

INVESTIGATION ON THE REAL STATE OF SOME RADIONUCLIDES IN VERY DILUTED WATERY SOLUTIONS IN THE PRESENCE OF SOME COMPLEXING AGENTS

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abstract: A general method of investigating of the real ionic state of the metallic radionuclides in very diluted watery solutions in the presence of some complexing agents was elaborated. To this purpose, using the ion exchange on the cation exchangers the overall stability constants of the complexes resulted from reaction of the $^{110}\text{Ag}^+$, $^{65}\text{Zn}^{2+}$, and $^{55+59}\text{Fe}^{3+}$ radionuclides with neutral or anionic complexing agents were obtained. Using these constants the fractions from the respective ion concentrations in solution, both in a simple ionic state and in every complex state too, at different concentrations of the complexant agent were estimated.

Introduction

It is known that in very diluted solutions the radionuclides react differently from the same non-radioactive metallic ions in usual concentrations. The metallic radionuclides which are to be found in microconcentrations in waters, besides a simple ionic state can also form radiocolloides pseudo-radiocolloides or complex compounds with different complexing agents which are likely to exist as impurity in waters. Such complexing agents can be the HO^- ions resulting from the ionization of the water as well as other neutral or anionic species in the waters.

Knowing the real state of the metallic radioactive ions in such systems is especially important while studying the radioactive pollution, as well as in the process of depollution with a view to protect the environment.

The previous papers [1,2] showed that the real state of metallic ions in very diluted watery solutions can be established if the overall stability constants of all complexes existing in the respective solution are known. The best way to obtain the values of these constants is the ion exchange on the cation exchangers and the anion exchangers as well [3÷5]. To this purpose the global distribution coefficient of the metallic ions between the ion exchanger and the solution, both in the absence of the complexing agent (P_0) and at different concentrations of the complexing agent in solution (P_i) has been determined [6÷9].

The advantage of this method is even greater if the metallic radionuclides are used because they are always in microconcentrations. That's why the variation of the concentration of the complexing agent as a result of the complexation of the radioactive metallic ions is to be

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neglected, because it is much higher than the concentration of the radionuclides under study. One may conclude that, at equilibrium, the concentration of the complexing agent is practically equal to the initial one.

Experimental

In this paper it has determined the global distribution coefficients P , of $^{110m}\text{Ag}^+$, $^{65}\text{Zn}^{2+}$, and $^{55+59}\text{Fe}^{3+}$ radioactive ions between the Dowex-50×8 (200 Mesh) cation exchanger and a watery solution both in the absence and in the presence of complexing agents at different concentrations: NH_3 and SCN^- for the $^{110m}\text{Ag}^+$ ions, HO^- for the $^{65}\text{Zn}^{2+}$ ions and Cl^- for the $^{55+59}\text{Fe}^{3+}$ ions. The necessary radionuclides, in tracer amounts, were supplied by IFIN-HH Magurele, Bucharest (Romania). The Dowex – 50×8 cation exchanger was purified being alternatively washed in solutions of HCl, distilled water and NaOH and, finally, it was obtained in the Na^+ form.

Before the experiment, the test tubes and the flasks were kept for two hours in AgNO_3 , ZnCl_2 and FeCl_3 inactive solutions having a $0.2 \text{ mol}\cdot\text{L}^{-1}$ concentration, to diminish the adsorption. The solutions meant to provide the ion exchange equilibria had a constant ionic strength. For every radionuclide and the respective complexing agent 12 solutions having the same amount of radionuclides but different amounts of ligand were prepared.

The first solution was used to determine the initial specific radioactivity, \dot{I}_0 of the solutions before the contact with the cation exchanger. The second solution didn't contain the complexing agent while the 3rd-12nd solutions had 10 different concentrations of the complexing agent. 40 mL from the 2nd-12nd solutions were poured into eleven 100 mL Erlenmeyer flasks provided with tops in which the same amount of cation exchanger (~0.15 g) was previously introduced. In order to provide the ion exchange the flasks were airtightly closed and then introduced into a thermostat and kept there for 6 hours at a temperature of 25°C. Every 10÷15 minutes the flasks were intensely stirred for 30÷40 seconds. As soon as the exchange equilibrium was established, 3 samples of 2 mL were taken from every flasks in order to measure the specific radioactivity using a mono-canal γ -spectrometer "Gamma NK-350".

