

Review

Stability of the emulsion (W/O): Application to the extraction of a Dawson type heteropolyanion complex in aqueous solution

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Abstract

Dawson type heteropolyanions form complexes with transition metals. These mixed complexes possess some remarkable electrocatalytic properties. Being soluble in aqueous and organic phases, they are used in homogeneous catalysis. In the setting of the recuperation and the regeneration of these complexes, the extraction of a mixed heteropolyanion ($\alpha_2\text{P}_2\text{W}_{12}\text{Mo}_5\text{O}_{61}\text{Fe}$)⁷⁻ is the subject of this work. This extraction was carried out by emulsified liquid membrane using (SPAN80) as surfactant and (TIBA) as extractant. Sulfuric acid was used as the internal phase. The stability of the emulsion was studied according to different parameters and the extracting efficiency in optimal conditions was found to be 70%.

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Keywords: Heteropolyanions; Dawson type; Homogeneous catalysis; Liquid surfactant membrane; Emulsion W/O

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1. Introduction

Since lately, polyoxometallates often known as heteropolyanions (HPA), are processing more and more applications well in homogeneous catalysis as in heterogeneous catalysis. The most utilized species are those of Keggin $(\text{PX}_{12}\text{O}_{40})^{n-}$ and Dawson–Wells $(\text{P}_2\text{X}_{18}\text{O}_{62})^{m-}$. Complexes $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ and $\text{K}_7\text{P}_2\text{W}_{17}\text{FeO}_{61}$ resulting from the saturated heteropolyanion $(\text{P}_2\text{W}_{18}\text{O}_{62})^{6-}$, catalyze the oxide-hydrogenation of isobutane to obtain isobutylene, this olefin is one of the important intermediaries in organic synthesis and especially in macromolecular synthesis. As catalysts these complexes are stable under conditions of oxidation until 500°C , but they become reactive when the reduction of their surfaces occurs and increases the contribution of an heterogeneous initiation of homogeneous reactions. The stability study of the structure has showed that beyond this temperature, the complex of the type Wells–Dawson $\text{K}_6\text{P}_2\text{W}_{18}\text{FeO}_{62}\cdot 10\text{H}_2\text{O}$ reacts and can be transformed into type of Keggin $\text{K}_3\text{PW}_{12}\text{O}_{40}$ [1]. In addition, during oxidation of isobutyric aldehyde to isobutyric acid using H_2O_2 in a solution of acetonitrile at 50°C , a study of the homogeneous catalysis in presence of $(\text{XM}_{12}\text{O}_{40})^{3-}$ and $(\text{X}_2\text{M}_{18}\text{O}_{62})^{6-}$ substituted with various metals in their incomplete structures (X: P^{5+} , Co^{3+} , Fe^{3+} , Cu^{2+} , Zn^{2+} and M: W^{6+}), has showed that the catalytic activity of catalyst, increases according reduction in the anion load. Moreover, by means of ^{31}P NMR and UV–vis, analysis has showed that a degradation of the structure of HPA $(\text{PZ(II)BrMo}_{11}\text{O}_{39})^{6-}$ (Z(II): Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}), could take place to give peroxide species of type $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$ [2]. In the literature it was indicated that the HPA of Keggin $[\text{SiW}_{11}\text{Mn}^{\text{III}}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$ had a certain pronounced selectivity in the oxidation of the lignin. This robust HPA which remains stable under the conditions of bleaching with the oxygen of an eucalyptus pulp can be re-used continuously during treatments knowing that the re-oxidation kinetics of the HPA by molecular oxygen is very slow [3].

The use of the polyanionic soluble species in homogeneous catalysis thus requires a treatment of recycling or regeneration adapted to separate catalyst from the products of the studied reaction. This operation constitutes a crucial stage in the continuation of the catalytic process. So the technique of separation by emulsified liquid membrane must be applied. From this point of view, an application was already carried out on the HPA of the type Dawson–Wells $(\alpha_1\text{P}_2\text{W}_{17}\text{O}_{61}\text{Fe})^{7-}$, the extraction efficiency of the polyanion exceeded 90% under optimal conditions with $(\text{NH}_4)_2\text{CO}_3$, (0.2 M) as internal phase. The regeneration of the membrane which depends on the concentration of the internal phase was carried out with a desextraction efficiency of 76% for the same internal phase but at 1 M [4].

