



NEW COMPLEXONE DERIVATIVES OF 8-HYDROXY- QUINOLINE AND THEIRS APPLICATION IN UO_2^{2+} EXTRACTION

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New complexone derivatives of 8-hydroxyquinoline (quinolinol) were synthesized by the Mannich reaction from secondary and primary amines. Our syntheses were carried out either at room temperature, at reflux or under microwave irradiation, in good yields. The use of the 7-(dioctylamino methyl) quinolin-8-ol (3f) as new extractant for the uptake and removal of UO_2^{2+} was investigated. Conditions for an effective sorption were optimized. The total sorption capacity was 102 (mg.g⁻¹) under optimum experimental conditions.

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Introduction

Complexones according to Schwarzenbach definition are small chelating agents able to form chelate with metal ions.^{1,2} One of the most well known examples of complexone is ethylenediaminetetraacetic acid (EDTA).³ It was used for the chelation of metallic ions in analytical chemistry and as antioxidative compound. More generally, complexones present many applications in analytical chemistry and are also used in prevention of action of metallic ions as stabilising, anti-oxidative product.

8-Hydroxyquinoline (**1**) (8-HQ or quinolinol) is a non-specific ligand chelating a large variety of metal ions.^{4,5} 8-Hydroxyquinoline is able to chelate essential metallic ions for metabolism of bacteria and fungi, so 8-HQ derivatives are used as antibacterial and antifungal. 8-HQ complexes of Zn or Mn can be also used for such applications.⁶

Polymer containing 8-HQ group have been described as chelating polymers.⁷ Generally these polymers were obtained by a Beckland reaction of 8-HQ with formaldehyde. Such chelating polymer derivatives can be used in hydrometallurgy for the extraction of metals, such as iron, copper, nickel and uranium.⁸

Recently, metal complexes of 8-hydroxyquinolines were used in supramolecular chemistry as luminescent or fluorescent solids.⁹ We are interested in the synthesis of new

chelating molecules possessing 8-hydroxyquinoline group for the metal extraction⁸ and as precursor of new luminescent complexes.^{10,11}

As application, we suggested applying the compound **3f** as an extracting agent for the uptake and removal of the uranyl ion, using liquid-liquid extraction.

Experimental

All commercial reagents were purchased from Agfa or Aldrich, and were used as received without further purification. Reaction times were monitored by TLC until no starting material remained. TLC was performed using Silica gel 60 F₂₅₄ precoated aluminium sheets. ¹H and ¹³C NMR spectra are recorded on a Bruker AC 400 spectrometers. Mass spectra were recorded on a QTOF Micro (Waters) spectrometer with electrospray ionization (ESI, positive mode), lockspray orthophosphoric acid, infusion introduction at 10 μL min⁻¹, a source temperature of 80°C and desolvation temperature of 120°C. Molecular modelisation and energy minimisations were performed with MP3 using Spartan Software. Microwave irradiations were performed at 2450 MHz with a Synthwave 402 oven (Prolabo). Analytik Jena SPECORD 210 Double Beam UV-VIS was used for spectra recording and absorbance measurements. Spectra were recorded in the range from 400 to 800 nm with 0.2 nm resolution in 10 mm quartz cells. Data were processed with WinLab software.

pH measurements for all solutions were taken on a potentiometer Consort C831, with combined glass electrode, that was calibrated with pH 4.00, 7.00 and 10.00 buffer standards.

7-(morpholinomethyl)quinolin-8-ol (3a, C₁₄H₁₆N₂O₂)

Morpholine (1.8 mL, 20 mmol) and aqueous solution of formaldehyde (37 %, 2.7 mL) were added to 8-hydroxyquinoline (2.90 g, 20 mmol) dissolved in 35 mL of

ethanol. The resulting mixture was stirred overnight (12 h) at room temperature (20 °C). After evaporation under vacuum, an orange viscous liquid was obtained. Yield: 4.73 g (97 %); mp=66 °C (ethanol-water) (lit: mp=66 °C);¹⁴ 1H NMR (400 MHz, $CDCl_3$): δ = 2.67 (m, 4H, NCH_2CH_2), 3.76 (m, 4H, CH_2O), 3.88 (s, 2H, NCH_2), 7.27 (s, 2H, H^5 and H^6), 7.38 (dd, 1H, $J=4.2$ Hz and $J=8.4$ Hz, H^3), 8.07 (dd, 1H, $J=1.2$ Hz and $J=8.4$ Hz, H^4), 8.85 (dd, 1H, $J=1.2$ Hz and $J=4.2$ Hz, H^2) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 152.8, 149.0, 148.7, 139.2, 135.8, 128.5, 128.1, 121.4, 117.7, 67.0, 60.1, 53.3 ppm. The NMR spectra were identical to the literature.¹⁴