The average value of the 3 samples represents the specific activity \dot{I} of the solution at the equilibrium with the cation exchanger. The distribution coefficients P , of the radionuclides under study were calculated by formula:

$$P = \frac{\dot{I}_0 - \dot{I}}{\dot{I}} \cdot \frac{V}{m}$$

where \dot{I}_0 and \dot{I} are the initial and equilibrium specific radioactivities, V is the volume of the solution and m is the mass of the air-dry cation exchanger.

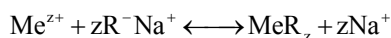
Results and Discussion

Table 1 presents the global distribution coefficients of the 3 radionuclides under study at different concentrations of the corresponding complexing agent. The overall stability constants of the complex compounds resulted from every radionuclide and the respective complexing agent have been calculated from the global distribution coefficients.

Table 1. The global distribution coefficients P_j for the $^{110m}\text{Ag}^+$, $^{65}\text{Zn}^{2+}$ and $^{55+59}\text{Fe}^{3+}$ radionuclides between the cation exchanger and the solution at different concentrations of the complexing agent in the watery solution.

Nuclide Ligand Sample	$^{110m}\text{Ag}^+$				$^{65}\text{Zn}^{2+}$		$^{55+59}\text{Fe}^{3+}$	
	$[\text{NH}_3] \cdot 10^4$ (mol·L ⁻¹)	P_j	$[\text{SCN}^-] \cdot 10^4$ (mol·L ⁻¹)	P_j	$[\text{HO}^-] \cdot 10^5$ (mol·L ⁻¹)	P_j	$[\text{Cl}^-] \cdot 10^2$ (mol·L ⁻¹)	P_j
2	0.0	1348.0	0.0	1348.0	~ 0	2151.0	0.0	2385.0
3	1.0	976.8	0.5	318.3	0.1	1756.0	1.0	1813.0
4	2.0	641.9	1.0	162.0	0.5	351.1	5.0	837.0
5	3.0	426.6	2.0	70.7	1.0	101.2	10.0	443.0
6	4.0	295.6	3.0	40.6	2.0	27.0	15.0	277.0
7	5.0	214.0	4.0	26.5	3.0	11.8	20.0	190.1
8	10.0	67.06	5.0	18.7	4.0	6.66	25.0	138.7
9	20.0	18.42	6.0	14.0	5.0	4.27	30.0	105.6
10	30.0	8.41	7.0	10.8	6.0	2.97	35.0	83.1
11	40.0	4.79	8.0	8.63	8.0	1.67	40.0	67.1
12	50.0	3.09	9.0	7.05	10.0	1.07	50.0	46.3

Considering the cation exchanger in the Na^+ form, and the radioactive metallic ion with the electric charge $z+$, the ion exchange reaction in the absence of the complexing agent is:

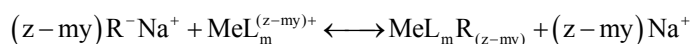


The global distribution coefficient is as follows:

$$P = \frac{[\text{MeR}_z]_{\text{exch}}}{[\text{Me}^{z+}]_{\text{sol}}} = K_0 \quad (1)$$

where $[\text{MeR}_z]_{\text{exch}}$ represents the concentration of the metallic ions in the cation exchanger, and $[\text{Me}^{z+}]_{\text{sol}}$ is the concentration of the metallic ions in the solution at the equilibrium with the cation exchanger.

If a ligand (complexing agent) having a negative charge L^{-y} is introduced in the solution, n complex species can result from this ligand and the Me^{z+} ions. All the complex species having a positive charge will participate to the ion exchange. The ion exchange reaction is:



The distribution constant of every complex species is:

$$K_m = \frac{[\text{MeL}_m \text{R}_{(z-my)}]_{\text{exch}}}{[\text{MeL}_m^{(z-my)+}]_{\text{sol}}} \quad (2)$$

in which m can be $0 \leq m \leq \frac{z-1}{y}$.

