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Kinetic study of zirconium (IV) extraction by two aqueous phases

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Abstract

Zirconium (IV) extraction from its aqueous solutions using polyethoxylated alcohols (CiEj) as a biodegradable non-ionic surfactant was investigated. According to the given surfactant concentration, the extracted solute arrived at 88.1% for $C_{13}E_{10}$, in one step. The kinetic study shows that the model of diffusion of ions in the micelles controls the extraction of zirconyl by coacervate. The kinetic study shows that the film-diffusion controls the extraction of zirconyl by coacervate, using $C_{13}E_{10}$. The film-diffusion control and the model of diffusion of ions in the micelles controls the extraction of zirconyl by coacervate, using $C_{12}E_{10}$

Keywords : Cloud point; Zirconium (IV); $C_{12}E_{10}$ non-ionic surfactant; $C_{13}E_{10}$ non-ionic surfactant; Extraction

1. Introduction

The cloud point extraction is then an interesting alternative to traditional liquid-liquid extraction is widely used in hydrometallurgy [1,2] and has certain advantages over a conventional liquid-liquid extraction including simplicity and safety process (using only water and excluding volatile and flammable organic solvents commonly used in conventional liquid-liquid extraction), and the biodegradability of nonionic surfactants.

The cloud point extraction can be used in environmental cleanup of industrial effluent, concentration or separation of fine chemical products. It can be used for example for preconcentration [3-6] separation and / or purification of metal ions [2, 7, 8] metal chelate [9-11] biological materials [12, 13] and the organic compounds [14].

At present, the development of clean technologies is increasingly desired to preserve the environment. It is in this spirit that we set ourselves the objective of developing a remediation technique for extraction of zirconium simple, efficient and environmentally friendly.

Zirconium is made of alloys and employed in nuclear applications [15-17], as it does not absorb neutrons. Moreover, it is used in catalytic converters, percussion hats, furnace bricks and fuel slaving in nuclear industry, for its strong resistance to corrosion. It is also used in the thermal ionization mass spectrometry [18], extraction by chelating ion-exchange resin [19] and by solvent extraction [20].

In the present work, a kinetic study of zirconium (IV) is performed. The aqueous phase extraction process was initially applied to the separation of metals ions, in the presence of a chelating agent [21]. Later, this process was used in the extraction of many other chemical species, such as various metal ions, small organic molecules and molecules of biological interest [22-25].

2. Experimental

2.1. Reagents

Two commercial non-ionic surfactants used as extracting agents are retained, namely $C_{13}E_{10}$ (non-ionic surfactant polyoxyethylene 10 tridecyl ether) (T_c = 67°C at 1 wt.% in water, M_W = 640.9 g/mol, (CAS 24938-91-8), and $C_{12}E_{10}$ (decaethylene glycol monododecyl ether) (T_c= 97°C at 1wt.% in water, M_W = 626.9 g/mol, (CAS 6540-99-4) were purchased from Sigma Aldrich. The zirconyl salt ($ZrOCl_2$. 8 H_2O), sodium chloride, sodium thiocyanate, sodium sulphate, potassium chloride and nitric acid (60%) were purchased from Merck.

2.2. Apparatus

The determination of the cloud point was carried out using a MPC 602 Tanaka apparatus. Zirconyl (II) concentration was analyzed by atomic absorption spectrometer compact continuous source of high-resolution technique, model GBC 906AA.

2.3. Extraction procedure

For extraction tests, in sealed tubes, were put the mixtures: 25 mL of solution containing the surfactant at different concentrations in wt. %, and the solute (0.15 wt. % zirconyl (II)) in dematerialized water). Mixtures are heated in an accurate oven, then cooled down, and kept in a thermostated bath for 24 h to reach equilibrium. The volumes of both phases were registered and the dilute phase was analysed.

3. Results and discussion

3.1. Extraction yield

In order to explain the performance of non-ionic surfactant during the extraction by cloud point, we calculate the extraction yield (see Figure1).

For a variable quantity of non-ionic surfactant from 1 to 7 % mass, the salt concentration of NaCl was 5% mass.

