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Flavonol assisted extraction of divalent and trivalent metal ions

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The work is devoted to investigations of extraction methods for the isolation and accumulation of divalent and trivalent metal ions Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Y^{3+} and Ce^{3+} in the absence and presence of flavonol derivatives with different numbers and locations of complexation sites. Two extraction methods were used and compared: the classical LL – water-organic phase (octanol) and the ATPS method – with two separated aqueous phases in the presence of polyethylene oxide 4000. It was shown that the presence of flavonols in the extraction system leads to a significant increase in the extraction efficiency with the exception of Ni^{2+} ions. It turned out that the most effective concentration of Zn^{2+} ions can be achieved using LL extraction, for other ions ATPS extraction is more effective. The use of flavonols to increase the efficiency of metal ion extraction allows increasing the sensitivity and selectivity of methods for quantitative analysis of the studied metal ions.

Keywords: flavonols, metal ion extractions, complexation, LL extraction, ATPS extraction.

Екстракція двох і трьох валентних іонів металів в присутності флавонолів. *О.О. Демідов, А.В. Краснопьорова, Г.Д. Юхно, Н.В. Єфімова, А.Д. Рошаль*

В роботі проведено дослідження екстракційних методів виділення та накопичення іонів двох і трьохвалентних іонів металів Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Y^{3+} и Ce^{3+} у відсутності та присутності похідних флавонолів з різною кількістю і розташуванням центрів комплексоутворення. Були використані і порівняні два екстракційних метода: класичний LL – вода-органічна фаза (октанол) та метод ATPS – з двома розділеними водними фазами у присутності поліетиленгліколю 4000. Було показано, наявність в екстракційній системі флавонолів приводить до значного збільшення ефективності екстракції за виключенням іонів Ni^{2+}. Виявилося, що найбільш ефективного концентрування іонів Zn^{2+}можна досягнути з використанням LL екстракції, для інших іонів більш ефективною є екстракція ATPS. Використання флавонолів для підвищення ефективності екстракції іонів металів дозволяє збільшити чутливість і селективність методів кількісного аналізу досліджуваних іонів металів.

1. Introduction

Derivatives of 2-phenylchromones – flavonoids, have attracted the attention of researchers for decades. The reason for this is the biological activity of these compounds, their ability to chemically bind metal ions, as well as unusual and complex spectral behavior. Most scientific works on flavonoids concern derivatives of 2-phenyl-3-hydroxychromone – flavonols, substances exhibiting P-vitamin activity, strong antioxidants, and fluorescent indicators for some metal ions [1-3].

Since natural flavonols contain from 3 to 5 hydroxyl groups and a carbonyl group, they are capable of forming metal ion complexes of various structures that have different spectral properties [4]. Previously, using unsubstituted flavonol (3-hydroxyflavone) and its derivatives, the complexation of these compounds in the ground and excited states were studied [5-7]. It was shown that flavonols demonstrate the behavior of “intelligent” ligands when forming complexes, i.e., depending on the ion parameters, they use for binding the most suitable complexation center. Depending on the size and charge of an ion, 3-hydroxyflavone derivatives form both chelate and non-cyclic complexes [5].

Later, studies of the complexation of a natural flavonol derivative – quercetin (3,5,7,3’,4’-pentahydroxyflavone) showed that this compound might form four types of complexes with metal ions. Three complexation centers of quercetin are located in the chromone fragment of the molecule (***A***, ***B***, ***D***) and one in the side phenyl fragment (***B***) (Figure 1).

Quantum-chemical calculations of the thermodynamic stability of latter complexes, as well as studies of ^{1}H NMR and electronic spectra have shown that, despite numerous references [8-10], complexes involving a side phenolic ring (site C) cannot be formed in neutral and acidic media [4,7,11]. In an alkaline medium, at pH sufficient for dissociation of the 4’-hydroxy group, the formation of complexes involving site C must be possible, however in this case, hydrolysis takes place, and the formation of metal hydroxy complexes or the corresponding hydroxides can be observed. In any case, the participation of the 3’ and 4’-hydroxy groups of the side phenyl fragment in the binding of metal ions remains controversial to this day.