The process of extraction with emulsified liquid membrane (ELM) which was produced for the first time by N.N. Li in 1968 [5], could currently reach the practical stage to which it was granted a great interest to its applications in various fields: In medicine for example, the hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ which is the main constituent of human bones and teeth, is very used as implants or layers on prostheses [6,7]. To study effect of Ca/P ratio on the texture and the morphology of this product, extraction by ELM was used with a biodegradable emulsifier and a fatty acid as extractant [8]. In hydrometallurgy, and by means of an ELM made up of Span80 (sorbitan mono-oleate) as surfactant, extraction of copper was carried out and effects of various parameters of the extraction process were studied, using LIX-84 and sulfuric acid, respectively as extractant and internal phase [9]. Using the same emulsifier, extraction of uranium from aqueous solution, was carried out with TOPO (trioctylphosphine oxide) as extractant in presence of a paraffin composed of (60%) C_{12} alkanes [10]. In addition, selective extraction of gallium from an acid solution containing other components (Fe, Co, Ni, Zn, Cd, Pb, Cu and Al), was carried out by ELM made up of the surfactant ECA4360J in kerosene, the extractant TOPO (trioctylphosphine oxide) and HCl as internal phase [11]. In biotechnology, extraction of penicillin G was optimized using an ELM made up of the emulsifying mixture Span80/ECA4360J in kerosene and Amberlite LA-2 as extractant [12,13]. Finally and generally in chemistry, organic acids, and many other products can be extracted by means of the emulsified liquid membranes [14].

By means of an extraction process using emulsified liquid membrane, the objective of this study was to recover a HPA of the type Dawson–Wells $(\alpha_2\text{P}_2\text{W}_{12}\text{Mo}_5\text{Fe})^{7-}$ which is a species having been the subject of an effective use in the electrocatalytic reduction of nitrates in a slightly acid phase [15]. This process consists in putting on contact the aqueous phase to treat with an emulsion water/oil (W/O) which composes the organic phase (membrane) and the internal aqueous solution. The phenomena brought into this process are physical (diffusion) and chemical (reaction with extractant) and they are very diversified. Before carrying out the extraction, a preliminary study of the stability of the emulsified liquid membrane was essential to determine the optimum conditions for a stable emulsion.

2. Experimental

2.1. Stability of the emulsion

To be ensured of the emulsion (W/O) stability, the method of the tracer which is in this case H^+ ion of the internal phase was applied because it is easily detectable by pH-meters. The

external phase was distilled water with known pH, the variation of its acidity would represent the rupture of the emulsion. Eq. (1) defines the rate of rupture (T_r) as the ratio of the volume (V_r) of the internal phase expelled by rupture towards the external phase, on the initial volume of the internal phase (V_{in}):

$$T_r = \frac{V_r}{V_{in}} \times 100 \quad (1)$$

2.1.1. Composition of the membrane

The membrane intended to extract the complex $(\alpha_2P_2W_{12}Mo_5O_61Fe)^{7-}$ was composed of tri-isobutylamine (TIBA) $[(CH_3)_2CHCH_2]_3N$ “Aldrich” as extractant, heptane “Riedel de Hean” as thinner and sorbitan mono-oleate (SPAN80) “Federated” as surfactant. This nonionic ester type emulsifier, was used in pH acid solution or slightly alkaline, and it favors an emulsion W/O due to its marked lipophilic character (HLB = 4.3).

2.1.2. Procedure

Emulsions were carried out by means of an homogenizer ULTRA-TURRAX T 18-10; A volume of 10 ml of H_2SO_4 (concentration to be optimized) and 10 ml of the organic phase (membrane) composed of (SPAN 80) 20%, (TIBA) 20% and heptane 60%, was introduced into a beaker with high form. The disperser was positioned on the level of the interface and was maintained during 5 min at constant temperature and speed (25 °C, 6000 rpm). Then, the prepared emulsion was dispersed into 200 ml of distilled water with known pH. The mixture was agitated, by a propeller agitator (type RW20 Kjank & Kunkel) with a speed of 200 rpm. The evolution of the pH of the external phase was followed by means of a pH meter (type HANA Hi 8519N) after 6 min of contact.

2.1.3. Determination of the volume of rupture (V_r)

According to the assessment matter (Eq. (2)), the volume expression of the internal phase expelled by rupture towards the external phase is given by Eq. (3).

$$V_r[H^+]_i = (V_r + V_{ex})[H^+]_t - V_{ex}[H^+]_o \quad (2)$$

$[H^+]_i$: concentration of H^+ ions in the intern phase before contact; $[H^+]_o$: concentration of H^+ ions in the aqueous phase before contact; $[H^+]_t$: concentration of H^+ ions in the extern aqueous phase at time (t); V_{ex} : volume of the extern phase before contact.

$$V_r = V_{ex} \frac{[H^+]_t - [H^+]_o}{[H^+]_i - [H^+]_t} \quad (3)$$

Knowing that $pH = -\log[H^+]$, the volume V_r is finally expressed directly according to the pH by Eq. (4).

