extraction of Cr(III) increases in the following order of anions: $ClO_4^- < NO_3^- < SO_4^{2-}$, and consequently, with the increase of their negative values of free energy of hydration equal to: −214 kJ/mol, −306 kJ/mol, −1090 kJ/mol, respectively [37]. Then, strongly hydrated sulphates which are

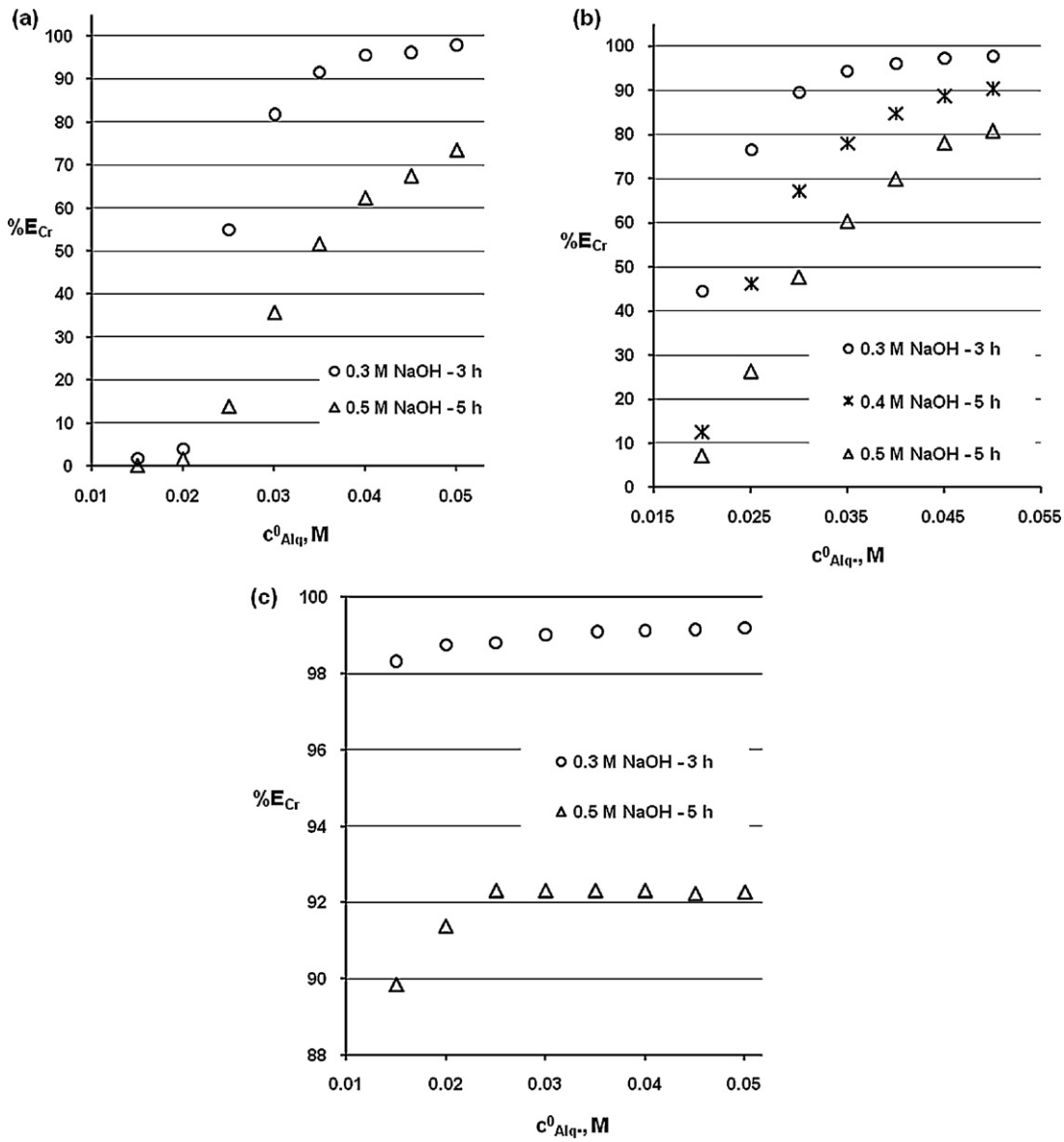

Fig. 2. Effect of concentration of Aliquat 336 in the organic phase on the extraction of chromium(III) (%E) from the alkaline aqueous solution of: (a) ClO_4^-; (b) NO_3^-; (c) SO_4^{2-}. $c^0_{Cr(III)} = 0.005$ M; temp. 25 ± 0.5 °C.

known in the Hofmeister series as kosmotropes ("water structure makers" and produce stabilizing and salting-out effects) favour the extraction of chromium(III) in the studied system while perchlorates and nitrates being chaotrope ("water structure breakers" and produce destabilizing and salting-in effects) affect negatively this process. Besides, the negative influence of perchlorates and nitrates comes also from their competition with hydroxochromates(III) in the extraction because as it is known anions of low negative free energy of hydration and of small ionic radius are extracted quicker than these other. We also found that formed in the organic phase trioctylmethylammonium perchlorates and/or nitrates species did not extract chromium(III) complexes on the contrary to sulphate and hydroxide species of the extractant.

3.1.2. *The effect of the extractant concentration*

The effect of concentration of Aliquat 336 in the organic phase on the extraction of chromium(III) from the alkaline aqueous phases prepared from the various selected Cr(III) compounds [$Cr(ClO_4)_3$, or $Cr(NO_3)_3$, and/or $KCr(SO_4)_2$] is shown in Fig. 2. The results reveal that an increase of the concentration of extractant from 0.015 M to 0.050 M in the organic phase leads to the considerable increase of the extraction of chromium(III) from the alkaline solutions of NO_3^- and ClO_4^- (Fig. 2(a) and (b)). This effect is slightly visible for the alkaline aqueous solutions of sulphates. Namely, in this system chromium(III) is extracted with almost constant and the highest yield within the whole examined range of the extractant concentration (Fig. 2(c)). Moreover, the results in Fig. 2 confirm our previous conclusion (see Section 3.1.1), that an increase of concentration of NaOH, and thus, the ionic strength of the aqueous phase, negatively affect the chromium(III) extraction, irrespective of the kind of anions present in the aqueous phase and of concentration of Aliquat 336 in the organic phase.