7-(thiomorpholinomethyl)quinolin-8-ol (3b, $C_{14}H_{16}N_2OS$)

Thiomorpholine (2.08 mL, 20 mmol) and aqueous solution of formaldehyde (37 %, 1.2 mL) was added to 8-hydroxyquinoline (2.90 g, 20 mmol) dissolved in 35 mL of EtOH. The resulting mixture was stirred 12 h at room temperature. After evaporation under vacuum, a yellow viscous liquid was obtained 5.14 g (99 %). 1H NMR (400 MHz, $CDCl_3$): δ = 2.82-2.83 (m, 4H, SCH_2CH_2), 2.94-2.95 (m, 4H, NCH_2CH_2), 3.95 (s, 2H, NCH_2Ar), 7.31 (s, 2H, H^5 and H^6), 7.39 (dd, 1H, $J=4.2$ Hz and $J=8.4$ Hz, H^3), 8.11 (dd, 1H, $J=1.6$ Hz and $J=8.4$ Hz, H^4), 8.88 (d, 1H, $J=1.6$ Hz and $J=4.2$ Hz, H^2) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 152.7, 148.9, 139.1, 135.7, 128.4, 127.9, 121.4, 117.7, 117.6, 60.8, 54.7, 28.1 ppm; IR (neat): ν = 3354, 2921, 2791, 1503, 1454, 1365, 1283 cm^{-1} ; MS (m/z) %: 261 (70 M+H), 158(100); ESI-HRMS calcd for $C_{14}H_{17}N_2OS$ 261.1062, found 261.1069.

7,7'-(piperazine-1,4-diylbis(methylene))diquinolin-8-ol (3c, $C_{24}H_{24}N_4O_2$)

Piperazine (0.86 g, 10 mmol) and aqueous solution of formaldehyde (37 %, 2.7 mL) were added to 8-hydroxyquinoline (2.90 g, 20 mmol) dissolved in 35 mL of EtOH. The resulting mixture was stirred overnight (12 h) at room temperature (20 °C). A yellow precipitate was observed; after filtration, it was washed with diethyl ether (25 mL) to give the product namely (3c) as a yellow solid, 2.48 g (62 %). m.p: 204 °C. 1H NMR (400 MHz, $DMSO-d_6$): δ = 2.50 (s, 2x4H, $NCH_2(CH_2N)$), 3.75 (s, 2x2H, $ArCH_2N$), 7.36 (d, 2xH, $J=8.4$ Hz, H^6), 7.47 (d, 2xH, $J=8.4$ Hz, H^5), 7.50 (dd, 2xH, $J=4.4$ Hz, and $J=8.4$ Hz, H^3), 8.28 (dd, 2xH, $J=1.6$ Hz and $J=8.4$ Hz, H^4), 8.82 (dd, 2xH, $J=1.6$ Hz and $J=4.4$ Hz, H^2) ppm; ^{13}C NMR ($DMSO-d_6$, 100.6 MHz) δ = 151.4, 148.1, 138.2, 135.9, 128.8, 127.6, 121.4, 119.6, 116.9, 56.5, 52.6 ppm; IR (neat): ν = 2947, 1504, 1464, 1376 cm^{-1} ; MS m/z (%): 401 (40, M+H), 244 (30), 158 (100); ESI-HRMS calcd for $C_{24}H_{25}N_4O_2$ 401.1978, found 401.1989.