It is known that quantitative analysis of metal ions uses two groups of methods. There are direct methods based on the complexation of metal ions with a ligand followed by further determination of complexes’ concentration, as well as indirect methods including extraction of metal complexes formed. These latter methods, despite the high labor intensity, allow to increase the selectivity of the analysis, as well as to concentrate the analyte, which is important when determining its low concentrations [12, 13]. It should also be noted that the evolution of extraction methods has led to the creation of “green” extraction methods, which do not use toxic organic solvents [14].

As is known, the logarithms of the complexation constants correlate with the logarithms of the constants of the inter-phase partition coefficients of metal ions [15, 16]. Thus, using extraction methods, in some cases it is possible to draw conclusions about the composition, and stability of complexes, as well as the participation of various complexation centers in the binding of metal ions. This work contains the results of a study of the complexation of flavonols in two-phase systems, in particular, data on the inter-phase partition of complexes with Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Ce^{3+}, and Y^{3+} ions. In this work, flavonols having different numbers of complexation centers both in the chromone part of the molecule and in the side phenyl fragment were used. These are three synthetic flavonols – 3-hydroxyflavone (flavonol) (***I***), 3,4’-dihydroxy-3’-methoxyflavone (***II***) and 3,3’,4’-trihydroxyflavone (***III***), as well as a natural flavonol – 3,5,7,3’,4’-pentahydroxyflavone (quercetin) (***IV***) (Figure 2).

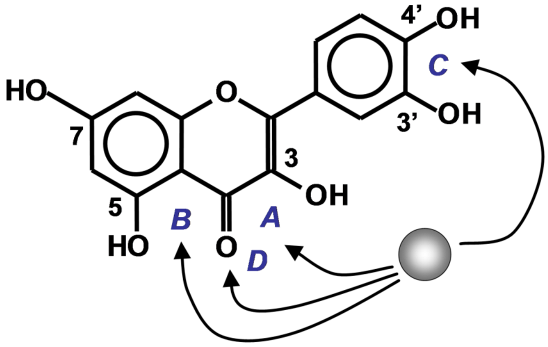


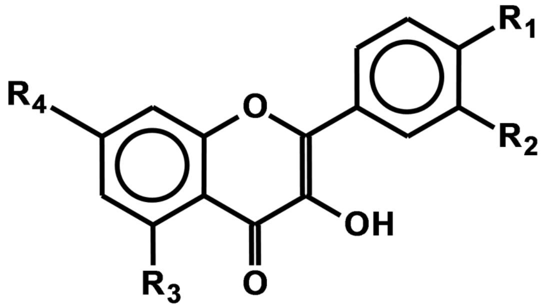
Fig. 1. Complexation sites of flavonols on the example of 3,5,7,3’,4’-flavone (quercetin)

In addition, in the presented work we have compared the complexation and the interphase distribution of metal ions and their flavonol complexes using both a conventional two-phase system – water/organic solvent, and the so-called “green” extraction – aqueous two-phase system (ATPS) extraction using polyethylene oxide.

2. Experimental

To study the complexation, commerce ligands ***I*** and ***IV*** (Aldrich) were used. Flavonols ***II*** and ***III*** were synthesized in three stages. Initially, chalcones with hydroxy groups protected by benzyl fragments were prepared via the Claisen–Schmidt reaction in DMF [17]. The chalcones then underwent an oxidative cyclization through a modified Algar–Flynn–Oyamada reaction [18, 19]. In the final step, deprotection of benzyl groups was performed in THF solutions following a standard protocol.

Initial concentrations of Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Y^{3+} и Ce^{3+} in their solutions were $1,0\text{-}1,5\times10^{-2}$ M. The solutions were pre-



	R$_1$	R$_2$	R$_3$	R$_4$
I	H	H	H	H
II	OH	OCH$_3$	H	H
III	OH	OH	H	H
IV	OH	OH	OH	OH

Fig. 2. Structures of studied flavonols.

pared from corresponding commercial salts $MnSO_4 \cdot 5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $YCl_3 \cdot 6H_2O$, and $Ce(NO_3)_3 \cdot 6H_2O$ (Merck). Commercial ammonium sulfate was dried at 100°C to constant weight before use.

