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V. I. Golovanov[a]; V. M. Shkinev[b]; B. Ya. Spivakov[b]; K. E. Geckeler[c]; E. Bayer[c]
[a] CHEMICAL DEPARTMENT, CHELYABINSK UNIVERSITY, CHELYABINSK, RUSSIA [b] VERNADSKY INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY ACADEMY OF SCIENCES, MOSCOW, RUSSIA [c] INSTITUTE OF ORGANIC CHEMISTRY UNIVERSITY OF TÜBINGEN, TÜBINGEN, GERMANY

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Mathematical Description of Metal Retention with Water-Soluble Polymers during Membrane Filtration

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V. I. GOLOVANOV
CHEMICAL DEPARTMENT
CHELYABINSK UNIVERSITY
CHELYABINSK 454014, RUSSIA

V. M. SHKINEV and B. YA. SPIVAKOV
VERNADSKY INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY
ACADEMY OF SCIENCES
MOSCOW 117975, RUSSIA

K. E. GECKELER* and E. BAYER
INSTITUTE OF ORGANIC CHEMISTRY
UNIVERSITY OF TÜBINGEN
W-7400 TÜBINGEN, GERMANY

ABSTRACT

A theoretical approach to the description of metal retention and enrichment in aqueous solution by soluble polymeric reagents during membrane filtration is proposed. The metal retention data obtained experimentally may be explained by using mathematical models based on the theory of kinetics of reactions in partially open systems.

INTRODUCTION

Membrane filtration processes can be successfully used for the separation of various species and for their enrichment from dilute solutions. More effective retention of certain inorganic ions and therefore their enrichment in a membrane filtration unit and separation from other solutes is achieved by using water-soluble polymeric reagents (1–3). Hydrophilic polymers with different complexing groups, including a variety of specially prepared complexing agents, have been tested to show the applicability of the method to the separation of various metal cations and anionic

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* To whom correspondence should be addressed.

species for analytical and technological purposes (3–5). This method, based on the retention of certain ions by a membrane which separates low molecular mass compounds from macromolecular complexes of the ions, is called liquid-phase polymer-based retention (LPR).

Different modes of separation by LPR can be used for inorganic ions and other microsolutes (1, 3, 6). To separate the components of a small volume sample in analytical chemistry (relative preconcentration), the liquid sample is placed in the polymer-containing cell solution and then washed with water (washing method). The pH is adjusted to a value at which the ions of interest are retained and the other species are removed. The washing method can also be applied to purify a macromolecular compound by eliminating the microsolutes while maintaining a constant cell volume. To achieve enrichment of metal ions, their solution can be passed from a reservoir into a smaller volume filtration unit in the presence of a complexing polymer. This concentration method (enrichment method) is designed for metal recovery from diluted technological solutions and for absolute preconcentration of elements in analytical chemistry. The ion separation process in LPR is a complex phenomenon and depends on the thermodynamic characteristics of the metal–ligand and other interactions in solution and at the membrane surface. The kinetic properties of the system are very important, particularly in the case of high flow rates and slow interactions. Therefore, the reported expressions (1, 3, 6) based on an assumption of zeroth or instant 100% metal binding with polymer ligands do not give an adequate description of real LPR separations.

This paper deals with both the washing method and the enrichment method, and it describes mathematical models of metal ion separation processes.

THE WASHING METHOD

In this method, a washing liquid is passed at a certain rate through the cell solution containing a polymer reagent and a mixture of ions which are separated owing to different thermodynamic stabilities of the high-molecular complexes formed in the cell and to different reactions rates. Retention of an ionic solute in the cell is often represented in the form of its retention coefficient

$$R = C_r C_0^{-1} \tag{1}$$

where C_r is the total ion concentration in the retentate (cell solution after a filtrate volume of V_f has been passed), and C_0 is the initial ion concentration in the cell. The cell solution volume V_c (retentate volume) and the fluid flow across the membrane as well as the retentate solution pH and ionic strength are usually maintained constant. In analytical separations it is of interest in most cases to retain trace elements to be determined for their separation from other sample constituents. In such separations the polymer reagent concentration in the cell solution is usually in the range of 1 to 4%, which is much higher than the retained ion concentration. Therefore, we assume that the free macromolecular ligand concentration (activity) is also constant during the filtration run. The filtration factor Z expressed in relative units is another convenient characteristic of the process:

$$Z = V_f V_c^{-1} = T^{-1} t \tag{2}$$

where $T = V_c F^{-1}$ is the time necessary for a washing fluid volume equal to V_c to pass through the cell, F is the flow rate across the membrane, and t is the total time of filtration. Some typical retention curves (R as a function of Z) are presented in Figs. 1 and 2.