7,7'-(ethane-1,2-diylbis(methylazanediy))bis(methylene)diquinolin-8-ol (3d, $C_{24}H_{26}N_4O_2$)

N,N'-dimethylethylenediamine (0.53 mL, 5 mmol) and aqueous solution of formaldehyde (37 %, 1 mL) was added to 8-hydroxyquinoline (1.45 g, 10 mmol) dissolved in 20 mL of EtOH. The resulting mixture was stirred and heated at 50 °C for 5 hours. After cooling and evaporation under vacuum, a brown viscous liquid was obtained, which

crystallizes at room temperature, 1.68 g (84 %). Mp= 60 °C (ethanol); 1H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 2x3H, NCH_3), 2.77 (s, 2x2H, NCH_2CH_2), 3.86 (s, 2x2H, $ArCH_2N$), 7.21 (d, 2H, $J=8.4$ Hz, H^6), 7.29 (d, 2xH, $J=8.4$ Hz, H^5), 7.36 (dd, 2xH, $J=4.2$ Hz and $J=8.4$ Hz, H^3), 8.07 (dd, 2H, $J=1.6$ Hz and $J=8.4$ Hz, H^4), 8.84 (dd, 2H, $J=2.5$ Hz and $J=4.2$ Hz, H^2) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 152.7, 148.8, 139.2, 135.8, 128.4, 128.3, 121.4, 118.9, 117.5, 58.6, 54.5, 42.4 ppm; IR (neat): ν = 2924, 1501, 1457, 1371, 1271 cm^{-1} ; SM: (m/z) %: 403 (80 M+H), 246 (100), 158 (60); ESI-HRMS calcd for $C_{24}H_{27}N_4O_2$ 403.2134, found 403.2125.

7-((dicyclohexylamino)methyl)quinolin-8-ol (3e, $C_{22}H_{30}N_2O$)

Dicyclohexylamine (3.98 mL, 20 mmol) and aqueous solution of formaldehyde (37 %, 1.7 mL) was added to 8-hydroxyquinoline (2.90 g, 20 mmol) dissolved in 17 mL of EtOH. The resulting mixture was stirred at 70 °C for 2 hours. After evaporation under vacuum and extraction with diethyl ether (25 mL), a brown viscous liquid is obtained 3.90 g (58 %). 1H NMR (400 MHz, $CDCl_3$): δ = 1.01-1.96 (m, 20 H, 2x(CH_2)₅), 2.74-2.81 (m, 2xH, NCH), 4.13 (s, 2H, $ArCH_2N$), 7.13 (d, 1H, $J=8.4$ Hz, H^6), 7.19 (d, 1H, $J=8.4$ Hz, H^5), 7.33 (dd, 1H, $J=4.4$ Hz and $J=8.0$ Hz, H^3), 8.04 (dd, 1H, $J=1.6$ Hz and $J=8.0$ Hz, H^4), 8.86 (dd, 1H, $J=1.6$ Hz and $J=4.4$ Hz, H^2) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 154.8, 149.0, 139.8, 135.6, 128.3, 126.9, 121.0, 119.5, 116.8, 58.2, 49.9, 30.6, 26.2, 26.1 ppm; IR (neat): ν = 3342, 2924, 2850, 1505, 1379, 1278 cm^{-1} ; SM (m/z) %: 339 (100 M+H), 182 (40), 158 (10); ESI-HRMS calcd for $C_{22}H_{31}N_2O$ 339.2436, found 339.2433.

7-((dioctylamino)methyl)quinolin-8-ol (3f, $C_{26}H_{42}N_2O$)

Dioctylamine (4.82 g, 20 mmol), and aqueous solution of formaldehyde (37 %, 1.7 mL) were added to 8-hydroxyquinoline (2.90 g, 20 mmol) dissolved in 40 mL of EtOH. 1.3 mL of hydrochloric acid (37%) was added to the mixture. The mixture was heated at 60°C for 6 hours under stirring. After cooling, a precipitate was observed. After filtration and washing with diethyl ether (25 mL), a yellow solid was obtained 4.61 g (58 %). m.p: 252 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 0.75-0.90 (m, 2x3H, CH_3), 1.10-1.40 (m, 2x10H, (CH_2)₅ CH_3), 1.86-1.90 (m, 2x2H, NCH_2CH_2), 2.87-2.89 (m, 2x2H, NCH_2), 4.48 (s, 2H, $NCH_2Ar_{o,p}$), 4.56 (s, 2H, $NCH_2Ar_{o,p}$), 7.10-7.60 (m, 2x3H, $ArH_{o,p}$), 8.02-8.18 (m, 2xH, $ArH_{o,p}$), 8.66-8.80 (m, 2xH, $Har_{o,p}$) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 149.6, 149.3, 139.3, 135.9, 128.0, 126.0, 121.2, 118.7, 118.0, 54.8, 50.5, 31.7, 30.5, 29.8, 28.0, , 27.1, 22.5, 14.0 ppm; IR (cm^{-1}): 3359, 2923, 1504, 1464, 1374; SM (m/z): 399 (30 M+H), 242 (100), 158 (30); ESI-HRMS calcd for $C_{26}H_{43}N_2O$ 399.3375, found 399.336. Ratio 60/40.