As mentioned above, to investigate the inter-phase partition of free metal ions and their complexes, two different extraction methods were used: liquid/liquid (LL) and aqueous two-phase system (ATPS) extractions. In the case of LL extraction in a water/organic solvent system, octanol (Aldrich) was used as the organic phase under the primary ratio of aqueous and organic phase equal to 5 : 1.

ATPS extraction was performed using polyethylene oxide (PEO) with a molecular weight of 4000 D (Merck). A two-phase system was obtained by mixing a 40% aqueous solution of PEO and a 40% aqueous solution of $(NH_4)_2SO_4$ containing metal ions, the concentrations of which were in the range of $0.5\text{-}1.5\times10^{-3}$ M. $(NH_4)_2SO_4$ was used as a phase separator, and its presence resulted in the formation of two phases: the aqueous one containing about 1.5% PEO and the "organic" one which is a 38% PEO aqueous solution. A primary ratio of $(NH_4)_2SO_4$ and PEO solutions was adjusted to obtain a ratio of aqueous to an "organic" phase equal to 5:1 after phase separation.

Flavonols were introduced into both extraction systems in one of two ways – either by adding concentrated alcohol solutions of the ligand to the aqueous phase (LL) or $(NH_4)_2SO_4$ solution (ATPS), or by dissolving a weighed sample of the ligand in the initial PEG solution or in octanol. Flavonols were added at a concentration twice higher than those of metal ions. To avoid hydrolysis of salt solutions, the extraction procedures were carried out in a weakly acidic medium at pH = 5.5.

The two-phase systems LL and ATPS were vigorously mixed for 6 hours, then poured into separatory funnels and left for 2 hours to separate the phases. The aqueous and organic phases were then separated, and the aqueous phase was further used to determine the concentration of metal ions.

The analyses of concentrations of Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} in the aqueous phase before and after the extraction were performed using an atom-absorption spectrometer AA-7050. Concentrations of Ce^{3+} and Y^{3+} ions were determined by a complexometric spectrophotometric method using arsenazo III as an indicator [20].

The efficiencies of the extraction methods were characterized by comparing the values of the ions' inter-phase molar partition coefficients (D) and the molar fraction of ions transferred into the organic phase (E%). The values of D and E% were calculated using equations (1) and (2), respectively:

$$D = \frac{C_0 - C_{aq}}{C_{aq}} \qquad (1)$$

$$E_{\%} = \frac{D}{D + \frac{V_{aq}}{V_{org}}} \times 100\% \qquad (2)$$

where C_0 and C_{aq} – concentrations of metal ions in the aqueous phase before and after the extraction, V_{aq} and V_{org} – volumes of the organic and aqueous phases after their separation.

3. Results and discussion

The inter-phase transfer of flavonol metal complexes is not the only possible way of ion transfer into the organic phase. A competing process is direct ion diffusion across the phase boundary. The ion transfer into the organic phase when using LL extraction is due to octanol saturation with water. The water

Table 1. Quantitative characteristics of LL and ATPS extraction methods

Metal ion	D	$E_{\%}$	D	$E_{\%}$	ω
	LL extraction		ATPS extraction		
Mn^{2+}	0.44	8.17	1.18	19.07	51.4
Ni^{2+}	2.92	36.88	3.09	38.17	5.8
Cu^{2+}	1.36	21.37	1.92	28.30	41.2
Zn^{2+}	2.19	30.44	2.25	30.99	2.7
Y^{3+}	0.08	1.54	0.16	3.11	100.0
Ce^{3+}	0.28	5.38	0.40	7.42	42.9

* D – molar partition coefficient; $E_{\%}$ – molar fraction of ions transferred into the organic phase (% mol.); ω – efficiency of the ATPS extraction relatively to the LL.