The aim of this work is to present a theoretical explanation of experimental retention curves by using mathematical modeling of physicochemical processes occurring in LPR systems.

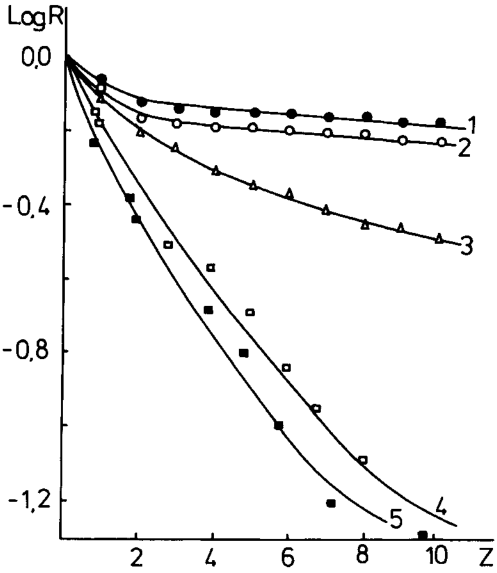

FIG. 1 Retention of Cr (1), Cu (2), Zn (3), Co (4), and Ni (5) by 2% poly(vinyl pyrrolidone) at pH 5 with the use of 0.15 M $NaNO_3$ as washing solution. Lines = calculated, points = experimental values.

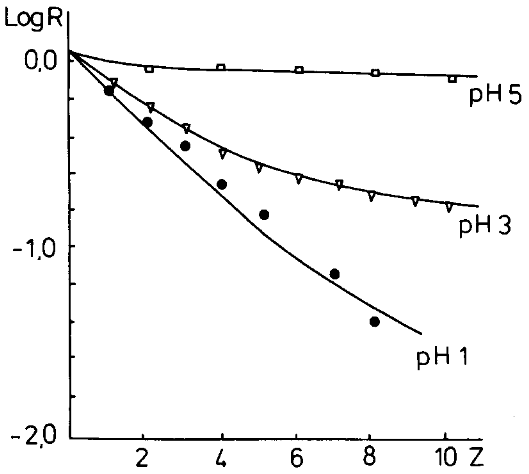

FIG. 2 Retention of zinc by 2% poly(ethyleneimine) at different pH values with the use of 0.15 M $NaNO_3$ as washing solution. Lines = calculated, points = experimental values.

Let us consider metal retention as a process dependent on polymer complex dissociation which is, in general, a case described by a reversible reaction (charges are omitted):

$$M + L \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} ML \tag{3}$$

In systems with metal concentrations which are small relative to the polymer concentration, only the formation of ML may be taken into account. Designate the concentrations of retained metal form ML as C_2 and of free metal forms M as C_1. The concentration of metal forms not complexed by the polymer in volume V_c is determined by two processes: Reaction (3) and irreversible transfer of M across the membrane. Therefore, we may base our model on the theory of kinetics of reactions in partially open systems (7). From the point of view of formal kinetics, such a model can be written as a system of differential equations:

$$V_c dC_1/dt = k_2' V_c C_2 - k_1' V_c C_1 - FC_f \tag{4}$$

$$V_c dC_2/dt = -k_2' V_c C_2 + k_1' V_c C_1 \tag{5}$$

where C_f denotes the metal concentration of the filtrate. To transfer to dimensionless parameters, let us use Eqs. (1) and (2) and take into account that the mass balance is expressed as

$$R = R_1 + R_2 \tag{6}$$

where R_1 and R_2 are retention values for M and ML, respectively. Then we can obtain a system of differential equations

$$dR_1/dZ = k_2'TR_2 - k_1'TR_1 - k_m'R_1 \tag{7}$$

$$dR_1/dZ = k_1'TR_1 - k_2'TR_2 \tag{8}$$

Here $k_m = C_f/C_r$ is the coefficient of distribution of the metal ions between the filtrate and the retentate, and which can be considered as a coefficient of membrane retardation. It is clear that k_m can have values from 1 to 0.