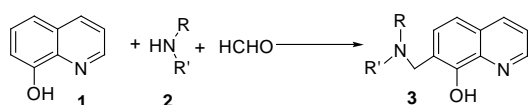
7-(octylamino) methylquinolin-8-ol (3g, $C_{18}H_{26}N_2O$)

N-octylamine (1.65 mL, 10 mmol) and aqueous solution of formaldehyde (37 %, 1.7 mL) was added to 8-hydroxyquinoline (1.45 g, 10 mmol) dissolved in 25 mL of EtOH. The resulting mixture was refluxed for 1 hour. After evaporation under vacuum, a yellow viscous liquid was obtained 2.80 g (98 %). 1H NMR (400 MHz, $CDCl_3$): δ =

0.84-0.87 (m, 3H, CH_3), 1.17-1.24 (m, $5 \times 2H$, $(CH_2)_5CH_3$), 1.57-1.63 (m, 2H, NCH_2CH_2), 2.80-2.83 (m, 2H, NCH_2CH_2), 4.15 (s, 2H, $ArCH_2N$), 7.14 (d, 1H, $J=8.4$ Hz, H^6), 7.31 (d, 1H, $J=8.4$ Hz, H^5), 7.38 (dd, 1H, $J=4.2$ Hz and $J=8.4$ Hz, H^3), 8.07 (dd, 1H, $J=1.6$ Hz and $J=8.4$ Hz, H^4) 8.89 (dd, 1H, $J=1.6$ Hz and $J=4.2$ Hz, H^2) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ = 149.6, 149.3, 139.3, 135.8, 128.0, 126.1, 121.1, 118.7, 118.1, 51.7, 50.5, 31.7, 29.4, 29.2, 28.1, 27.1, 22.5, 14.0 ppm; IR (neat): ν =3370, 2923, 2852, 1501, 1463, 1371 cm^{-1} ; SM (m/z) %: 287 (45 M+H), 158 (100); ESI-HRMS calcd for $C_{18}H_{27}N_2O$ 287.2123, found 287.2135.

Results and Discussion

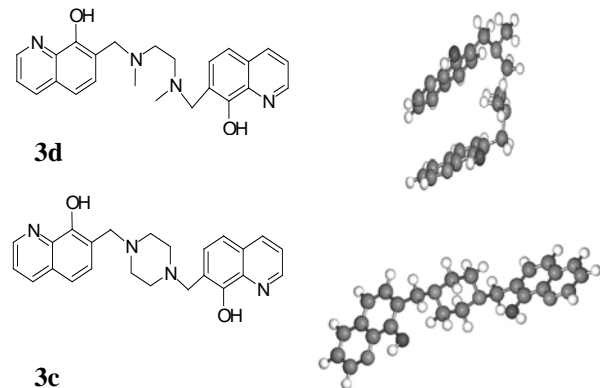
8-Hydroxyquinoline is a phenol able to react in a reaction of Mannich.¹² The reaction of 8-HQ was described with different aldehydes (Betti reaction¹³) and some amines.



Scheme 1: Synthesis of 8-hydroxyquinoline derivatives (**3**) from secondary amines by Mannich reaction

In our work, we have studied the reaction of formaldehyde and different amines in order to obtain molecules with one or two 8-HQ units for the coordination of metal ion. The reaction of morpholine with formaldehyde and 8-hydroxyquinoline was already described and was used as a basis of our work.¹⁴

First, we have been interested in using new 8-HQ derivatives as ligand of metals in complexes formation. We have synthesized ligands with a second site of coordination in the molecule (oxygen with morpholine, sulfur with thiomorpholine) or with two HQ units with diamines. The reaction with thiomorpholine introduced a sulfur atom, a soft site of coordination on the ligand according to R.G. Pearson.^{15,16} With diamine such as piperazine (**2c**) a compound (**3c**) with two 8-HQ units, is obtained. The N,N' -1,2-dimethylenediamine (**2d**) is not so reactive so the reaction required heating. By comparison by molecular modelisation, the compound (**3d**) obtained with N,N' -1,2-dimethylenediamine is more flexible than the preceding one with piperazine.



Scheme 2. Molecular representation of (**3c**) and (**3d**).