concentration in octanol after phase separation is approximately 4.9 wt.% [21], which leads to an increase in the polarity of the alcohol and improved conditions for preserving the hydration shell of metal ions in the organic phase. In the case of using ATPS, the “organic” phase contains 62% water, which further contributes to the uniform distribution of metal ions between the phases. In addition, in the last case, the migration of metal ions from the aqueous phase to the “organic” one is facilitated by their interaction with PEO molecules, accompanied by the formation of a helicoidal conformation of the polyester chains that leads, in turn, to the formation of like-crown coordination compounds [22]. As shown in [22] using alkali metals as an example, the stability of PEO complexes depends on the diameters of the ions and size of the helical cavity of the PEO, as well as on the number of oxygen bridges inside the helical cavity per metal ion. There is no data on the stability of PEO complexes with *d*- and *f*-element ions, so it is impossible to quantitatively evaluate the effects of PEO on the transport of metal ions.

Table 1 shows the molar coefficients of the inter-phase partition of metal ions in the absence of additional complexing agents, as well as the molar fraction of ions transferred into the organic phase. To compare the LL and ATPS methods, the relative extraction efficiency ω was used, showing how much the concentration of metal ions in the organic phase after ATPS extraction is greater than that obtained with LL extraction. The value of ω was calculated using the equation:

$$\omega = \frac{E_{\%}(ATPS) - E_{\%}(LL)}{E_{\%}(LL)} \cdot 100\% \ , \qquad (3)$$

According to the D and E% values listed in the table, metal ions can be divided into two groups depending on their charge. Thus, Ni^{2+} and Zn^{2+} ions in the water-octanol system have partition coefficients in the range from 2 to 3. Thus, taking into account the ratio of phase volumes, 30-40% of free ions pass into water-saturated octanol. On going to the ATPS extraction, the partition coefficients of Ni^{2+} and Zn^{2+} ions do not change significantly, and the number of ions transferred to the PEO-containing phase increases insignificantly compared to LL extraction – by 1-3%. This allows us to conclude that solvation effects play the greatest role in the partition of these ions between the phases, while the influence of ion complexation by PEO molecules is insignificant.

The partition coefficients of Cu^{2+} and Mn^{2+} ions in the octanol-water system are 2.1 and 6.8 times lower, respectively, than in the case of Ni^{2+} ion. Accordingly, using the LL extraction, 21% and 8% ions approximately can be collected in the organic phase. When using ATPS, the partition coefficients increase, and $E_{\%}$ values increase up to 28% and 20%, respectively. Although the concentrations of Cu^{2+} and Mn^{2+} ions transferred to the organic phase are lower in absolute values than in the case of Ni^{2+} and Zn^{2+} ions, the efficiency of ATPS extraction of Cu^{2+} and Mn^{2+} is 40–50% higher.

Trivalent ions Y^{3+} and Ce^{3+} have even lower partition coefficients (0.08 and 0.28), and the fraction of their extraction by the organic phase does not exceed 1.5–5%. In the presence of a PEO-using system, the partition coefficients also remain low, although the relative efficiency of ion extraction by the organic phase increases by 1.5–2 times.

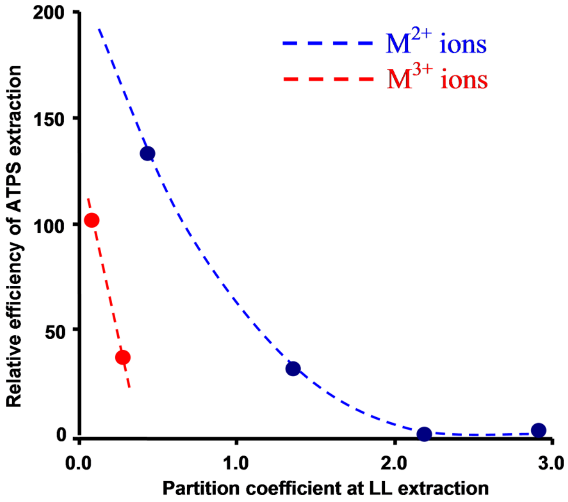


Figure 3. Plot of relative efficiency of the ATPS extraction on molar partition coefficient of ions under the LL extraction

The plot in Figure 3 shows that with a decrease in the ion partition coefficients, and consequently, the fraction of ions transferring into the organic phase, an increase in the relative efficiency of ATPS extraction ω is observed. This shows that when extracting ions with low partition coefficients, the contribution of metal ion complexation with PEO to the inter-phase transfer of ions becomes more pronounced.