$$V_r = V_{ex} \frac{10^{-pH} - 10^{-pHo}}{[H^+]_i - 10^{-pH}} \quad (4)$$

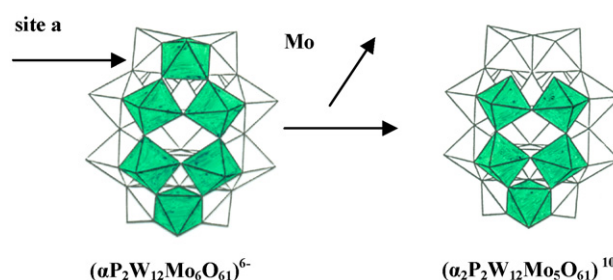


Fig. 1. Structure of heteropolyanions: saturated $(\alpha_2P_2W_{12}Mo_6O_61)^{6-}$ and lacunar $(\alpha_2P_2W_{12}Mo_5O_61)^{10-}$.

2.2. Extraction of $(\alpha_2P_2W_{12}Mo_5Fe)^{7-}$

2.2.1. Preparation of the heteropolyanion

The heteropolyanion $(\alpha_2P_2W_{12}Mo_5O_61Fe)^{7-}$ was prepared by addition of iron nitrate on the lacunar compound $(\alpha_2P_2W_{12}Mo_5O_61)^{10-}$, according to methods described in the literature [16]. The monovacant complex $(\alpha_2P_2W_{12}Mo_5O_61)^{10-}$ was obtained by reaction of elimination of the molybdate ion MoO_4^{2-} which was occupying the site “a” in the saturated complex $(\alpha_2P_2W_{12}Mo_6O_61)^{6-}$. The signs “ α ” and “2” in “ α_2 ”, indicate, respectively, that the two complexes have the same structure and that the lacuna is located in the site “a” (Fig. 1).

2.2.2. Procedure of extraction

The selected membrane was made up 20% of SPAN80 and 25% of TIBA in heptane as solvent. The internal phase was a solution of H_2SO_4 (1.5 M). By means of a mechanical agitator, the emulsified membrane was dispersed in a beaker containing 200 ml of solution to be treated (external phase). The initial concentration of the complex in the external phase was equal to 100 mg/l. To follow the extraction kinetics of the complex, samples taken away from the external phase, were analyzed according different times of contact from 2 to 8 min. Residual iron was detected by atomic absorption spectrophotometer (PerkinElmer). The initial concentration 1.5 mg/l of iron in the complex considered, was based as reference by atomic absorption. The kinetics of extraction should be presented as extraction rate constant which can be calculated from the data of $[Fe]$ and time. All tests were repeated and confirmed, the accuracy was less than 3% for $[Fe]$ and less than 2% for the yield of extraction.

3. Effects of operational parameters on the emulsion stability

To determine optimal conditions giving a stable emulsion, the following factors were followed: concentration of the tracer, stirring velocity, ratio of the volume of the membrane on the volume of the aqueous phase interns (O/A), ratio of the volume of the external phase on volume of the emulsion (V_{ex}/V_{em}), mass of extractant, mass of surfactant, choice of thinner and time of contact. Effects of these various parameters were studied by

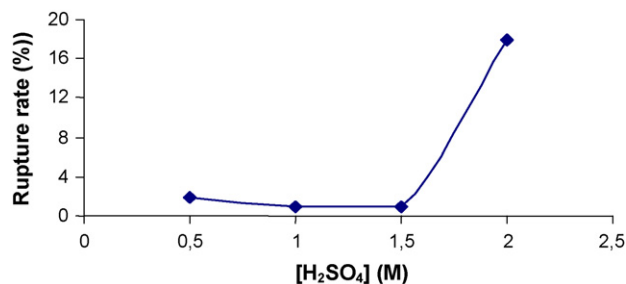


Fig. 2. Influence of the acid concentration on the rupture rate (stirring velocity = 200 rpm, (O/A) = 1, (V_{ex}/V_{em}) = 10, TIBA = 20%, SPAN80 = 20%, thinner: heptane, t = 6 min).

determining rates of rupture from measurements of pH of the external phase. The accuracy of the values of rupture rate was in the order of 12%.

3.1. Concentration of (H_2SO_4) in internal phase

The concentration of the acid from 0.5 to 2 M of the internal phase was studied under the following operating conditions: stirring velocity = 200 rpm, (O/A) = 1, (V_{ex}/V_{em}) = 10, TIBA = 20%, SPAN80 = 20%, thinner: heptane, time of contact = 6 min.

The obtained experimental results (Fig. 2) showed a constant rupture rate (approximately 1%) until 1.5 M concentration of H_2SO_4 . Beyond this concentration, the rate increased abruptly reaching approximately 18% for 2 M concentration of acid. This rupture with relatively high concentrations of acid in internal phase could be explained by a partial hydrolysis of the SPAN80 catalyzed by proton [17]. Products of the reaction would probably degrade the emulsified properties of the SPAN80, and destabilize the emulsion generating a high rupture rate. The concentration 1.5 M in acid of the internal phase can be regarded as a limiting concentration not to exceed. It would be selected as one of the operating conditions.