Assuming that the extraction equilibrium of chromium(III) in the each studied system can be described by the general Eq. (1):

$$x\mathrm{R_4NCl}_{(o)} + [\mathrm{Cr}_n(\mathrm{OH})_{(3n+x)}]^{x-}_{(a)} = [(\mathrm{R_4N})_x\mathrm{Cr}_n(\mathrm{OH})_{(3n+x)}]_{(o)} + x\mathrm{Cl}^-_{(a)} \quad (1)$$

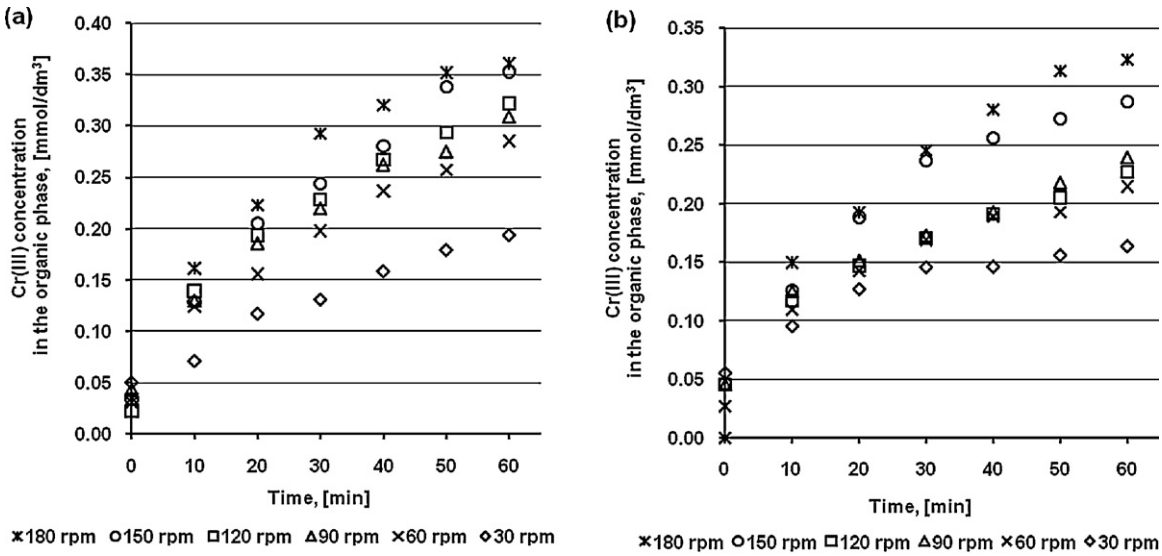

Fig. 3. Effect of stirring speed on the extraction of chromium(III) with 0.05 M solution of Aliquat 336 from the alkaline aqueous solutions of sulphates at concentrations of NaOH equal to: (a) 0.3 M; (b) 0.5 M. $c^0_{Cr(III)} = 0.005$ M; temp. 25 ± 0.5 °C.

and using a course of action like that given in our work [31], the numbers of molecules of quaternary ammonium salt, forming complexes with chromium(III) in the organic phases, were estimated from slope of the following function:

$$\log D = f\left\{\log \frac{[R_4NCl]_o}{[Cl^-]_a}\right\} \quad (2)$$

where: indices "a" and "o" relate to the aqueous and organic phases, respectively, D is distribution ratio of chromium(III) at the equilibrium, $[R_4NCl]_o$ stands for the equilibrium concentration of free Aliquat 336, $[Cl^-]_a$ denotes the equilibrium concentration of chlorides. The slope of the function (2) represents also the coefficient x in Eq. (1).

Considering term reflecting the effect of the ionic strength (I) of the aqueous phase on the extraction of Cr(III) and using the multiple regression analysis, the following relations were established from the results obtained at temperature 25 °C (Fig. 2(a) and (b)) in the studied system with:

- alkaline aqueous solutions of ClO_4^-

$$\log D = (6.69 \pm 0.34) + (3.46 \pm 0.18)\log \frac{[R_4NCl]_o}{[Cl^-]_a} - (15.01 \pm 0.88)\frac{\sqrt{I}}{1+\sqrt{I}}; \quad R^2 = 0.9853;\ \text{S.D.} = 0.092;\ F = 369;\ N = 12 \quad (3)$$

- alkaline aqueous solutions of NO_3^-

$$\log D = (7.01 \pm 0.34) + (3.49 \pm 0.13)\log \frac{[R_4NCl]_o}{[Cl^-]_a} - (15.40 \pm 0.87)\frac{\sqrt{I}}{1+\sqrt{I}}; \quad R^2 = 0.9812;\ \text{S.D.} = 0.101;\ F = 522;\ N = 21 \quad (4)$$

where: R^2, S.D., F, and N mean the determination coefficient, the standard deviation, the Fisher–Snedecor test function, and number of experimental points, respectively.

On the base of coefficients involving term $\log \frac{[R_4NCl]}{[Cl^-]}$ in Eqs. (3) and (4), it can be supposed that ionic pairs containing, on average, three trioctylmethylammonium cations prevail in the loaded organic phases in the extraction system with alkaline aqueous solutions prepared from $Cr(NO_3)_3$ and $Cr(ClO_4)_3$, e.g. the following formula $(R_4N)_3Cr(OH)_6$ may be proposed for them at the assumption that coefficient "n" in Eq. (1) is equal to one.