It is logical to assume that the use of flavonols as ligands for binding metal ions should lead to the appearance of an additional path for the transfer of ions into the organic phase, which should result in an increase in the distribution coefficients. To study the efficiency of ion transfer due to complex formation, we used flavonols with different numbers of chelating centers:

1) unsubstituted flavonol ***I***, having one chelation site ***A*** (see Figure 1), formed by the carbonyl and 3-hydroxy groups.

2) 3'-methoxy-4'-hydroxyflavonol ***II***, having the same chelation site ***A*** and electron-donating substituents in the side phenyl ring.

3) 3',4'-dihydroxyflavonol ***III***, having a chelation site ***A***, as well as a chelation center ***C*** due to the presence of 3' and 4'-hydroxy groups.

4) 3,5,7,3',4'-pentahydroxyflavone, having four different complexation sites: the same as in ***III*** – ***A***, ***C***, and site ***B***, formed by the carbonyl and 5-hydroxy groups. In addition, in the case of large-radius ions, the formation of a non-chelate complex directly with the carbonyl group is possible – site ***D***.

The formation of chelates of type ***B*** in the presence of a methoxy group in the side ring, as in compound ***II***, is unlikely and has not been described in publications. Non-cyclic complexes with a carbonyl group at the center of ***D*** have low stability [7] and their formation also seems unlikely.

It is known that complexes of flavonols with divalent ions, as a rule, have the composition ML, while with trivalent ions not only mono- but also biligand complexes ML_2 can be formed [4, 7]. In the experiments, the concentration of flavonols was twice as high as the concentration of metal ions. Taking into account the values of $E_{\%}$ for free ions (Table 1), the concentration of flavonol in the organic phase should be at least 5 times higher than the concentration of metal ions, which ensures maximum complete binding of flavonol ligands with ions.

The effect of flavonol complexation on the inter-phase partition of metal ions was estimated with a Δ value calculated by equation 4 and showing an increase in the concentration of the metal ion in the organic phase in the presence of flavonol relative to the concentration of the metal ion in the absence of the ligand:

$$\Delta = \frac{E_{\%,lig} - E_{\%}}{E_{\%}} \times 100\,, \qquad (4)$$

where $E_{\%,lig}$ and $E_{\%}$ are the molar fractions of ions transferred into the organic phase in the presence and absence of flavonols, correspondingly.

Considering that the dispersion of values in parallel measurements was 3-5%, Δ values below 5% were considered equal to zero, and it was believed that the addition of flavonol, in this case, affected insignificantly additional partition of ions between phases.

The parameters of metal ion extraction in the presence of flavonols are listed in Table 2. It should be noted that the values of D and $E_{\%}$ for Ni^{2+} ions did not change in fact upon the addition of flavonols, and the value of Δ was <3%. This allowed us to conclude that there was no effect of complexation on the extraction of these ions. In this regard, there are no data on the extraction of Ni^{2+} ions in Table 2.

As shown by the Δ values for LL extraction of Mn^{2+}, Cu^{2+} and Zn^{2+} ions, in the presence of flavonols, the concentration of metal ions in the organic phase increases on average by 86%, 28% and 63%, respectively. The Δ values upon addition of ***I***, ***II*** and ***III*** differ from each other by ±10%, which allows us to conclude that the effect of these flavonols on the extraction efficiency is approximately the same. In the case of quercetin ***IV***, the ligand addition leads to a lower extraction efficiency compared to other flavonols for Zn^{2+} ions, and a higher one for Cu^{2+} and Mn^{2+} ions.