3.2. Stirring velocity

Using fixed concentration of acid in the internal phase (1.5 M) and maintaining the other parameters operational identical to those of the preceding experiment, the effect the stirring velocity (Fig. 3) on the rupture rate, was followed.

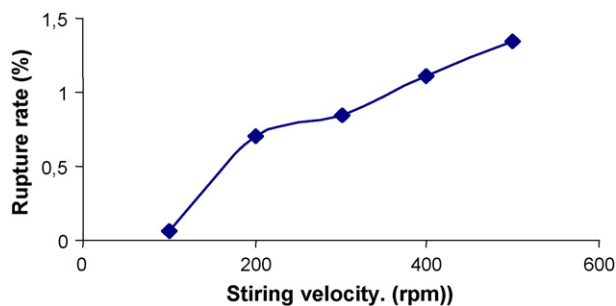


Fig. 3. Influence of the stirring velocity on the rupture rate ($[H^+] = 1.5$ M, (O/A) = 1, (V_{ex}/V_{em}) = 10, TIBA = 20%, SPAN80 = 20%, thinner: heptane, t = 6 min).

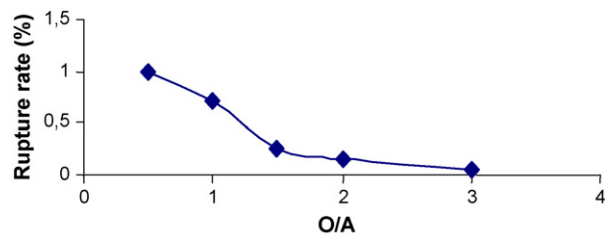


Fig. 4. Influence of the O/A ratio on the rupture rate ($[H^+] = 1.5$ M, stirring velocity = 300 rpm, (V_{ex}/V_{em}) = 10, TIBA = 20%, SPAN80 = 20%, thinner: heptane, t = 6 min).

The stirring velocity had not a great influence on the rupture rate; indeed, until a speed of 500 rpm, the rupture rate did not exceed 1.35%. A mean velocity of 300 rpm was selected for two reasons; first a high speed had being avoided because it would cause an important shearing of the inter-facial film, and second a low speed was not recommended for kinetics of appreciable extraction.

3.3. (O/A) ratio

In the conditions chosen up to now, the effect of the ratio O/A of volumes (membrane: (O) and intern aqueous phase: (A)) was followed. The results which were obtained, showed that the increase in ratio O/A implies a reduction in the rupture rate (Fig. 4), this reduction can be explained by the fact that the increase in the volume of the membrane involves an increase in the viscosity of the emulsion (a high viscosity is generally favorable to the stability of the emulsion). The viscosity of the membrane phase has a large effect on the mass transfer rate. An increase in membrane phase viscosity decreases the diffusion coefficient and mass transfer coefficient [18]. However a high ratio O/A generates a very thick film of the membrane, which would slow down the transfer of the aqueous solution. The O/A ratio equal 2 would be thus a good choice according to the stability of the membrane and the kinetics of the extraction.

3.4. (V_{ex}/V_{em}) ratio

For V_{ex}/V_{em} ratios going from 5 to 20, an optimum appears in the neighborhoods of 10 as shown in Fig. 5. Beyond this value, the emulsion becomes unstable and the considerable increase in the value of the rupture rate can be explained by diffusion of the

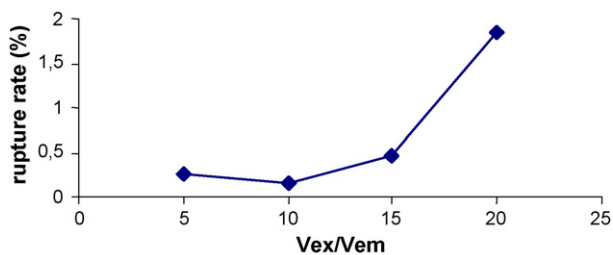


Fig. 5. Influence of the V_{ex}/V_{em} ratio on the rupture rate ($[H^+] = 1.5$ M, stirring velocity = 300 rpm, (O/A) = 2, TIBA = 20%, SPAN80 = 20%, thinner: heptane, t = 6 min).