Moreover, the results obtained in the system with alkaline aqueous solutions of SO_4^{2-} (see Fig. 2(c)) were added to the results from our previous work [31,32] and the following new correlation was found:

$$\log D = (6.91 \pm 0.12) + (1.00 \pm 0.09)\log \frac{[R_4NCl]_o}{[Cl^-]_a} - (14.05 \pm 0.33)\frac{\sqrt{I}}{1+\sqrt{I}}; \quad R^2 = 0.9827;\ \text{S.D.} = 0.111;\ F = 1080;\ N = 39 \quad (5)$$

From Eq. (5) it appears that coefficient concerning term $\log \frac{[R_4NCl]}{[Cl^-]}$ is equal to (1.00 ± 0.09) and it does not differ from that

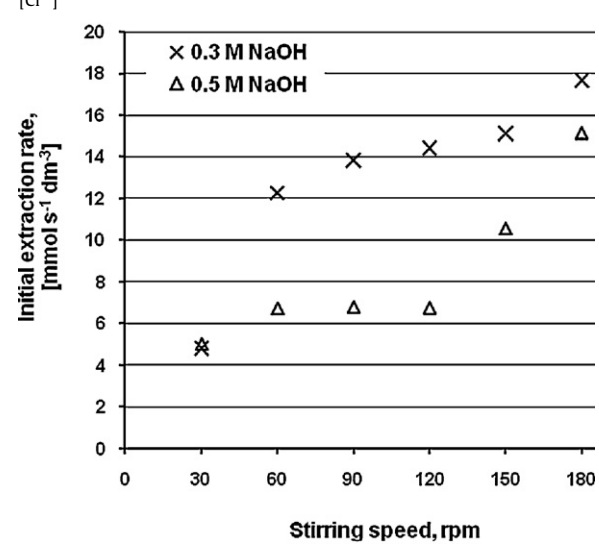

Fig. 4. Effect of stirring speed on the initial rate of the extraction of chromium(III) with 0.05 M solution of Aliquat 336 from the alkaline aqueous solutions of sulphates. $c^0_{Cr(III)} = 0.005$ M; temp. 25 ± 0.5 °C.

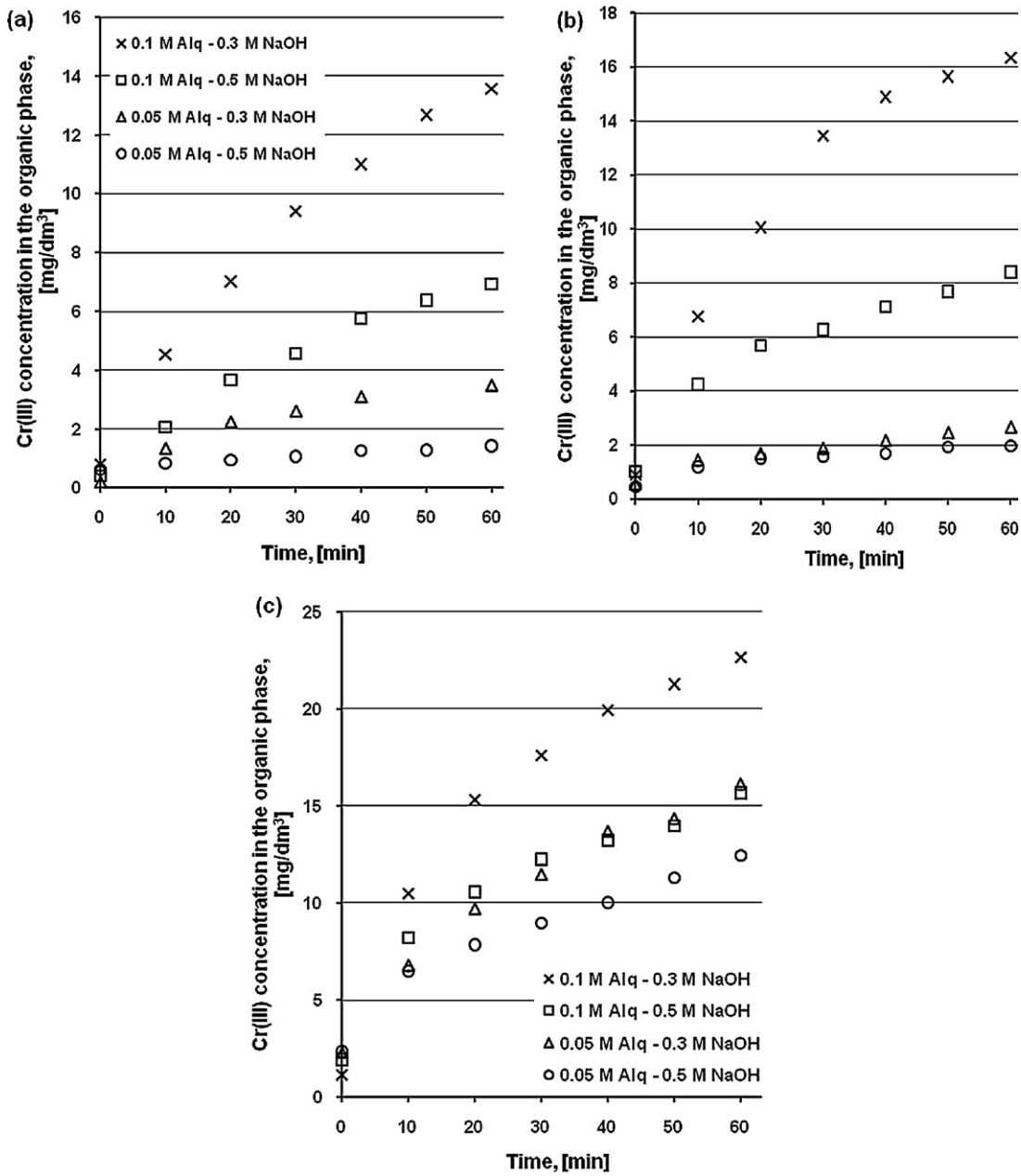

Fig. 5. Effect of concentrations of NaOH in the aqueous phases and of Aliquat 336 in the organic phase on amount of chromium(III) extracted from the alkaline solutions of:(a) ClO_4^-; (b) NO_3^-; (c) SO_4^{2-} in the Lewis cell at rotation speed equal to 90 rpm. $c^0_{Cr(III)} = 0.005$ M.

one (0.96 ± 0.07) established in our earlier work [32]. Then, this value reveals that ion-pair complexes of chromium(III) with one trioctylmethylammonium cation dominate in the loaded organic phase in the extraction system with the alkaline aqueous solutions prepared from $KCr(SO_4)_2$.