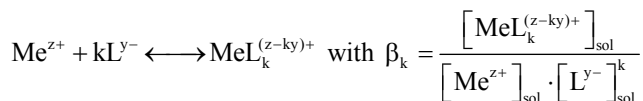
The distribution constants defined for every species charged positively, can't be directly measured experimentally. That's why the global distribution coefficient shown by the relation:

$$P = \frac{\sum_{i=0}^m [\text{MeL}_i \text{R}_{(z-iy)}]_{\text{exch}}}{\sum_{k=0}^n [\text{MeL}_k^{(z-ky)+}]_{\text{sol}}} \quad (3)$$

is more convenient. The numerator represents the total concentration of the metallic ions in the cation exchanger and the denominator represents the total concentration of the metallic ions in the solution at the equilibrium with the cation exchanger. These total concentrations are directly proportional to the specific activities, \dot{I} , experimentally measured, for the 2 phases in equilibrium. In order to eliminate the proportionality factor the specific activities for the solution and the ion exchanger should be measured in identical conditions. If \dot{I}_0 represents the specific activity of the solution before coming into contact with the ion exchanger, and \dot{I} represents the specific activity of the solution after the distribution equilibrium was established, the difference $(\dot{I}_0 - \dot{I})$ represents the specific activity of the cation exchanger at equilibrium.

For every radionuclide, 10 values of the global distribution coefficient were determined, corresponding to 10 different concentrations of the respective ligand.

The equilibrium concentrations of the complex species in the solution can be expressed by the corresponding overall stability constant, β_k :



results:

$$[\text{MeL}_k^{(z-ky)+}]_{\text{sol}} = \beta_k \cdot [\text{Me}^{z+}]_{\text{sol}} \cdot [\text{L}^{y-}]_{\text{sol}}^k \quad (4)$$

where $0 \leq k \leq n$.

Considering the relations (3) and (4) after some simple maths operations the result is:

$$P_j = \frac{P_0 + \sum_{i=1}^m K_i \beta_i [L_j^{y-}]_{\text{sol}}^i}{1 + \sum_{k=1}^n \beta_k [L_j^{y-}]_{\text{sol}}^k} \quad (5)$$

This very general expression of P_j corresponding to a certain concentration of the ligand in solution, $[L_j^{y-}]_{\text{sol}}$, is greatly simplified for the concrete situations, if the necessary condition, $m \leq \frac{z-1}{y}$ is considered. If there are bivalent metallic ions ($z=2$) and monovalent anionic ligands ($y=1$) m has only one value, $m=1$, and the relations (5) becomes:

$$P_j = \frac{P_0 + K_1 \beta_1 [L_j^{y-}]_{\text{sol}}}{1 + \sum_{k=1}^n \beta_k [L_j^{y-}]_{\text{sol}}^k} \quad (6)$$

Considering the values of the distribution constants for all the complex specia being much lower than the respective global distribution coefficients the relation (6) is as follows:

$$\frac{P_0 - P_j}{P_j} = \sum_{k=1}^n \beta_k [L_j^{y-}]_{\text{sol}}^k \quad (7)$$

This relation is valid for every value of y , including the neutral ligands ($y=0$) when $m=n$. The experimental determination of the global distribution coefficients P_j for n different values of the ligand concentration $[L_j]$, has as a result a system of n linear equations. The solutions to these equations are the n overall stability constants β_k of the complex specia formed by the metallic ion Me^{z+} and the respective ligand.

Ten P_j values for 10 different concentrations $[L_j]$ of the ligand were determined for every radionuclide under study. Four systems of n linear equations solved by means of a computer programme were drawn up. The average between the 4 values of overall stability constant is used further on. Table 2 presents these results.

Table 2. The overall stability constants of the complex compounds formed by the $^{110\text{m}}\text{Ag}^+$, $^{65}\text{Zn}^{2+}$, and $^{55+59}\text{Fe}^{3+}$ radionuclides with different ligands.