Table 2. Parameters of metal ion extraction in the presence of flavonols*

Ligand	D	$E_{\%}$	Δ	D	$E_{\%}$	Δ
	LL			ATPS		
Mn^{2+}						
I	0.75	13.1	59.7	1.01	14.7	80.0
II	0.84	14.2	74.2	1.18	15.0	83.2
III	0.83	14.2	73.4	1.32	18.0	120.3
IV	1.21	19.4	137.6	1.64	21.6	163.9
Cu^{2+}						
I	1.95	28.0	31.0	2.13	30.8	9.0
II	1.72	25.5	19.5	2.43	45.0	59.1
III	1.83	26.5	24.2	3.29	43.7	54.4
IV	2.07	29.2	36.7	2.64	36.8	30.2
Zn^{2+}						
I	4.95	49.7	63.4	3.25	39.4	27.2
II	5.84	53.8	76.9	3.43	40.7	63.4
III	5.53	52.5	72.5	3.86	39.6	59.3
IV	3.67	42.3	39.0	3.80	43.2	39.4
Ce^{3+}						
I	0.56	25.10	366.5	1.56	48.35	551.6
II	0.28	5.92	10.0	0.59	10.84	46.1
III	0.21	4.96	2.4	0.43	8.18	10.2
IV	0.49	22.85	324.7	0.27	13.85	86.7
Y^{3+}						
I	0.22	11.51	270.1	0.38	18.68	1113.0
II	0.03	0.50	88.7	0.03	0.50	67.6
III	0.13	2.22	46.0	0.13	2.22	140.0
IV	0.37	18.11	249.5	0.37	18.11	454.0

* D, E% and Δ designations are given in the text.

Trivalent ions have low inter-phase partition coefficients, and after extraction only 1.5% (Y^{3+}) to 5.5% (Ce^{3+}) of ions pass into octanol. In the presence of ***I*** and ***IV***, the ion transfer in the organic phase increases from 10 to 25%. Thus, the addition of these flavonols leads to an increase in the extraction efficiency by approximately 5 (Ce^{3+}) and 10-20 times (Y^{3+}). At the same time, as follows from Tables 1 and 2, flavonols ***II*** and ***III*** do not affect the extraction efficiency of trivalent ions.

The use of ATPS extraction with flavonols also allows for an increase in the efficiency of ion extraction. It can be seen that in most cases (except for Zn^{2+} ions) the partition coefficients and ion concentrations in the organic phase for ATPS extraction are higher than in the case of the LL one. The highest efficiency of Cu^{2+} and Mn^{2+} ion extraction is achieved when using flavonols ***II*** and ***III*** as complexing agents. An increase in the efficiency of ATPS extraction of triply charged ions is observed only in the case of using unsubstituted flavonol ***I***. Other ligands show either low extraction efficiency or do not affect the ion transfer between phases at all.

The analysis of the values presented in Table 2 shows that finding a general trend in the change in the partition coefficients and the extraction efficiency depending on the ligand structure does not seem possible. It would be logical to consider that the extraction efficiency should correlate with the complexation constants of the corresponding flavonols and metal ions. Moreover, as shown in the works [15, 23], there is a dependence of lgD and $lgE_{\%}$ on the value of the logarithm of the stability constant of the complex. The latter, in turn, depends on the electron configuration of the ion, the correspondence between ion diameter and the size of the chelation site cavity, as well as on the electron-releasing ability of the carbonyl and hydroxyl groups of the ligand. The latter factor is largely determined by the presence of different number of electron-donor hydroxy and R-oxy groups in the flavonol molecules.

However, to compare the extraction efficiency in the presence of different flavonols, in our opinion, it is necessary to take into account own flavonols' degree partition between the phases. If unsubstituted flavonol ***I*** is lipophilic

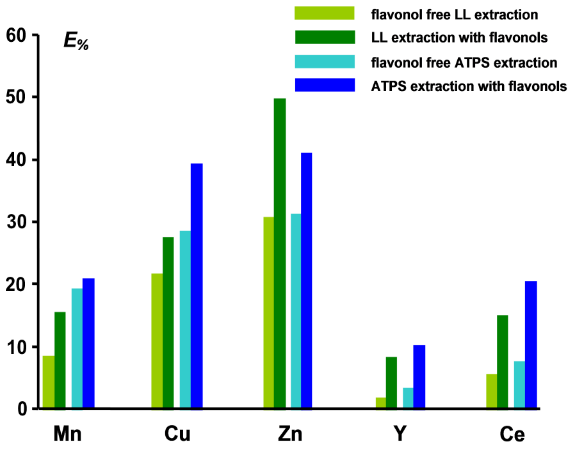


Fig. 4. Relative values of the extraction efficiency under LL and ATPS extractions of metal ions with and without using flavonol ligands.