A differential form of the retention function can be obtained from Eqs. (7) and (8):

$$d \ln R/dZ = -k_mR_1/R = -k_m\alpha \tag{9}$$

where α represents the free metal fraction of the total metal concentration in the cell solution. In a general case, α can be considered as a dissociation degree under nonequilibrium conditions. The integral retention function can be found by solution of the given system of equations. Solution of a system of such equations as Eqs. (6) and (7) in a general form is known:

$$R_1 = Q_1'e^{r_1Z}\, Q_2'e^{r_2Z} \tag{10}$$

$$R_2 = Q_1''e^{r_1Z} + Q_2''e^{r_2Z} \tag{11}$$

Therefore, by substitution into Eq. (6), we have for R:

$$R = Q_1e^{r_1Z} + Q_2e^{r_2Z} \tag{12}$$

Coefficients r_1 and r_2 are roots of a characteristic equation $r^2 + pr + q = 0$:

$$r_1 = -p/2 + \sqrt{(p/2)^2 - q} \tag{13}$$

$$r_2 = -p/2 - \sqrt{(p/2)^2 - q} \tag{14}$$

In our case:

$$p = k_1 + k_2 + k_m \tag{15}$$

$$q = k_2k_m \tag{16}$$

where $k_1 = k_1'T$ and $k_2 = k_2'T$.

Concrete expressions for Q_1 and Q_2 are obtained by solving a system of equations:

$$\left.\begin{aligned} Q_1 + Q_2 &= 1 \\ r_1Q_1 + r_2Q_2 &= -k_m\alpha_0 = -A \end{aligned}\right\} \tag{17}$$

which corresponds to the boundary conditions for R and $(d \ln R)/dZ$ at $Z = 0$. The expression for α_0 can be written as $\alpha_0 = k_2/(k_1 + k_2)$ if the equilibrium is attained in the cell solution. The solution of the equation system will be

$$\left.\begin{aligned} Q_1 &= (r_2 + A)/(r_2 - r_1) \\ Q_2 &= (r_1 + A)/(r_1 - r_2) \end{aligned}\right\} \tag{18}$$

The ultimate expression for the retention function is written as

$$R = Qe^{r_1Z} + (1 - Q)e^{r_2Z} \tag{19}$$

where

$$Q = (r_2 + A)/(r_2 - r_1) \tag{20}$$

It follows from Eqs. (13)–(20) that the retention function is determined by three parameters, k_1, k_2, and k_m, if $\alpha_0 = k_2/(k_1 + k_2)$.

The parameters can be found by using one of nonlinear least-squares methods (8). We have used the distorted polyhedron method to develop software for the purpose. Tables 1 and 2 give parameters of the retention functions and the estimates of ML stability constants ($K = k_1'/k_2' = k_1/k_2$) calculated for the systems based on poly(vinyl pyrolidone), poly(ethyl-

TABLE 1
Parameters of the Functions of Metal Retention by Poly(Vinyl Pyrrolidone) at pH 5 and an Ionic Strength of 0.15 mol·L^{-1} (NaNO$_3$)

Metal	R (Z = 10)	k_m	$k_1 \times 10^2$	$k_2 \times 10^2$	K
Cr(III)	0.70	0.98	3.6	1.2	3.0
Cu(II)	0.63	0.98	2.3	1.1	2.1
Zn(II)	0.50	0.97	35.0	42.0	0.8
Cd(II)	0.34	0.74	8.2	7.2	1.1
Co(II)	0.15	0.63	2.9	9.3	0.3
Ni(II)	0.01	1.00	52.0	64.0	0.8

TABLE 2
Parameters of the Functions of Metal Retention by Poly(Vinyl Alcohol) at pH 5 and an Ionic Strength of 0.15 mol·L^{-1} ($NaNO_3$)

Metal	R (Z = 10)	k_m	$k_1 \times 10^2$	$k_2 \times 10^2$	K
Fe(III)	0.93	1.0	1.58	0.106	14.90
Cr(III)	0.92	0.95	4.07	0.246	16.50
Cu(II)	0.69	0.64	3.22	1.080	2.98
Co(II)	0.33	0.70	0.41	0.757	0.55
Cd(II)	0.32	0.82	13.50	9.510	1.42
Ni(II)	0.22	0.62	12.40	50.80	0.24
Zn(II)	0.11	0.53	1.92	9.40	0.20

eneimine) (PEI), poly(vinyl alcohol), and various metal ions. The model proposed has been shown to be adequate to the experimental results for the systems studied. The experimental retention curves have been obtained using a procedure described below.

If the thermodynamic equilibrium is attained during the ultrafiltration process, Eq. (21) can be used instead of Eq. (19);

$$R = e^{-Z/(1+\tilde{k})} \tag{21}$$

at $k_m = 1$. This may be shown by integration of Eq. (9). Eq. (21) is obtained from Eq. (19) if $|r_1| \ll |r_2|$. This conclusion, as follows from consideration of Eqs. (13)–(16), is valid at $T > 1/k'_1$ and $T > 1/k'_2$. In other words, the "lifetime" of complex ML ($1/k_2$) and metal ions M, not bound by the ligands, must be less than the time of complete substitution of the cell solution volume.