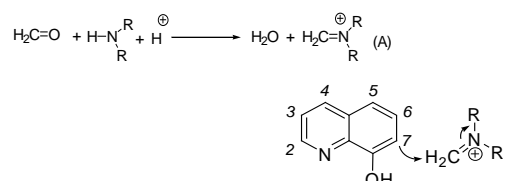
In a second approach, we were interested in the synthesis of a lipophilic molecule with 8-HQ ligand, such molecule can be used as metal extractant in liquid-liquid extraction process. In this aim, we have used bicyclohexylamine, bisoctylamine and mono-octylamine as starting amines.

Table 1. New complexone derivatives of 8-hydroxyquinoline obtained under Mannich conditions.

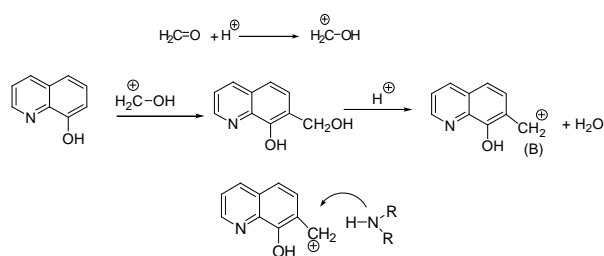
| Amine, 2 | Product (3) | Condi-tions | Yield (%) |
|-----------------|----------------------|-------------|-----------|
| 2a | 3a | 12 h, 20 °C | 97 |
| 2b | 3b | 12 h, 20 °C | 99 |
| 2c | 3c | 12 h, 20 °C | 62 |
| 2d | 3d | 5 h, 50 °C | 84 |
| 2e | 3e | 2 h, 70 °C | 58 |
| 2f | 3f | 6 h, 60 °C | 58 |
| 2g | 3g | 1 h, 78 °C | 98 |

Under microwave irradiation (10min, 300W) the yield obtained were similar to those obtained under classical conditions. In all the products synthesized by the Mannich reaction, the addition of amine was at the position 7 of 8-hydroxyquinoline. However, in the case of dioctylamine (**2f**), two products (substituted in 5 or 7 position) were obtained in a mixture.

We can propose two probable mechanisms: the first involved the attack of the iminium (A) by 8-hydroxyquinoline and the second one the reaction of benzyl cation (B) with amine in this Mannich reaction.



Scheme 3: Mechanism (A).



Scheme 4. Mechanism (B)

The new compound (**3f**) was used in the liquid-liquid extraction of uranyl ion: **3f** which is soluble in ethyl acetate, was taken as the organic solvent throughout this study. Equal volumes of organic and aqueous phases (5 mL) were agitated for 30 minutes (enough for equilibrium) at 22 °C under the desired experimental conditions. The two phases were then separated by decantation and assayed by taking known aliquots from the aqueous phases. The concentration of UO_2^{2+} in the sample was determined by Arsenazo(III) visible spectrophotometric analysis at 650 nm,¹⁷ and that in the organic phase was obtained by subtracting the aqueous concentration from the total initial aqueous concentration of UO_2^{2+} .

Effect of molar ratio Q

The extraction experiment results are discussed in term of the extraction yield (Y) defined as follows:

$$Y(\%) = 100 \frac{(m_i - m_f)}{m_i} \quad (1)$$

where

m_i = initial mass of UO_2^{2+} in aqueous phase and
 m_f = mass of UO_2^{2+} after extraction.

The variable Q is the ratio of the number of moles of ligand in organic phase to the number of moles of metal in aqueous phase before extraction; $Q = n_{\text{ligand}}/n_{\text{metal}}$.

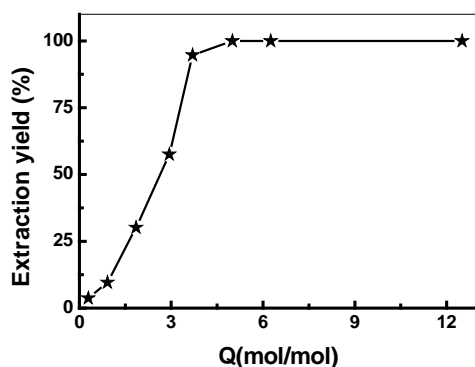


Figure 1. Extraction yield of UO_2^{2+} by **3f** as a function of Q . $V_{\text{org}} = 5.0$ mL, $[\text{Ex}] = 1.0$ mmol L^{-1} , $V_{\text{aq}} = 5$ mL, $\text{pH}^i = 0.6$, $t = 30$ min, $T = 22$ °C.