and is almost entirely concentrated in the organic phase, then ***IV***, which has 5 hydroxyl groups, has a higher solubility in water and is present in the aqueous phase in fairly significant concentrations. Perhaps this explains the higher efficiency of using ***I*** in LL extraction of Zn^{2+} and Cu^{2+}, ***II*** and ***III*** in ATPS extraction of Cu^{2+}, and polyhydroxylated ***III*** and ***IV*** in ATPS extraction of Mn^{2+}. As mentioned above, in the case of ATPS extraction it is also necessary to take into account the presence of competing complexation of ions with PEO molecules, and therefore, to adequately describe the ion extraction process, the values of not one, but two complexation constants should be considered.

Flavonols can be quite easily modified by the introduction of additional hydroxy and R-oxy substituents both in the bicyclic chromone moiety of the molecule and in the side phenyl fragment. Therefore, in order to have a general view of the effect of flavonol ligands on extraction processes, we used the values of partition coefficients and ion concentrations in the organic phase averaged for all the flavonols studied. The diagram in Figure 4 shows the differences between the efficiencies of metal ion extraction in the absence and presence of flavonols.

The diagram shows that the use of flavonols leads to an increase in the concentration of metal ions in the organic phase. Moreover, the most effective is the use of flavonols for the extraction of zinc, copper and cerium.

The comparative extraction efficiencies of LL and ATPS methods for averaged D and $E_{\%}$ values of all studied flavonols are presented in Figure 5

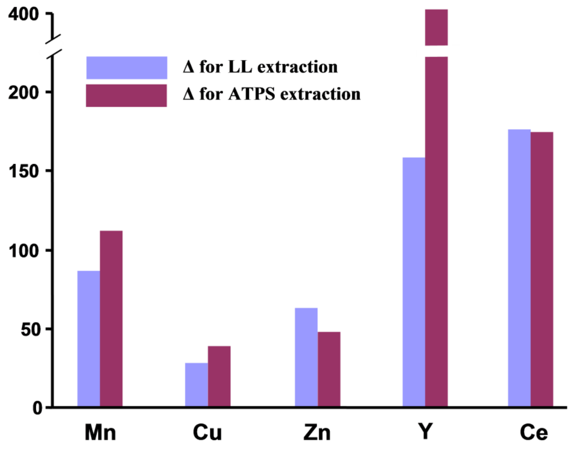


Fig. 5. Average efficiencies of ion extraction using LL and ATPS methods

The following practical conclusions can be drawn from the presented data: for the concentration and analysis of Mn^{2+}, Cu^{2+}, and Y^{3+} ions in the presence of flavonols, the use of ATPS extraction is more preferable, while Zn^{2+} is better extracted in the form of flavonol complexes when using LL extraction.

4. Conclusions

The studies have clearly shown that the use of flavonols as ligands leads to more effective extraction of most metal ions into the organic phase. It should also be noted that flavonols can be used both in conventional LL extraction and when using “green” methods of extracting ions from aqueous solutions. Special attention should be paid to the extraction of triply charged ions, which are much worse transferred to the organic phase. The use of flavonols can increase the sensitivity of yttrium and cerium determination when using analytical methods which involve LL or ATPS extraction.

Taking into account the different solubility of flavonols in aqueous and organic phases, different stability constants of complexes depending on the nature and number of substituents in ligands, the possibility of “switching” the complexation center depending on the geometric parameters and charges of ions, it can be concluded that individual selection of cation-flavonol derivative pairs is necessary. Such an approach will ensure not only high extraction efficiency, but also its selectivity with respect to ions of a certain type.

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