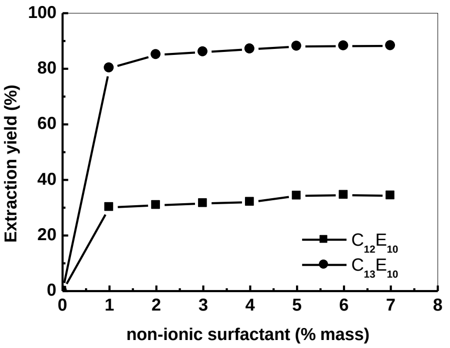

Fig 1. Effect of non-ionic surfactant concentration on the yield of extraction in $H_2O/C_{13}E_{10}/ZrO^{2+}$ at 60°C and $H_2O/C_{12}E_{10}/ZrO^{2+}$ at 70°C; 5% de NaCl

Figure 1 shows that the best extraction yield was obtained by the addition of NaCl 5% to $C_{13}E_{10}$.

The extraction increases gradually until reaching one to mitigate for the zirconyl representing the power of maximum extraction [26,27].

We also notice during the analysis of Figure 1 that the surfactant $C_{13}E_{10}$ is an excellent extractant for ZrO^{2+}. With $C_{13}E_{10}$, zirconyl is extracted up to 88.1 %; and with $C_{12}E_{10}$ only 34.0 % was extracted. These extractions were realized in one step.

3.2. Kinetics of phase separation

The kinetic study has been realized by stirring a mixture of surfactant solutions and zirconyl (II). We followed the evolution of the voluminal fraction of coacervate at different time intervals for the water/surfactant/electrolyte system (Figure 2).

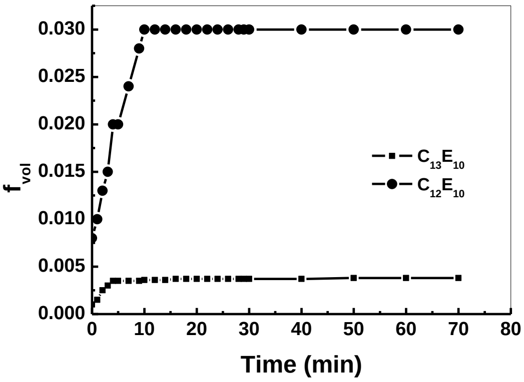

Fig 2. Evolution of the voluminal fraction of coacervate according to time; $[ZrO^{2+}] = 1.5$ g/l; $C_{13}E_{10} = 1\%$ & T = 60°C; $C_{12}E_{10} = 1\%$ & T = 70°C; 5% of NaCl.

In Figure 2 we can see that the evolution of the voluminal fraction of coacervate is not the same for $C_{13}E_{10}$ and $C_{12}E_{10}$. We notice that the interfaces are already formed after 10 min with $C_{12}E_{10}$ and 5 min with $C_{13}E_{10}$. This is very favourable from the hydrodynamic point of view. Coacervate is already limpid while the diluted phase remains still opaque because of the presence of some coacervate droplets.

3.3. Order of the reactions

The study of the order of the reaction of zirconyl extraction was realized using various forms of Nerst-Planck equation, as well as the mode of micelle diffusion.

The extraction by coacervate must be seen as a liquid-liquid reaction which includes several stages: diffusion of the zirconyl ions of the diluted phase towards micellar surface, diffusion of the zirconyl ions in coacervate, the chemical reaction between the metal ions and the functional groupings of surfactant (micelles).

The zirconyl extraction is governed by the slowest of these processes.

The kinetic models and the constants of equations for the three cases above were established. The exchange can be described by the equations of Nerst-Planck which apply to the diffusion of two species in almost homogeneous mediums [28].

This model was selected for its simplicity and its application in the field of adsorption of metal compounds on various adsorbents [28-30].

3.4. Diffusion of the ions of the diluted phase towards micellar surface

To represent the kinetic rate evolution in terms of fractional attainment at equilibrium, a simplified rate equation has been derived from one of the approaches suggested in [31]. In this approach, the ionic process is considered formally analogous to a reversible, pseudo-first order chemical reaction:

$$M \underset{K'_f}{\overset{K_f}{\rightleftharpoons}} \overline{M} \qquad (1)$$

where M is zirconyl cation, K_f and K'_f are forward (from the diluted phase to coacervate) and reverse (from coacervate to the diluted phase) constants, which include constant geometric factors, such as the interfacial area and the solution volume.