The extraction results of uranyl ion as a function of Q , are reported in Fig.1. We observe that the best performance is achieved for Q equal to 5.0. For the extraction of one mole of UO_2^{2+} in aqueous phase, 5.0 mol of extractant in organic phase are required, under the operating conditions listed above.

Effect of initial concentration of UO_2^{2+}

Figure 2 shows that the extraction yield of UO_2^{2+} extracted by the **3f** increased from 0.0 % to 100.0 % with an increase in the initial concentration from 0.00 (mol.L^{-1}) to 16.2 ppm, and thereafter remains constant at 41.59 ppm. At initial concentrations, higher than 41.59 ppm, the extraction yield decreases. With increasing concentrations, the ratio of the available sorption sites of ligand to the initial number of moles of metal ions becomes lower, and hence, the extent of metal removal depends on the initial concentration.

The extraction results of uranyl ions as a function of Q are reported in Fig. 2.

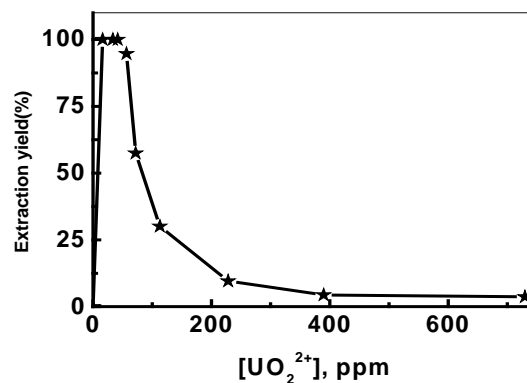


Figure 2. UO_2^{2+} extraction yield versus initial molar UO_2^{2+} concentration. $V_{\text{org}} = 5.0$ mL, $[\text{Ex}] = 1.0$ mmol L^{-1} , $V_{\text{aq}} = 5.0$ mL, $\text{pH}^i = 0.65$, $t = 30$ min, $T = 22$ °C

The curve in Figure 2 shows that the extraction is quantitative for dilute solutions of UO_2^{2+} .

Effect of initial pH

The effect of the initial pH on the extraction yield of UO_2^{2+} was studied in the pH range of 0.65 to 1.67 (see Figure 3). The extraction yield (99.4 %) was found to be higher at $\text{pH} = 1.13$. The extractant is suitable for chelate formation with UO_2^{2+} ions, as it has a nitrogen atom and an OH group. As the complex formation is strongly pH dependent, careful adjustment of proper pH was necessary.¹³ The extraction results of UO_2^{2+} ion as a function of pH are reported in Figure 3.

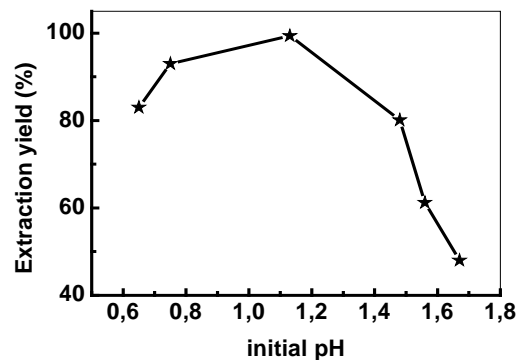


Figure 3. pH effect on the extraction of UO_2^{2+} . $V_{\text{org}} = 5.0$ mL, $[\text{Ex}] = 1.0$ mmol L^{-1} , $V_{\text{aq}} = 5$ mL, $[\text{UO}_2^{2+}]_{\text{initial}} = 60$ ppm, $t = 30$ min, $T = 22$ °C

The negative effect of pH increase on the extraction yield can be attributed to the formation, in aqueous phase, of hydroxide species like $UO_2(OH)_2$ and $(UO_2)_6(OH)_{12}$, larger and more stable than UO_2^{2+} and $UO_2(OH)^+$ majority in the more acidic medium.

In conclusion, the Mannich reaction of 8-hydroxyquinoline, formaldehyde and amines allowed a rapid, convenient and easy synthesis of new ligands and new extractants.

The 7-(dioctylaminomethyl)quinolin-8-ol obtained has exhibited high efficiency for the uptake and removal of uranyl ion from water and the recovery was quantitative ($\approx 100\%$).

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