Consequently, comparing correlations (3) and (4) with Eq. (5), it can be assumed that the equilibrium of extraction of chromium(III) in the system with $Cr(NO_3)_3$ and $Cr(ClO_4)_3$ differs significantly from that one established for the extraction of chromium(III) from the alkaline solutions of sulphates. Moreover, it can be noted that negative terms relating to the ionic strength in dependencies (3)–(5) confirm its negative effect on the extraction of chromium(III) in the each of studied systems.

Further studies are planned to explain the differences observed in behavior of Cr(III) during extraction in the system with alkaline solutions of sulphates and in these other with alkaline solutions of nitrates or perchlorates.

3.2. Kinetic studies

3.2.1. The effect of stirring speed of phases

The dependence of the extraction of chromium(III) with Aliquat 336 on time and on stirring speed of the aqueous and organic phases in the modified Lewis cell is shown in Fig. 3. These experiments were performed only in the extraction system with the alkaline aqueous solutions of SO_4^{2-} at concentration of NaOH equal to 0.3 M and 0.5 M. The results in Fig. 3 reveal that amount of chromium(III) extracted to the organic phase depends on contact time of phases and on their stirring speed. Then, an elongation of extraction time up to 60 min and an increase of the stirring

Table 1
The mass transfer coefficient, k, determined on the base of results obtained by the Lewis cell in the studied extraction systems of chromium (III).

c^0_{NaOH} (M)	c^0_{Alq} (M)	Mass transfer coefficient, k, (m/s)		
		$KCr(SO_4)_2$	$Cr(NO_3)_3$	$Cr(ClO_4)_3$
0.3	0.01	2.94×10^{-7}	–	–
0.3	0.05	1.62×10^{-6}	2.35×10^{-7}	2.05×10^{-7}
0.3	0.10	3.38×10^{-6}	1.58×10^{-6}	9.22×10^{-7}
0.5	0.01	1.43×10^{-7}	–	–
0.5	0.05	1.17×10^{-6}	3.72×10^{-7}	5.87×10^{-8}
0.5	0.10	1.77×10^{-6}	8.12×10^{-7}	4.35×10^{-7}

Table 2
Some of the most important rate equations (models) proposed for kinetic analysis of heterogeneous processes [39].

Kind and symbol of kinetic model	Mechanism	Integral form $g(\alpha) = k_T \times t$
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)	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$
'Order of reaction' models		
F1/A1	First order/Avrami-Erofeev equation, $n = 1$	$-\ln(1-\alpha)$
F2	Second order	$\left[\frac{1}{(1-\alpha)}\right]-1$
F3	Third order	$\left[\frac{1}{(1-\alpha)^2}\right]-1$

speed from 30 to 180 rpm affect positively the extraction of chromium(III), irrespective of the initial concentration of NaOH in the system. Moreover, the most considerable changes of amount of chromium(III) extracted to the organic phase were observed within period of time from 0 to 30 min.

So that, from the slope of the linear relationships (presented in Fig. 3) within the period of extraction time from 0 to 30 min, the initial rates (v) of chromium(III) extraction, and consequently, the fluxes of chromium(III) transfer (J) from the aqueous to the organic phase can be determined according to the following equations:

$$v = \frac{dc_o}{dt} \tag{6}$$

$$J = \frac{V_o}{S} \times v \tag{7}$$

where: c_o – concentration of Cr(III) in the organic phase after appropriate period of time; V_o – volume of the organic phase; t – time of extraction; S – interfacial surface.

The correlations established between the initial rate of Cr(III) extraction and the stirring speed of phases in the modified Lewis cell in the system with alkaline solutions of sulphates are shown in Fig. 4. The results indicate that determined for the both concentration of NaOH in the aqueous phase, values of the initial rate of chromium(III) extraction with Aliquat 336 are not proportional to the stirring speed of the phases within the whole examined range from 30 to 180 rpm. However, the plateau region within 60–120 rpm is better seen in the plot obtained for the extraction system with 0.5 M solution of NaOH and it might be attributed to the limiting of reaction due to the true kinetics or to the "slip effect" described by Danesi [38]. This effect means that in spite of the existence of the plateau region, the rate of extraction may be also limited by diffusion. Then, it can be supposed that the studied extraction of chromium(III) can occur probably in the mixed diffusion-kinetic regime.

The successive kinetic experiments were performed at the stirring speed equal to 90 rpm.

3.2.2. *The effect of time and composition of the aqueous and organic phases*

The influence of time, concentration of NaOH in the aqueous phases, and concentration of Aliquat 336 in the organic phases in the systems with different anions (sulphates, or nitrates, or perchlorates) on amount of chromium(III) extracted to the organic phase in the modified Lewis cell is illustrated in Fig. 5. The results appear that an elongation of contact time of phases and an increase

Table 3
Fitting of the experimental results obtained by the Lewis cell in the system: 0.005 M Cr(III)–0.3 M NaOH–0.05 M Aliquat 336, to the selected kinetic models.

Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	$\alpha = 0.0106–0.0746$, $t = 0–60$ min		$\alpha = 0.0020–0.0092$, $t = 0–60$ min		$\alpha = 0.0007–0.0113$, $t = 0–60$ min	
D1	1.56 ± 0.03	0.9977	0.022 ± 0.000	0.9860	0.038 ± 0.002	0.9926
D2	0.80 ± 0.01	0.9978	0.011 ± 0.000	0.9861	0.018 ± 0.000	0.9748
D3	0.18 ± 0.00	0.9979	0.002 ± 0.000	0.9861	0.004 ± 0.000	0.9749
D4	0.16 ± 0.00	0.9981	0.001 ± 0.000	0.9479	0.002 ± 0.000	0.9420
F1	17.5 ± 1.9	0.9358	1.83 ± 0.22	0.9160	2.86 ± 0.50	0.8621
F2	18.3 ± 1.9	0.9407	1.84 ± 0.22	0.9167	2.88 ± 0.51	0.8632
F3	38.4 ± 3.8	0.9455	3.70 ± 0.45	0.9174	5.80 ± 1.01	0.8643
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	$\alpha = 0.0314–0.0746$, $t = 10–60$ min		$\alpha = 0.0050–0.0092$, $t = 10–60$ min		$\alpha = 0.0044–0.0113$, $t = 10–60$ min	
D1	1.56 ± 0.03	0.9978	0.021 ± 0.000	0.9833	0.038 ± 0.002	0.9926
D2	0.80 ± 0.02	0.9979	0.010 ± 0.000	0.9832	0.018 ± 0.000	0.9584
D3	0.18 ± 0.00	0.9980	0.002 ± 0.000	0.9832	0.004 ± 0.000	0.9586
D4	0.16 ± 0.00	0.9982	0.001 ± 0.000	0.9638	0.002 ± 0.000	0.9807
F1	14.6 ± 1.2	0.9657	1.44 ± 0.04	0.9962	2.22 ± 0.40	0.8830
F2	15.5 ± 1.3	0.9679	1.46 ± 0.04	0.9962	2.24 ± 0.40	0.8837
F3	32.7 ± 2.6	0.9700	2.93 ± 0.08	0.9962	4.52 ± 0.80	0.8845

Table 4
Fitting of the experimental results obtained by the Lewis cell in the system: 0.005 M Cr(III)–0.5 M NaOH–0.05 M Aliquat 336, to the selected kinetic models.

Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0086–0.0455 t = 0–60 min		α = 0.0015–0.0064 t = 0–60 min		α = 0.0021–0.0050 t = 0–60 min	
D1	0.52 ± 0.02	0.9898	0.0103 ± 0.0000	0.9341	0.0054 ± 0.0000	0.9816
D2	0.27 ± 0.01	0.9900	0.0051 ± 0.0000	0.9342	0.0027 ± 0.0000	0.9816
D3	0.06 ± 0.00	0.9901	0.0011 ± 0.0000	0.9344	0.0006 ± 0.0000	0.9816
D4	0.06 ± 0.00	0.9970	0.0003 ± 0.0000	0.8736	0.0001 ± 0.0000	0.6719
F1	9.42 ± 1.16	0.9152	1.21 ± 0.23	0.8156	0.76 ± 0.06	0.9696
F2	9.70 ± 1.17	0.9188	1.21 ± 0.23	0.8162	0.76 ± 0.06	0.9697
F3	20.0 ± 2.4	0.9223	2.43 ± 0.46	0.8168	1.53 ± 0.11	0.9698
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0238–0.0455 t = 10–60 min		α = 0.0039–0.0064 t = 10–60 min		α = 0.0029–0.0050 t = 10–60 min	
D1	0.50 ± 0.02	0.9904	0.0086 ± 0.0000	0.9541	0.0054 ± 0.0000	0.9694
D2	0.25 ± 0.01	0.9901	0.0043 ± 0.0000	0.9541	0.0027 ± 0.0000	0.9694
D3	0.06 ± 0.00	0.9898	0.0010 ± 0.0000	0.9541	0.0006 ± 0.0000	0.9694
D4	0.06 ± 0.00	0.9971	0.0004 ± 0.0000	0.9489	0.0001 ± 0.0000	0.8865
F1	7.41 ± 0.12	0.9986	0.82 ± 0.09	0.9409	0.69 ± 0.05	0.9700
F2	7.68 ± 0.12	0.9987	0.83 ± 0.09	0.9410	0.70 ± 0.05	0.9700
F3	15.9 ± 0.3	0.9987	1.67 ± 0.18	0.9411	1.40 ± 0.11	0.9701

Table 5
Fitting of the experimental results obtained by the Lewis cell in the system: 0.005 M Cr(III)–0.3 M NaOH–0.10 M Aliquat 336, to the selected kinetic models.

Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0053–0.1051 t = 0–60 min		α = 0.0031–0.0569 t = 0–60 min		α = 0.0026–0.0439 t = 0–60 min	
D1	3.32 ± 0.12	0.9919	1.00 ± 0.04	0.9887	0.52 ± 0.01	0.9962
D2	1.72 ± 0.06	0.9926	0.51 ± 0.02	0.9890	0.26 ± 0.01	0.9960
D3	0.39 ± 0.01	0.9932	0.12 ± 0.01	0.9892	0.06 ± 0.00	0.9958
D4	0.36 ± 0.01	0.9942	0.10 ± 0.00	0.9899	0.06 ± 0.00	0.9853
F1	26.7 ± 4.5	0.8502	14.8 ± 2.4	0.8654	11.5 ± 1.2	0.9464
F2	28.5 ± 4.6	0.8620	15.3 ± 2.4	0.8703	11.8 ± 1.2	0.9496
F3	60.8 ± 9.3	0.8734	31.7 ± 4.8	0.8751	24.2 ± 2.4	0.9527
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0486–0.1051 t = 10–60 min		α = 0.0235–0.0569 t = 10–60 min		α = 0.0146–0.0439 t = 10–60 min	
D1	3.32 ± 0.13	0.9919	1.00 ± 0.05	0.9887	0.58 ± 0.01	0.9980
D2	1.72 ± 0.07	0.9926	0.51 ± 0.02	0.9890	0.29 ± 0.01	0.9981
D3	0.39 ± 0.01	0.9932	0.12 ± 0.01	0.9892	0.07 ± 0.00	0.9982
D4	0.36 ± 0.01	0.9942	0.10 ± 0.01	0.9899	0.06 ± 0.00	0.9980
F1	19.4 ± 2.4	0.9298	11.4 ± 1.9	0.8773	9.96 ± 0.95	0.9647
F2	21.1 ± 2.5	0.9349	11.9 ± 1.9	0.8801	10.3 ± 1.0	0.9666
F3	45.9 ± 5.2	0.9399	24.9 ± 4.0	0.8828	21.2 ± 1.9	0.9685
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0711–0.1051 t = 20–60 min		α = 0.0350–0.0569 t = 20–60 min		α = 0.0228–0.0439 t = 2–60 min	
D1	2.51 ± 0.12	0.9906	1.00 ± 0.05	0.9887	0.58 ± 0.02	0.9965
D2	1.31 ± 0.06	0.9911	0.51 ± 0.03	0.9889	0.30 ± 0.01	0.9967
D3	0.31 ± 0.01	0.9915	0.12 ± 0.01	0.9892	0.07 ± 0.00	0.9969
D4	0.29 ± 0.01	0.9915	0.10 ± 0.01	0.9904	0.06 ± 0.00	0.9980
F1	15.5 ± 1.2	0.9786	8.97 ± 1.90	0.8417	8.88 ± 0.92	0.9681
F2	17.1 ± 1.2	0.9802	9.42 ± 1.98	0.8443	9.19 ± 0.93	0.9696
F3	37.4 ± 2.6	0.9817	19.8 ± 4.1	0.8470	19.0 ± 1.9	0.9711

Table 6
Fitting of the experimental results obtained by the Lewis cell in the system: 0.005 M Cr(III)–0.5 M NaOH–0.10 M Aliquat 336, to the selected kinetic models.

Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0071–0.0574 t = 0–60 min		α = 0.0033–0.0274 t = 0–60 min		α = 0.0014–0.0239 t = 0–60 min	
D1	0.83 ± 0.06	0.9682	0.20 ± 0.01	0.9830	0.16 ± 0.01	0.9947
D2	0.42 ± 0.03	0.9691	0.10 ± 0.01	0.9834	0.08 ± 0.00	0.9946
D3	0.10 ± 0.01	0.9701	0.02 ± 0.00	0.9838	0.02 ± 0.00	0.9886
D4	0.09 ± 0.01	0.9758	0.02 ± 0.00	0.9936	0.02 ± 0.00	0.9721
F1	12.5 ± 2.2	0.8412	6.03 ± 0.97	0.8620	6.29 ± 0.53	0.9584
F2	13.0 ± 2.2	0.8473	6.13 ± 0.98	0.8648	6.37 ± 0.53	0.9597
F3	26.9 ± 4.5	0.8534	12.5 ± 2.0	0.8676	12.9 ± 1.1	0.9610
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0300–0.0574 t = 10–60 min		α = 0.0138–0.0274 t = 10–60 min		α = 0.0071–0.0239 t = 10–60 min	
D1	0.75 ± 0.05	0.9787	0.18 ± 0.01	0.9924	0.18 ± 0.01	0.9938
D2	0.38 ± 0.02	0.9788	0.09 ± 0.00	0.9925	0.09 ± 0.00	0.9938
D3	0.09 ± 0.01	0.9790	0.02 ± 0.00	0.9926	0.02 ± 0.00	0.9939
D4	0.08 ± 0.01	0.9794	0.02 ± 0.00	0.9937	0.02 ± 0.00	0.9932
F1	8.86 ± 0.81	0.9595	4.40 ± 0.34	0.9706	5.60 ± 0.51	0.9604
F2	9.27 ± 0.83	0.9609	4.49 ± 0.34	0.9713	5.70 ± 0.51	0.9614
F3	19.4 ± 1.7	0.9623	9.18 ± 0.69	0.9720	11.6 ± 1.0	0.9624
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.0387–0.0574 t = 20–60 min		α = 0.0185–0.0274 t = 20–60 min		α = 0.0127–0.0239 t = 20–60 min	
D1	0.70 ± 0.06	0.9679	0.17 ± 0.01	0.9924	0.16 ± 0.00	0.9970
D2	0.36 ± 0.03	0.9676	0.09 ± 0.00	0.9923	0.08 ± 0.00	0.9970
D3	0.08 ± 0.01	0.9674	0.02 ± 0.00	0.9971	0.02 ± 0.00	0.9885
D4	0.08 ± 0.01	0.9668	0.02 ± 0.00	0.9912	0.02 ± 0.00	0.9896
F1	7.66 ± 0.64	0.9723	3.83 ± 0.14	0.9951	4.86 ± 0.41	0.9723
F2	8.05 ± 0.68	0.9724	3.92 ± 0.14	0.9951	4.95 ± 0.41	0.9727
F3	16.9 ± 1.4	0.9724	8.02 ± 0.28	0.9951	10.1 ± 0.8	0.9732

