

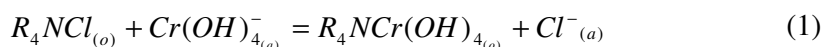
DEPENDENCE OF CHROMIUM(III) EXTRACTION FROM ALKALINE SOLUTIONS ON TEMPERATURE

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INTRODUCTION

In the previous studies [1,2,3] on extraction of chromium, it was proved that chromium(III) is effectively extracted with trioctylmethylammonium chloride (Aliquat 336) from alkaline aqueous solutions as tetrahydroxochromate(III) anions. As the initial concentration of chromium(III) in the aqueous phase is lower than the initial concentration of extractant and concentration of Aliquat 336 in the organic phase does not exceed 0.05 M, the equilibrium of extraction of Cr(III) from alkaline media can be described as follows [3]:



It has been found that experimental values of conditional extraction constants of chromium(III) (K_{ex}) determined at 25°C strongly depended on the ionic strength (I) of the aqueous phase in accordance with the following dependence [3]:

$$\log K_{ex} = (6.09 \pm 0.38) - (10.04 \pm 1.68) \frac{\sqrt{I}}{1 + \sqrt{I}} - (1.86 \pm 0.65)I; \quad (2)$$

$$R^2 = 0.9878; \text{ S.D.} = 0.10; \text{ F} = 1219; \text{ N} = 31.$$

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

In this work, I analyse the effect of temperature on equilibria of extraction of chromium(III) with Aliquat 336 from alkaline aqueous solutions.

EXPERIMENTAL

In all experiments, the initial concentrations of chromium(III) in the aqueous phases were kept within the range 0.003 – 0.024 M and were always lower than the initial concentration of Aliquat 336 varying from 0.02 to 0.05 M. The organic phases, solutions of Aliquat 336 in n-heptane, were modified with 1% (v/v) 1-decanol. The initial aqueous phases of chromium(III) were prepared from reagent

grade $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, NaOH , and distilled water. Their ionic strength ranged from 0.1 to 0.8 M.

Experiments were carried out at constant phase volume ratio of $V_o/V_a = 1:1$ and in constant time (3 h) while temperature varied from 0 to 50°C (273 – 323 K).

RESULTS AND DISCUSSION

Experimental values of extraction constants of chromium(III) (K_{ex}) were correlated with the reciprocal of absolute temperature (T) and the ionic strength (I) of the aqueous phase. The calculations have been performed according to the following model:

$$\log K_{\text{ex}} = f(1/T, \phi(I)) \quad (3)$$

where: $\phi(I)$ stands for the linear combination of terms involving ionic strength of the aqueous phase.

The following correlation was found:

$$\log K_{\text{ex}} = (19.44 \pm 0.38) - \frac{3887.0 \pm 84.6}{T} - (11.62 \pm 1.02) \frac{\sqrt{I}}{1 + \sqrt{I}} - (1.33 \pm 0.30)I; \quad (4)$$

$$R^2 = 0.9741; \text{ S.D.} = 0.15; \text{ F} = 1984; \text{ N} = 159.$$

The fitting of experimental values of extraction constants of Cr(III) (K_{ex} , observed) to these predicted from correlation (4) is presented in Fig.1.

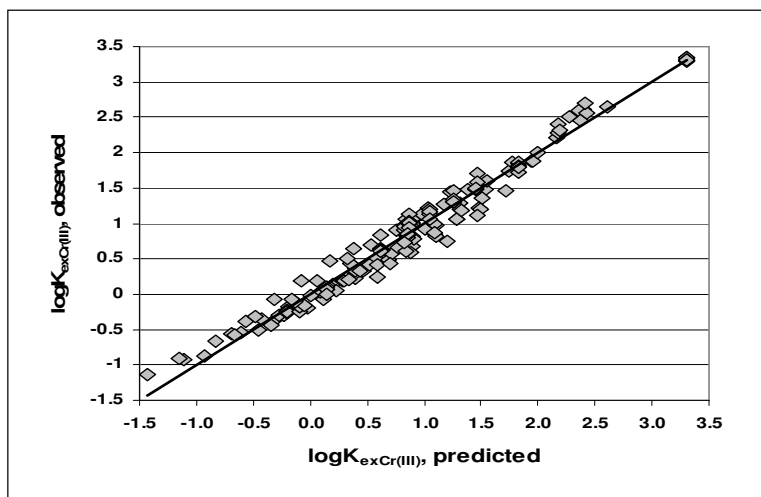


Fig.1. The fitting of the experimental extraction constants of Cr(III) to those calculated from dependence (4)