Therefore, deviations from the simple Eq. (21) become noticeable when the rate constants are comparable in order of magnitude with min^{-1}. Such deviations were observed in our experiments (see Figs. 1 and 2).

The quality of the model may be estimated by comparison of the experimental points and calculated retention functions, given in Figs. 1 and 2 in the form of points and solid lines, respectively. The relative deviations of the experimental results from the calculated values are not greater than 5% in these examples.

In conclusion to this part of the paper, it is worth noting that the metal retention orders may be different from the thermodynamic complex stability orders for corresponding metal ions. The k_m values are significantly different from the units in some cases. The reasons for such deviations should be especially investigated.

THE ENRICHMENT METHOD

The model proposed and the parameters obtained can be used to calculate enrichment factors for metal ions concentrated by using the enrichment variant of LPR.

In this method a solution with a metal concentration of C°_M is passed from the reservoir into the membrane filtration cell. The cell solution volume V_c is usually kept constant. Under such conditions, the enrichment factor is expressed as

$$E = C_r/C^\circ_\mathrm{M} \tag{22}$$

As in the previous model, we may assume that the metal ions are concentrated due to a reversible complexation reaction (3). The ions are also partially retained as low-molecular species owing to the so-called membrane effect ($k_m < 1$). Taking this into account and using Eq. (2), we can write Eqs. (22) and (23) instead of Eqs. (4) and (5):

$$V_c dC_1/dZ = k_2 V_c C_2 - k_1 V_c C_1 - FC_f + FC^\circ_\mathrm{M} \tag{23}$$

$$V_c dC_2/dZ = -k_2 V_c C_2 + k_1 V_0 C_1 \tag{24}$$

where F is the average flow rate.

The form of the system of Eqs. (22) and (24) is not different from that of Eqs. (4) and (5). A similar solution gives the following expressions:

$$C_1 = Q'_1 e^{r_1 Z} + Q'_2 e^{r_2 Z} + C^\circ_\mathrm{M}/k_m \tag{25}$$

$$C_2 = Q''_1 e^{r_1 Z} + Q''_2 e^{r_2 Z} + k_1 C^\circ_\mathrm{M}/k_2 k_m \tag{26}$$

where r_1 and r_2, assigned by Eqs. (13)–(16), are dependent on k_1, k_2, and k_m. Taking into account that

$$C_r = C_1 + C_2 \tag{27}$$

and substituting Eqs. (25) and (26) into Expression (22), we have

$$E = Q_1 e^{r_1 Z} + Q_2 e^{r_2 Z} + (k_1 + k_2)/k_2 k_m \tag{28}$$

The differential form of the enrichment function can be obtained by summarizing Eqs. (23) and (24) and using the definitions of Eqs. (22) and (27):

$$dE/dZ = 1 - k_m \alpha E \tag{29}$$

The form of concrete expressions for Q_1 and Q_2 depends on the enrichment procedure used. If the cell is filled with water before the filtration process starts (that is, $E = 0$ at $Z = 0$), then it follows from Eqs. (28) and (29) that

$$\left.\begin{array}{l} Q_1 + Q_2 + A^{-1} = 0 \\ r_1Q_1 + r_2Q_2 = 1 \end{array}\right\} \tag{30}$$

The simultaneous solution of the above expressions gives

$$Q_1 = Q - Q/A \tag{31}$$

$$Q_2 = (Q - 1)/A \tag{32}$$

where Q is preset by Expression (20). By substitution of Eqs. (30) and (32) into Eq. (28), we ultimately obtain

$$E = -1/A[1 - Qe^{r_1Z} - (1 - Q)e^{r_2Z}] \tag{33}$$

or

$$E = -1/A(1 - R) \tag{34}$$

The interrelation between E as a function of Z and R as a function of Z is an important consequence from Eq. (34). This enables the design of experimental studies of metal enrichment and *a priori* prediction of the results if parameters k_1, k_2, and k_m are known. It is convenient to find these parameters from the R–Z function.