Radionuclide	$^{110\text{m}}\text{Ag}^+$		$^{65}\text{Zn}^{2+}$	$^{55+59}\text{Fe}^{3+}$
Ligand	NH_3	SCN^-	HO^-	Cl^-
Values	$\beta_1 = 2.1 \times 10^3$	$\beta_1 = 5.6 \times 10^4$	$\beta_1 = 2.5 \times 10^4$	$\beta_1 = 30.2$
	$\beta_2 = 1.7 \times 10^7$	$\beta_2 = 1.7 \times 10^8$	$\beta_2 = 2.0 \times 10^{11}$	$\beta_2 = 135.0$
		$\beta_3 = 2.8 \times 10^9$	$\beta_3 = 1.4 \times 10^{13}$	$\beta_3 = 13.6$
		$\beta_3 = 4.7 \times 10^9$	$\beta_4 = 4.6 \times 10^{14}$	$\beta_4 = 0.06$

Using the values of these overall stability constants, the fractions α_i (%) for every radionuclide existent in the solution either as a simple uncomplexed ion or in every possible complex state depending on the ligand concentration in the solution, were calculated.

If the Me^{z+} metallic ions and the ligand L form many complex specia MeL_i with $0 \leq i \leq n$, the fraction α_i of these ions existing in a complex state in the solution is represented by the ratio between the concentration of this complex and the absolute concentration of the respective ions in a system at equilibrium.

$$\alpha_i (\%) = \frac{[MeL_i]_{sol}}{\sum_{k=0}^n [MeL_k]_{sol}} \cdot 100 \quad (8)$$

Expressing the concentrations of the complex specia in the solution by the respective stability constants and the concentration of the ligand the result is:

$$\alpha_i (\%) = \frac{\beta_i}{\sum_{k=0}^n \beta_k [L]^{k-i}} \cdot 100 \quad (9)$$

The fractions α_i for the radionuclides and the corresponding ligands at different concentrations in the solution were calculated by means of the overall stability constants (see Table 2 and the relation 9).

The tables 3÷6 show the results.

The complexation of the $^{110m}Ag^+$ ions in $5 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ concentration of the ammonia in ammoniacal solutions is considerable. If the concentration is higher $10^{-5} \text{ mol} \cdot \text{L}^{-1}$ the whole amount of Ag is complexed (see Table 3). The complexation of the Ag ions with SCN^- ions begins right at $10^{-6} \text{ mol} \cdot \text{L}^{-1}$ concentrations. At $5 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ all the positive Ag ions are to be found as neutral or anionic complex compounds (see Table 4). For SCN^- ion concentrations higher than $10^{-2} \text{ mol} \cdot \text{L}^{-1}$ there are only anionic complex specia in the solution. The complex $[^{110}Ag^+(SCN)_2]^-$ is over 80% predominant.

Table 5 shows that the $^{65}Zn^{2+}$ radioactive ions are to be found in the solution in this simple state only for $pH < 8$. There are also more than 10% cationic specia for pH values up to 9. For pH 9÷10 there are only neutral complex compounds in the solution. For $pH > 11$ the anionic complex compounds are present in the solution in a considerable number. The $^{65}Zn^{2+}$ radioactive ions from the polluted waters can be separate on the cation exchangers only if the pH is neutral or acid. For $pH > 13$ the above mentioned radioactive ions can be separated on the anion exchangers. For pH 8÷13 these radioactive ions can't be entirely separated from the polluted waters either on the cation exchangers or the anion exchangers.

Regarding the $^{55+59}\text{Fe}^{3+}$ radioactive ions in solutions containing Cl^- at a lower than $10^{-3} \text{ mol} \cdot \text{L}^{-1}$ concentration the whole Fe^{3+} amount is uncomplexed. There are only cationic species in the solution having $1 \text{ mol} \cdot \text{L}^{-1}$ concentration of the Cl^- ions. At very high concentrations, over $10 \text{ mol} \cdot \text{L}^{-1}$, there are $[\text{}^{55+59}\text{FeCl}_4]^-$ anionic complex compounds in the solution.

Conclusion

This method makes the study of the real ionic state of metallic radionuclides in very diluted watery solutions possible. The data presented in this paper offer the best conditions and the most efficient method of separating the radionuclides which can be found in microconcentrations in polluted waters.

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