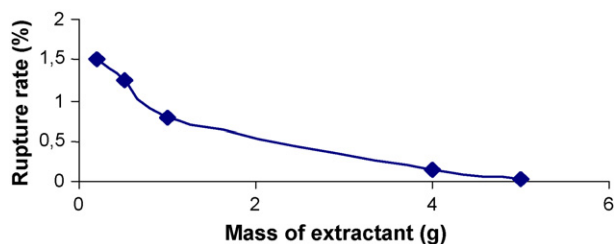


Fig. 6. Influence of the quantity of extractant on the rupture rate ($[H^+] = 1.5$ M, stirring velocity = 300 rpm, $(V_{ex}/V_{em}) = 10$, $(O/A) = 2$, SPAN80 = 20%, thinner: heptane, $t = 6$ min).

H^+ ions towards the least concentrated phase (phenomenon of osmosis).

3.5. Masses of extractant and surfactant

The increase in the mass of extractant which has a raised viscosity, improves the stability of the emulsion. Indeed, starting from 5 g corresponding to 25%, the rupture rate reaches a very low value (Fig. 6). On the other hand, the mass of the surfactant which is more viscous than extractant, stabilizes the membrane; for masses going from 1 to 8 g, the rupture rate as shown in Fig. 7, lies between 0.2% and approximately 0%. Knowing that for 4 g (20%) of surfactant, the rupture rate is about 0.03%, this percentage can be regarded as optimum.

Values of 25% of TIBA and 20% of SPAN80 will be thus selected for the extraction.

3.6. Thinner

A comparative study between two thinners *n*-heptane and *n*-hexane was undertaken while following the rupture rate. The experimental results which were obtained, showed that the membrane is slightly more stable in heptane than in hexane (Fig. 8). This phenomenon could be probably explained by the improvement of certain physical properties of the membrane and in particular its viscosity.

3.7. Time of contact

According to time of contact from 2 to 12 min, the rupture rate varies very slightly (Fig. 9) and did not exceed 0.12%. This is why; selected parameters gave satisfaction for a stable emulsion in this time interval of contact. The time of optimal contact will thus be dictated by the kinetics of extraction.

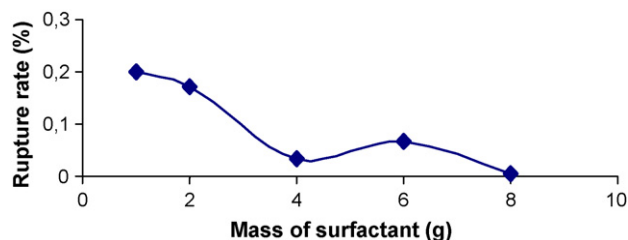


Fig. 7. Influence of the quantity of surfactant on the rupture rate ($[H^+] = 1.5$ M, stirring velocity = 300 rpm, $(V_{ex}/V_{em}) = 10$, $(O/A) = 2$, TIBA = 25%, thinner: heptane, $t = 6$ min).

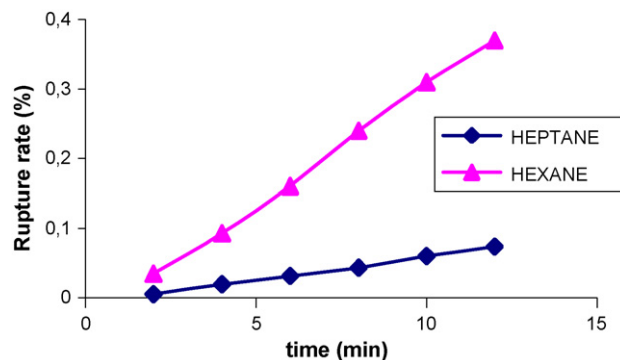


Fig. 8. Effect of the thinner on the rupture rate ($[H^+] = 1.5$ M, stirring velocity = 300 rpm, $(V_{ex}/V_{em}) = 10$, $(O/A) = 2$, TIBA = 20%, TIBA = 25%, SPAN80 = 20%, $t = 6$ min).

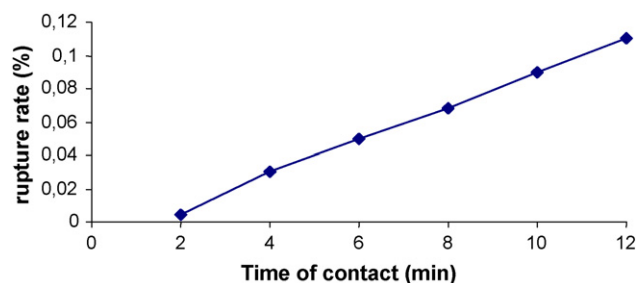


Fig. 9. Influence of the time on the rupture rate ($[H^+] = 1.5$ M, stirring velocity = 300 rpm, $(V_{ex}/V_{em}) = 10$, $(O/A) = 2$, TIBA = 25%, SPAN80 = 20%, thinner: heptane).

4. Optimal conditions of the extraction

The extraction of the complex by emulsified liquid membrane has been studied according to the following factors: ratio of the organic phase on the internal phase (O/A), stirring velocity, ratio of the external phase volume on the emulsion volume (V_{ex}/V_{em}), mass of the extractant (TIBA) and pH of the external phase.