Using the mass balance relation, valid throughout the uptake process,

$$(C = ([M]v_d / v_t + [\overline{M}]v_c / v_t) \qquad (2)$$

Over bar refers to the zirconyl (II) in the coacervate, v_t is the total volume, v_d and v_c are the volumes of the dilute phase and coacervate, respectively, C is the total concentration of zirconyl (II) in the system. It follows that:

$$\frac{d[\overline{M}]}{dt} = K_1 \cdot C - \left(K_f + k_{f'}\right)[\overline{M}] \qquad (3)$$

Which upon integration with the initial condition [M] = 0 at t = 0 and rearrangement, gives

$$\ln\left(1 - \frac{\left(K_{f+K_{f'}}\right) \cdot [\overline{M}]}{K_f \cdot C}\right) = -\left(K_f + k_{f'}\right) \cdot t \qquad (4)$$

By introducing the equilibrium condition, we can determine $\overline{D}$ and F, the distribution coefficient of zirconyl and the fractional attainment of equilibrium, respectively:

$$\overline{D} = \frac{K_f}{K_{f'}} = \frac{[\overline{M}]_{eq}}{[M]_{eq}} \qquad (5)$$

and

$$F = \frac{[\overline{M}]_t}{[\overline{M}]_{eq}} \qquad (6)$$

So, we obtain the rate equation as following:

$$\ln(1 - F) = -\left(K_f + K_{f'}\right) \cdot t = -K \cdot t \qquad (7)$$

where K (s^{-1}) is the experimentally observed overall rate constant.

The obtained equation is identical to the rate law proposed by Boyd, Adamson and Meyers [32], for a film-diffusion control when the ingoing ion is a microcomponent of the system.

For an isotropic exchange under film-diffusion control, it has been demonstrated [33] that:

$$K \propto \frac{D \cdot C}{r_0 \cdot \delta \overline{C}} \qquad (8)$$

where D is the diffusion coefficient, C the concentration of the incoming ion in solution, r_0 is the radius of ZrO_2^{2+}, δ the diffusion film thickness and C the counter-ion concentration in the ion-exchanger.

The application of the equation (7) to zirconyl (II) extraction by coacervate, leds to the results exposed in Figure 3.

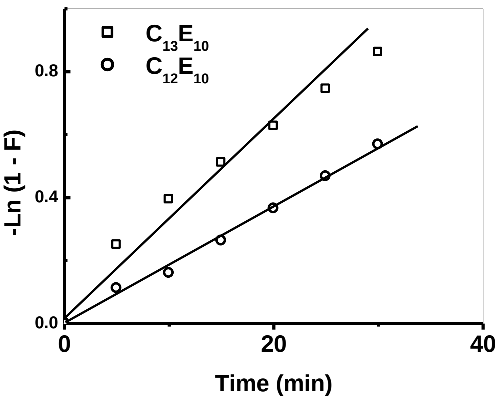

Fig 3. Plot of equation (7) for ZrO^{2+} extraction; $[ZrO^{2+}]$ = 1.5 g/l; NaCl = 5%; $C_{13}E_{10}$ = 1% and T = 60°C; $C_{12}E_{10}$ = 1% and T = 70°C.

3.5. Diffusion of ions in coacervate

When the inside diffusion is the rate controlling process, for the limiting case of isotropic exchange, a more appropriated rate equation is reported [33]:

$$-Ln\left(1 - F^2\right) = K \cdot t \qquad (9)$$

where, the constant K has the following meaning.

$$K \propto \frac{\overline{D}}{r_0^{\,2}} \qquad (10)$$

and D is the diffusion coefficient in the coacervate phase.

The application of equation (9) to zirconyl extraction by coacervate for the two surfactants, is given in Figure 4.