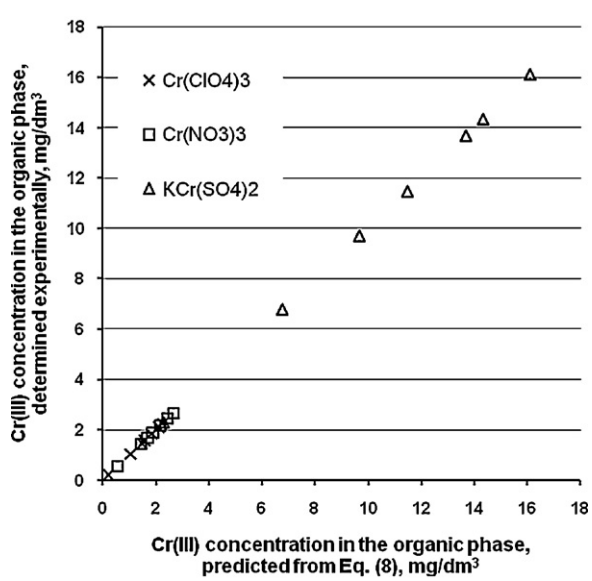

Fig. 6. The fitting of experimental values of concentration of chromium(III) extracted to the organic phase with these values predicted from the theoretical model (8). The organic phase: $c^0_{Alq} = 0.05$ M. The aqueous phases: $c^0_{Cr(III)} = 0.005$ M and $c^0_{NaOH} = 0.3$ M.

of the extractant concentration as well as a decrease of NaOH concentration affect positively the extraction of chromium(III) in the each examined system. However, comparing results obtained under the same conditions it should be noted that the most amount of chromium(III) is extracted to the organic phase in the system with the alkaline solutions of sulphates.

Taking into account small changes of concentration of chromium(III) in the organic phase and assuming that distribution ratio (D) is constant in the experiment, Eq. (8), given below, can be used for the estimation of mass transfer coefficients (k) by fitting theoretical results with the experimental data:

$$c_o(t) = \frac{D(c^0_o V_o + c^0_a V_a)}{DV_o + V_a} - \frac{V_o(Dc^0_a - c^0_o)}{DV_o + V_a} \exp\left[-\frac{ktS(DV_o + V_a)}{DV_o V_a}\right] \quad (8)$$

where: superscript “0” means initial value.

The calculated values of mass transfer coefficients are presented in Table 1. These results confirm findings coming from Fig. 5 that quantity of Cr(III) transferred from the aqueous to the organic phase depends on composition of these phases. Namely, values of k increase:

- with the decreasing concentration of NaOH in the aqueous phase,
- with the increasing concentration of Aliquat 336 in the organic phase, and
- in the following order of anions occurring in the aqueous phase: $ClO_4^- < NO_3^- < SO_4^{2-}$.

Table 7
Fitting of the experimental results received from the equilibrium experiments in the system: 0.005 M Cr(III)–NaOH–0.05 M Aliquat 336, to the selected kinetic models.

Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.733–0.959 t = 5–60 min		α = 0.693–0.986 t = 5–60 min		α = 0.642–0.949 t = 5–60 min	
0.3 M NaOH						
D1	98.9 ± 22.9	0.7470	116 ± 16	0.8893	124 ± 17	0.8998
D2	121 ± 22	0.8275	131 ± 14	0.9382	130 ± 13	0.9413
D3	85.5 ± 9.5	0.9297	81.1 ± 4.1	0.9849	72.2 ± 4.2	0.9797
D4	39.9 ± 6.2	0.8686	41.3 ± 3.5	0.9587	39.5 ± 3.4	0.9578
F1	528 ± 58	0.9327	498 ± 27	0.9828	446 ± 29	0.9744
F2	6401 ± 158	0.9964	4407 ± 119	0.9956	2954 ± 116	0.9907
F3	129,549 ± 16,100	0.9152	85,389 ± 10,979	0.9084	44,398 ± 4489	0.9416
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.439–0.928 t = 5–300 min		α = 0.325–0.807 t = 5–300 min		α = 0.310–0.794 t = 5–300 min	
0.5 M NaOH						
D1	35.8 ± 5.7	0.7930	31.3 ± 3.5	0.8761	31.8 ± 2.7	0.9307
D2	34.7 ± 4.4	0.8624	25.1 ± 2.3	0.9139	24.7 ± 1.7	0.9541
D3	17.8 ± 1.4	0.9380	9.60 ± 0.65	0.9514	9.11 ± 0.45	0.9762
D4	10.2 ± 1.1	0.8922	6.68 ± 0.56	0.9283	6.50 ± 0.40	0.9628
F1	114 ± 11	0.9141	71.5 ± 6.7	0.9121	70.7 ± 5.1	0.9507
F2	684 ± 13	0.9964	216 ± 9	0.9795	234 ± 6	0.9955
F3	10,167 ± 607	0.9655	1421 ± 18	0.9982	1141 ± 51	0.9861
Model	$KCr(SO_4)_2$		$Cr(NO_3)_3$		$Cr(ClO_4)_3$	
	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2	$(k_T \pm S.D.) \times 10^{-6}$ (s^{-1})	R^2
	α = 0.439–0.683 t = 5–30 min		α = 0.325–0.670 t = 5–90 min		α = 0.310–0.673 t = 5–120 min	
0.5 M NaOH						
D1	181 ± 6	0.9961	66.1 ± 3.6	0.9797	52.5 ± 1.8	0.9914
D2	135 ± 7	0.9896	47.1 ± 1.8	0.9900	37.3 ± 0.9	0.9960
D3	57.6 ± 3.3	0.9871	15.4 ± 0.4	0.9955	12.2 ± 0.3	0.9954
D4	34.7 ± 2.1	0.9858	11.9 ± 0.4	0.9928	9.41 ± 0.21	0.9965
F1	376 ± 16	0.9926	136 ± 7	0.9804	109 ± 4	0.9927
F2	907 ± 83	0.9670	295 ± 8	0.9946	234 ± 6	0.9955
F3	4683 ± 264	0.9875	1321 ± 71	0.9804	1141 ± 51	0.9861

These conclusions correspond very well with these one established on the base of results obtained in the equilibrium studies described in Sections 3.1.1 and 3.1.2.

Moreover, the values of mass transfer coefficients determined from the model (Eq. (8)) are fitted quite well to the experimental data. Examples of matching of the experimental results with values of concentrations of chromium(III) in the organic phase predicted from the model (8) are illustrated in Fig. 6.