On the basis of assumptions used to obtain Eq. (21), a partial expression of Eq. (35) for equilibrium conditions will be

$$E = (\tilde{k} + 1)(1 - e^{-Z(\tilde{k}+1)}) \tag{35}$$

A Zn–PEI–0.15 M $NaNO_3$ system (Fig. 2) was used as an example of the application of the values of R as a function of Z to predict E–Z functions. The conditional stability constants for the complexes formed in the system have been evaluated (from the experimental data presented in Fig. 2) to be $K = 23$ (pH 5) and $K = 0.33$ (pH 3). Taking into account the competitive reaction

$$\mathrm{H} + \mathrm{L} = \mathrm{HL} \tag{36}$$

the expression for a conditional constant can be written as

$$K = K'(1 + 10^{\mathrm{p}K_a - \mathrm{pH}})^{-1} \tag{37}$$

where pK_a relates to the protonated form of PEI. By solving Eq. (37) relative to K and pK_a, and using the two K values, we obtain $K' = 69$ and p$K_a = 5.3$. The enrichment functions for the Zn–PEI system calculated by

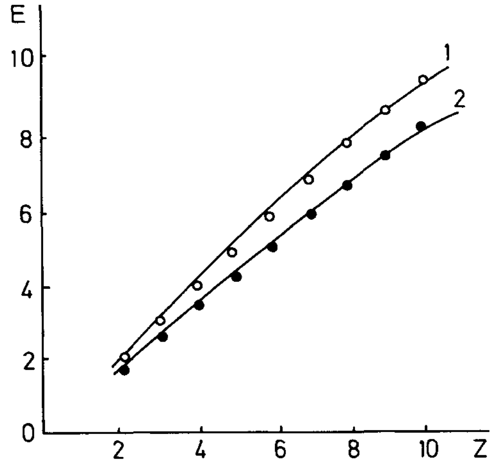

FIG. 3 Enrichment of zinc by 2% poly(ethyleneimine) at pH 7 (1) and 5 (2) from 0.15 M $NaNO_3$. Lines = calculated, points = experimental values.

Eq. (36) for the two pH values are given in Fig. 3 as solid lines. The experimental points, also presented in Fig. 3, are in good agreement with the values evaluated from the calculated functions.

The maximum enrichment factor E, which can be obtained experimentally, is an important characteristic of the system used. In our example, the problem was solved by using Eq. (36). The maximum enrichment factor of 70 for Zn at pH 7 can be achieved at $Z = 72$.

EXPERIMENTAL

Reagents

Poly(vinyl pyrrolidone), poly(vinyl alcohol), and poly(ethyleneimine), used for metal retention, had a molecular mass in the 30,000–40,000 $g \cdot mol^{-1}$ range; they were dissolved in water and membrane-filtered prior to use.

All salts were of analytical-reagent grade and used as received. The individual radionuclides ^{51}Cr, ^{59}Fe, ^{60}Co, and ^{65}Zn were applied to study the distribution of the corresponding elements between the cell solution and the permeate.

Instrumentation

The unit used for separation and enrichment studies consisted of a filtration cell with a magnetic stirrer, a membrane with an exclusion rate of 10,000 (Amicon PM-10 or equivalent), and a reservoir. The system has been described in more detail elsewhere (2, 5). The nitrogen pressure was kept constant (300 kPa) during membrane filtration.

Radiometric measurements were made with an NRG-603 automatic γ-counter (Tesla) or with a Ge(Li) detector connected to a multichannel Nokia LP-4900 analyzer (for simultaneous measurements). Concentrations of some elements were measured on an ICAP 9000 simultaneous ICP atomic emission spectrometer (Allied Analytical Systems).

Procedures

The washing procedure was as follows. An aliquot of a nitrate solution of one or several elements was placed in the filtration cell, which also contained the polymer reagent solution, to make a total constant volume of 2 or 4 mL. The filtration flux was 1–10 $\mathrm{mL \cdot min^{-1}}$. It was kept constant during filtration.

The metal concentration was 10 $\mu\mathrm{g \cdot mL^{-1}}$, and the reagent concentration was 2% in all instances. The pH values of the cell and reservoir solutions were adjusted to be the same, and the nitrate concentration ($NaNO_3$ + HNO_3) was adjusted to give a constant ionic strength of 0.15. The cell solution was stirred for 5 minutes and then washed with the reservoir fluid under pressure. The filtrate (permeate) fractions and cell solution were subjected to radiometric or ICP measurements.

In the enrichment procedure, a nitrate solution of zinc and PEI was mixed, stirred for 5 minutes, placed in the reservoir, and passed into a filtration cell containing 2–4 mL of 0.15 M $NaNO_3$. The metal-to-polymer ratio was the same as in the washing method. The filtrate and cell solution were analyzed as described above.

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