4.1. O/A ratio

In order to study the influence of the O/A ratio on the kinetics of extraction, different values from 1 to 3 of this active ratio have been reported. Results of the influence of the O/A ratio on the

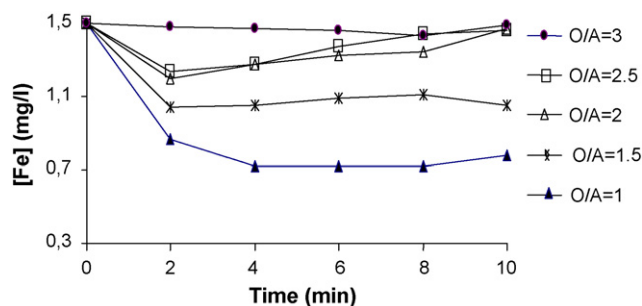


Fig. 10. Influence of the (O/A) ratio on the extraction of iron ($[H^+] = 1.5$ M, stirring velocity = 300 rpm, $(V_{ex}/V_{em}) = 10$, TIBA = 25%, SPAN80 = 20%, thinner: heptane).

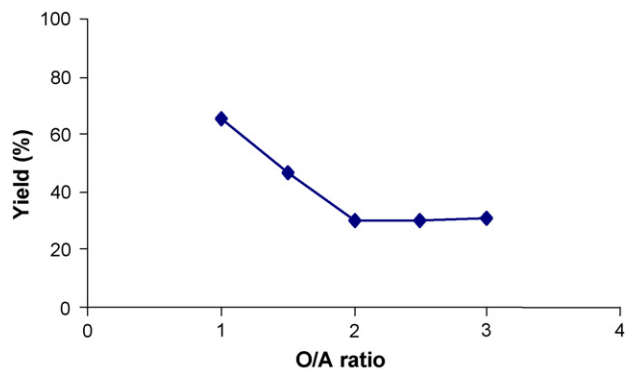


Fig. 11. Influence of (O/A) ratio on the yield of extraction at 8 min.

kinetics of extraction are represented by curves in Fig. 10 and the yield in Fig. 11.

Results showed that for ratios (O/A) higher than the unit, the kinetics of the extraction becomes slow, this phenomenon can be explained by the increase of the membrane thickness involving an increase of the thickness of the inter-facial film of the globules and consequently, it slows down the diffusion of the aqueous solution in the globules. The optimal ratio O/A of extraction is thus equal to the unit and the corresponding yield is equal to 65%.

4.2. Stirring velocity

Speeds used were: 150, 200, 250, 300 and 350 rpm. Results of the stirring velocity influence on the extraction kinetics are represented in Fig. 12.

The increase of stirring velocity beyond 250 rpm would cause an important shearing, involving the rupture of the emulsion from where the expulsion of the aqueous solution already extracted the internal phase towards the external phase. This phenomenon affects the stability of the emulsion and increases the osmotic swelling of the membrane and makes the emulsion unstable [19,20]. It involves a reduction of the yield of extraction. For low stirring velocities, the kinetics is slow. Its optimal value is thus about 250 rpm for a yield of extraction approximately equals to 70% (Fig. 13).

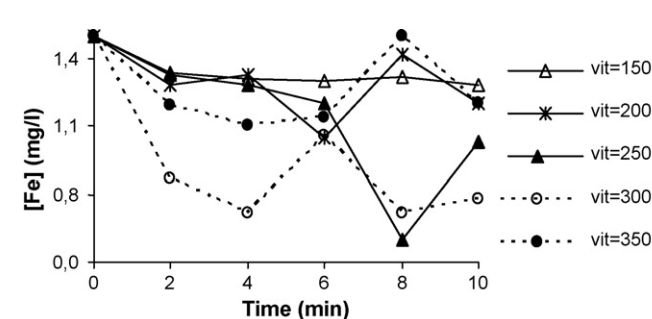


Fig. 12. Kinetics of the extraction at different stirring velocities ($[H^+] = 1.5$ M, (O/A) = 1, (V_{ex}/V_{em}) = 10, TIBA = 25%, SPAN80 = 20%, thinner: heptane).

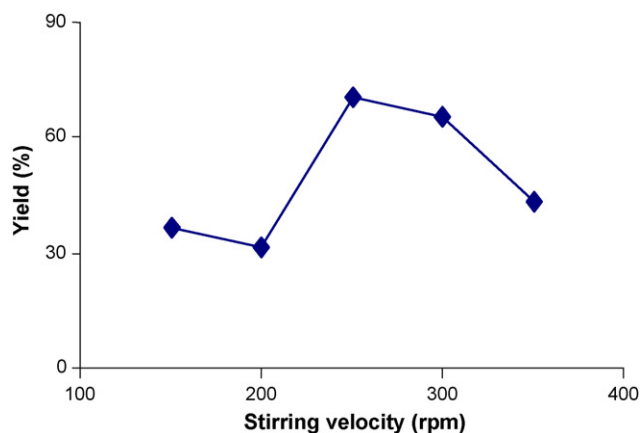


Fig. 13. Effect of stirring velocity on the yield of extraction.