The very good statistical quality of correlation (4) allows for its use to determine the enthalpy change (ΔH_{ex}) of extraction of chromium(III) with Aliquat 336 from alkaline solutions. The value of enthalpy change calculated from Eq. (4) is positive and equal to 74.42 ± 1.62 kJ/mol, which indicates that extraction of chromium(III) with Aliquat 336 described by Eq. (1) is endoergic. Therefore, it should be expected that this process is entropy driven. Indeed, the values of entropy change (ΔS_{ex}) in the studied extraction system, calculated from Eq. (5)

$$\Delta S_{ex} = R \ln K_{ex} + \frac{\Delta H_{ex}}{T}, \quad (5)$$

are always positive and varying from 242.0 to 313.7 J/(mol.K). Entropy change depends only on ionic strength of the aqueous phase and decreases with the increase of ionic strength according to the following correlation:

$$\Delta S_{ex} = (380.7 \pm 3.4) - (265.0 \pm 10.2) \frac{\sqrt{I}}{1 + \sqrt{I}} - (14.0 \pm 3.0) I^2; \quad (6)$$

$$R^2 = 0.9637; \text{ S.D.} = 2.87 \text{ J/(mol} \cdot \text{K)}; \text{ F} = 2097; \text{ N} = 159.$$

Good accordance of the values of ΔS_{ex} determined from experimental data (Eq. 5) and these calculated from dependence (6) is illustrated in Fig.2.

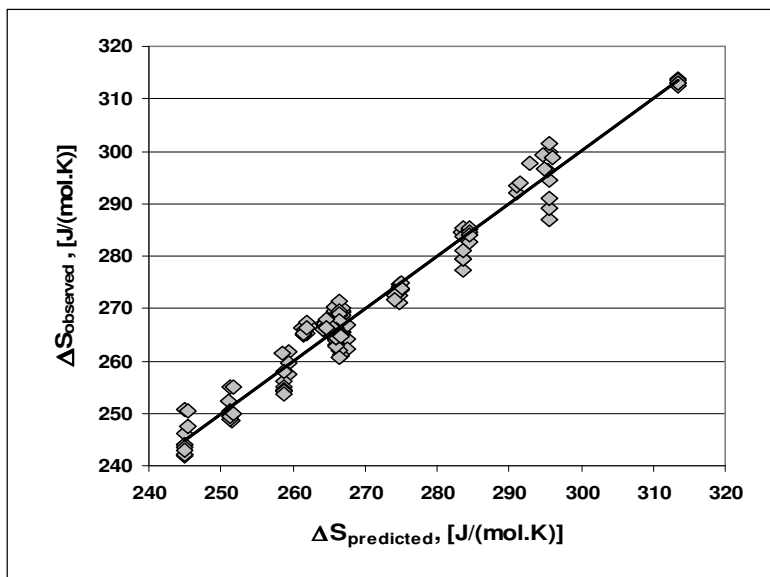


Fig.2. The fitting of entropy change calculated from Eq. (5) (ΔS_{ex} , observed) to those predicted from correlation (6).

The high and positive values of entropy change indicate that in Eq. (7) the negative term $T\Delta S_{\text{ex}}$ should prevail over value of ΔH_{ex} giving negative values of free energy (ΔG_{ex}) in the studied extraction process.

$$\Delta G_{\text{ex}} = \Delta H_{\text{ex}} - T\Delta S_{\text{ex}} \quad (7)$$

However, at suitably high ionic strength of aqueous phases and at lower temperatures, values of ΔG_{ex} are positive, which means, that equilibrium of extraction of chromium(III) shifts to the left side of Eq. (1). The mean values of the ionic strength and entropy change as well as temperature at which ΔG_{ex} is positive are presented in Table 1.

Table 1. Values of free energy (ΔG_{ex}) of extraction of chromium(III) with Aliquat 336 from alkaline solutions. (Negative values of ΔG_{ex} are indicated by “-“)

I mol/dm ³	ΔS_{ex} J/(mol·K)	ΔG_{ex} [J/mol]										
		273 K	278 K	283 K	288 K	293 K	298 K	303 K	308 K	313 K	318 K	323 K
0.82	245	5972	4806	4729	3144	2885	1732	1089	-	-	-	-
0.72	252	4794	3531	2978	2413	1023	-	-	-	-	-	-
0.61	259	2963	1716	932	93	-	-	-	-	-	-	-
0.57	262	2002	411	-	-	-	-	-	-	-	-	-
0.54	264	1822	354	-	-	-	-	-	-	-	-	-
0.52	266	1389	1348	-	-	-	-	-	-	-	-	-
0.51	266	1807	1046	-	-	-	-	-	-	-	-	-
0.50	267	1596	871	-	-	-	-	-	-	-	-	-
0.41	275	388	-	-	-	-	-	-	-	-	-	-
0.32	284	-	-	-	-	-	-	-	-	-	-	-
0.22	296	-	-	-	-	-	-	-	-	-	-	-
0.12	314	-	-	-	-	-	-	-	-	-	-	-

CONCLUSIONS

Analysis of the effect of temperature on extraction of chromium(III) with Aliquat 336 from alkaline solutions allows for estimation of thermodynamic functions involved. The positive value of ΔH_{ex} indicates the endoergic character of extraction described by Eq. (1) under studied conditions. At lower ionic strength of the aqueous phase, the high and positive values of entropy change indicate that the negative term $T\Delta S_{\text{ex}}$ prevails over positive ΔH_{ex} , which means, that extraction of chromium(III) with Aliquat 336 is an entropy driven process. An increase of ionic strength over 0.6 M leads to positive values of ΔG_{ex} and shifts the equilibrium of

extraction process towards formation of substrates. This negative effect of the ionic strength can be compensated in part for elevation of extraction temperature.

ACKNOWLEDGEMENTS

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