3.3. Kinetic models for chromium(III) extraction

As an enhancement of the kinetic studies we have attempted to define the factors limiting the rate of the chromium(III) extraction in the examined systems using the rate equations (kinetic models) applied usually for the kinetic analysis of heterogeneous processes or reactions. The different models describing the mechanism of such processes are proposed in literature [39].

The rate of heterogeneous process under conditions far from equilibrium can be kinetically described by the following general equation in the differential form [40]:

$$\frac{d\alpha}{dt} = k_T f(\alpha) \tag{9}$$

where: α is an extent (progress) of process/reaction varying from 0 at the beginning of it to 1 when it is over, k_T is named the rate constant and it describes the dependence of the rate of process/reaction on temperature, $f(\alpha)$ is a term describing the relation between the rate of process/reaction and its mechanism.

After integration and introduction to the Eq. (9) the following designation:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) \tag{10}$$

the total integral form of the Eq. (9) is as follows:

$$g(\alpha) = k_T t \tag{11}$$

The integral forms of kinetic models which were selected by us for the kinetic analysis of the experimental results received from both the equilibrium and kinetic studies on the chromium(III) extraction in the tested systems are specified in Table 2.

An extent of the chromium(III) extraction (α) was measured by dimensionless fraction of Cr(III) extracted to the organic phase after any period of the extraction time and it was calculated according to Eq. (12):

$$\alpha = \frac{c_o}{c_a^0} \tag{12}$$

To select which of the rate equations given in Table 2 describes the most precisely the changes of α with time we examined the accuracy of mathematical fit of the experimental data to the relations between α and time expressed by the diffusion (D1–D4) and

order of reaction (F1–F3) models. The standard statistical criteria were used as a measure of linearity of the relations across defined α range. The rate constants (k_T) determined from the each of tested kinetic models (Table 2) and estimated for them values of standard deviations (S.D.) as well as determination coefficient (R^2) are presented in Tables 3–6 for the results obtained by the modified Lewis cell and in Table 7 for the data received using the typical extraction equipment.

From the kinetic analysis of results given in Tables 3–6, it comes that the diffusion models (D1–D4) are fitted the most precisely to the experimental data within the whole range of α or extraction time, irrespective of the composition of the aqueous and organic phases used. However, it can be noted (Tables 3–6) that within smaller ranges of α, which correspond to the period of time 10–60 min, the accuracy of fitting of experimental results with the reaction order models is already much better than this determined within time from 0 to 60 min. An improvement of the quality of fitting of data of α-time to the reaction order models (F1–F3) for the decreasing ranges of α is clearly seen in Tables 5 and 6 for the extraction of Cr(III) with 0.1 M solution of Aliquat 336. Namely, under these conditions, the fitting of experimental data to the reaction order models across the smallest ranges of α (or within 20–60 min) is very well, excepting results obtained in the system with nitrates and 0.3 M NaOH (Table 5).

The results in Table 7, determined from the classic extraction experiments, reveal that within the periods of time needed to reach the equilibrium (5–60 min and 5–300 min), the second order reaction expression (F2) from among the reaction models and the three-dimensional diffusion equation (D3) from among the diffusion models are the best descriptions of the extraction of chromium(III) in the all tested systems with 0.3 M and 0.5 M solutions of NaOH. However, it is evident that the accuracy of fitting of F2 model is much better than D3 model in the all systems. Besides, it should be noted that within these periods of time, satisfactorily linear relations are obtained also for the first-order reaction model (F1) in the system with 0.3 M NaOH and for the third-order reaction model (F3) in the systems with 0.5 M NaOH. Moreover, from Table 7 it comes that across the similar ranges of α (0.3–0.7), the all selected diffusion and reaction order models give very well fitting to the changes of α-time in the each system with 0.5 M NaOH.

Taking into account all results presented in Tables 3–7, it may be assumed that irrespective of the kind of anions present in the aqueous phase, the extraction of chromium(III) from alkaline media with Aliquat 336 is limited by both diffusion and chemical reaction and their contribution depends on the extent of process. This supposition is in a good agreement with the results obtained by the modified Lewis cell which indicate that the studied extraction of Cr(III) occurs in the mixed diffusion-kinetic regime (see Section 3.2.1).

4. Conclusions

It was shown that the equilibrium and the kinetics of chromium(III) extraction with Aliquat 336 from the alkaline aqueous solutions containing anions of different complexing abilities and solvating properties (nitrates, or perchlorates, or sulphates) depend strongly on compositions of the aqueous and organic phases as well as on the contact time of these phases. On the other hand, an increase of the extractant concentration in the organic phase, a reduction of NaOH concentration in the aqueous phase, and as a consequence, a decrease of the ionic strength of the aqueous phase as well as an elongation of contact time of phases have a positive effect on the kinetics and the equilibrium of chromium(III) extraction in the each studied systems.

Furthermore, under the same conditions the yield and the rate of Cr(III) extraction as well as values of mass transfer coefficient of Cr(III) calculated according to the theoretical model, increase in the following order of anions occurring in the aqueous phase: perchlorates < nitrates < sulphates, and consequently with the increase of their negative values of free energy of hydration.

It was found that the equilibrium of extraction of chromium(III) in the systems with perchlorates and/or nitrates differs considerably from that one established for the extraction of Cr(III) from the alkaline aqueous solutions of sulphates. Ionic pairs containing three trioctylmethylammonium cations prevail probably in the loaded organic phase in the systems with perchlorates and/or nitrates while the ion-pair complexes of Cr(III) with one trioctylmethylammonium cation dominate in the loaded organic phase in the system with sulphates.

Taking into account the mathematical kinetic models as well as the experimental results obtained by the modified Lewis cell it may be assumed that irrespective of the kind of anions present in the aqueous phase, the extraction of chromium(III) from alkaline media with Aliquat 336 is limited both by diffusion and chemical reaction and their contribution depends on the extent of process.

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