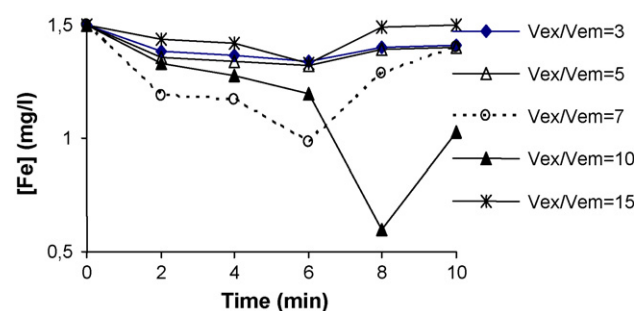


Fig. 14. Influence of the V_{ex}/V_{em} ratio on the kinetics of extraction ($[H^+] = 1.5$ M, stirring velocity = 250 rpm, (O/A) = 1, TIBA = 25%, SPAN80 = 20%, thinner: heptane).

4.3. V_{ex}/V_{em} ratio

In this experiment, ratios of volumes which varied from 3 to 10 (volume of the external phase on the volume of emulsion), have different effects on the extraction of iron (Fig. 14). Results showed that for high V_{ex}/V_{em} ratios, the yield of extraction is weak (35% for a ratio of 15). That can be explained by the instability of the membrane (Fig. 5). The increase in the volume of the emulsion for low V_{ex}/V_{em} ratios, would cause more thickness of the membrane film, involving low kinetics and decreasing the yield of extraction. The optimal value is about 10 and the yield is thus around 70% (Fig. 15).

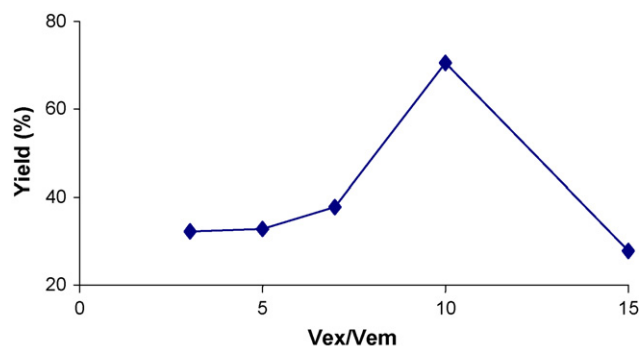


Fig. 15. Effect of the V_{ex}/V_{em} ratio on the yield of extraction.

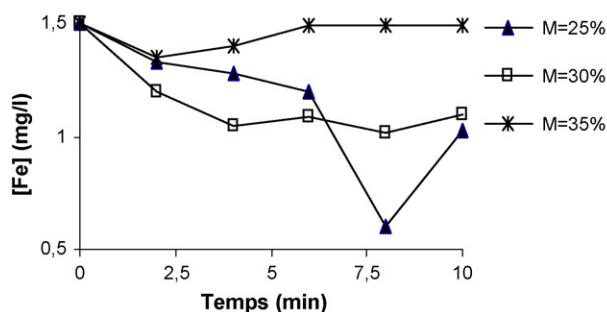


Fig. 16. Influence of the extractant mass on the kinetics of extraction ($[H^+] = 1.5$ M, stirring velocity = 250 rpm, $(V_{ex}/V_{em}) = 10$, $(O/A) = 1$, SPAN80 = 20%, thinner: heptane).

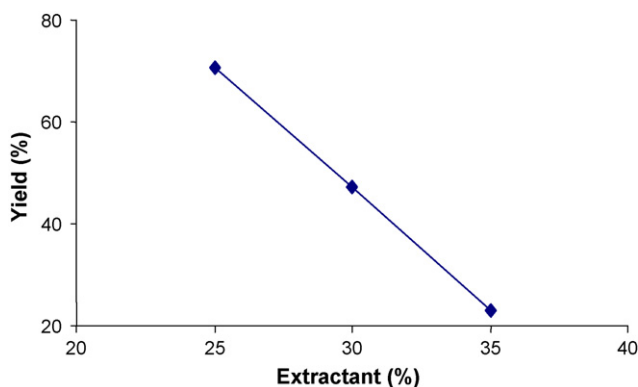


Fig. 17. Effect of the extractant mass on the yield of extraction.