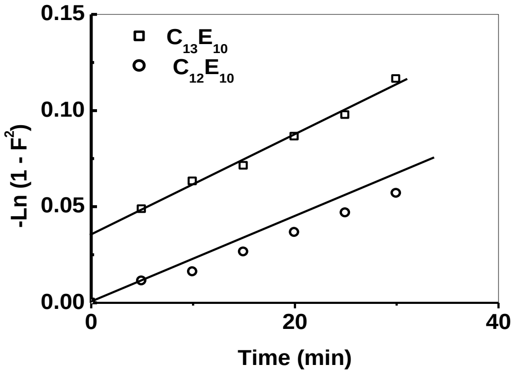

Fig 4. Plot of equation (9) for ZrO^{2+} extraction: $[ZrO^{2+}]$ = 1.5 g/l; NaCl = 5%; $C_{12}E_{10}$ = 1% and T = 70°C.; $C_{13}E_{10}$ = 1% and T= 60°C.

3.6. Mass transfer by chemical reaction

When the adsorption of metal ion involves mass transfer accompanied by chemical reaction, the process can be explained by the moving boundary model. This model assumes a sharp boundary that separates a completely reacted shell from an unreacted core and that advances from the surface toward the center of the solid with the progression of adsorption. In this case, the rate equation is given by:

$$3 - 3 \cdot (1 - F)^{2/3} - 2 \cdot F = K \cdot t \qquad (11)$$

The graphical correlation (Figure 5) given by equation 11, shows that the moving boundary particle diffusion model fits, only the initial adsorption of the tow aqueous phases.

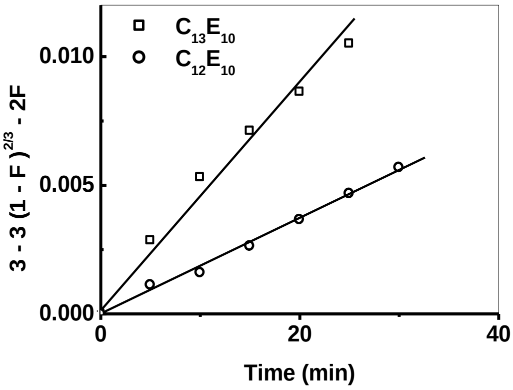

Fig 5. Plot of equation (11) for ZrO^{2+} extraction $[ZrO^{2+}]$ =1.5 g/l; NaCl =5%; $C_{12}E_{10}$ =1% and T= 70°C; $C_{13}E_{10}$ = 1% and T = 60°C

The linear regression analysis of functions was also given in Table 1.

Table-1-Constant rate and coefficient of correlation

Equation		$C_{13}E_{10}$	$C_{12}E_{10}$
-ln (1-F) = K t	K (mn^{-1}).10^2	2.72	1.87
	r^2	0.98943	0.99717
-ln (1- F^2) = K t	K (mn^{-1}).10^3	3.36	1.87
	r^2	0.95972	0.99717
3 - 3$(1-F)^{2/3}$- 2F = K t	K (mn^{-1}).10^4	4.8019	1.8707
	r^2	0.97931	0.99713

Table 1 shows that the film-diffusion control process is that best describes the extraction of zirconyl by coacervate, using $C_{13}E_{10}$ (r^2 = 0.98943). In contrast, the film-diffusion control and the model of diffusion of ions in the micelles are appropriate for the extraction of zirconyl by coacervate when $C_{12}E_{10}$ (r^2 = 0.99717) is used.

The surfactant $C_{13}E_{10}$ presents a very interesting industrial property because only the film-diffusion control process was determinant, in one step.

4. Conclusion

The results of the present study indicate that the extraction, in one step, of zirconium (IV) from chloride medium by cloud-point vary from 34.0% to 88.1% and the best performances are obtained for zirconyl using $C_{13}E_{10}$.

The optimal conditions for the extraction of zirconium (IV) by coacervate were determined and correspond to the following: the use of oxo-$C_{13}E_{10}$ as surfactant, an average concentration into non-ionic surfactant (1 wt %), 5 % wt of NaCl, a temperature lower by about 7°C than the cloud point of the used surfactant (T= 60°C) and 24 hours as time of decantation.

The kinetic study shows that the film-diffusion control describes the extraction of zirconyl by coacervate, using $C_{13}E_{10}$. The film-diffusion control and the model of diffusion of ions in the micelles describe the extraction of zirconyl by coacervate, using $C_{12}E_{10}$.

Acknowledgements

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