4.4. Mass of extractant

The mass percentages of extractant in the membrane, tested were: 25%, 30%, 35%. The results obtained are illustrated in Fig. 16.

The mass of extractant increases the viscosity of the membrane that slows down the kinetics of extraction. The optimal mass in this case and which gives the best yield (70%), is 5 g correspondent to 25% (Fig. 17).

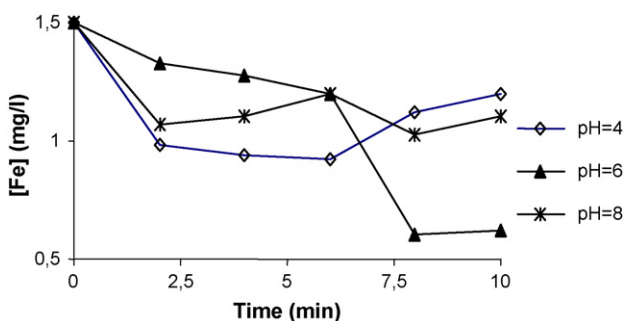


Fig. 18. Influence of pH on the kinetics of extraction ($[H^+] = 1.5$ M, stirring velocity = 250 rpm, $(V_{ex}/V_{em}) = 10$, $(O/A) = 1$, TIBA = 25%, SPAN80 = 20%, thinner: heptane).

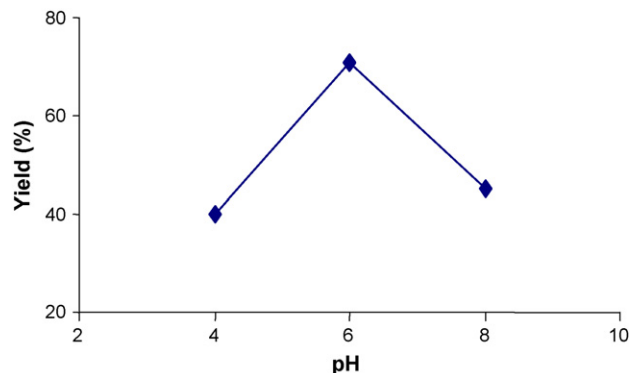


Fig. 19. Effect of pH on the yield of extraction.

4.5. pH of the external phase

In this experiment the kinetics of extraction of iron was studied according to different pH (Fig. 18). Indeed, the pH of the external phase influences the yield of the extraction; among the three values used, pH 6 seems to give the best result (Fig. 19).

The poor performance at low pH could be explained by the competition of H^+ ions with the solute due to the release of H^+ ions from extractant to the external phase. At high pH, the extraction efficiency is low and this is probably due to the instability of the emulsion; indeed, at these pH, the SPAN-80 loses its emulsified properties. The optimum pH is of the order of 6 for a yield of extraction of approximately 70%.

4.6. Time of contact

For a stirring velocity of 300 rpm, the yield of extraction reached about 65% during an optimal contact time of 4 min as showed in Figs. 10 and 12. On the other hand for a best performance under the optimized conditions, a time of extraction of 8 min became necessary. This time of contact is thus optimal for the highest yield of 70% (Figs. 14, 16 and 18).

5. Conclusion

After using Dawson–Wells heteropolyanions (HPA) as catalysts, their recovery becomes an essential stage before a probable industrialization of the process. The extraction by emulsified liquid membrane of the HPA ($\alpha_2P_2W_{12}Mo_5Fe$)⁷⁻ which could serve with effective manner in the electrocatalytic reduction of nitrates in a slightly acid solution, was the object this work. The study of a membrane made up of SPAN 80 as surfactant and TIBA as extractant according to the various important parameters, showed that the stability of emulsion W/O requires certain operating conditions. Indeed; for high concentrations of H_2SO_4 , the SPAN 80 would lose its surfactant properties. The increase of the stirring velocity would cause a shearing and the phenomenon of osmosis (swelling), involving a rupture of the emulsion. The increase in O/A ratio involves an increase in the viscosity of the emulsion making probably the transfer slow. The increase in the V_{ex}/V_{em} ratio would cause the instability of the membrane. The increase in the concentration of extractant and surfactant stabi-

lizes the emulsion and consequently, it returns the membrane viscous thus involving the deceleration of the solute diffusion. Taking account the stability of the emulsified liquid membrane, the optimal operating conditions for a maximum yield (70%) of extraction of the complex $(\alpha_2P_2W_{12}Mo_5O_{61}Fe)^{7-}$ are as follows:

Concentration of the acid in the interne phase: 1.5 M.
 Stirring velocity: 250 rpm.
 O/A ratio: 1.
 V_{ex}/V_{em} ratio: 10.
 Percentage of extractant in the membrane: 25%.
 Percentage of surfactant in the membrane: 20%.
 pH of the external phase: 6.
 Thinner: *n*-heptane.

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