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Study of Polyelectrolytes

for

LOS ALAMOS NATIONAL LABORATORY

Final Report

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MASTER

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INTRODUCTION

To assess the safety of a potential radioactive waste repository, analyse of the fluid solution containing low levels of activity need to be performed. In some cases, the radioactivity would be so weak (3 - 30 pCi/L) that the solution must be concentrated for measurement. For this purpose, Los Alamos National Laboratory scientists are synthesising some water soluble polyelectrolytes, which, because they are strong complexing agents for inorganic cations, can concentrate the radioelements in solution.

To assist in characterisation of these polyelectrolytes, we have performed experiments to determine physico-chemical constants, such as pKa values and stability constants.

DESCRIPTION OF THE POLYMERS

The table below lists some properties of the polyelectrolytes.

abbreviation	name	weight	appearance	vapor pressure	water solubility	stability
PEI C	polyethylenamine-functionalised with acetic acid groups	>30,000	whitish solid odorless	high	soluble	stable
PEI PO3	polyethylenamine-functionalised with phosphonic acid groups	>30,000	yellow-gold solid odorless	high	soluble	stable

Parameters of PEI PO3 and PEI C

(Los Alamos National Laboratory)

Some H-NMR spectra have been done on both compounds. There are presented in the following pages. The solvent used was D₂O and the reference was 3(Trimethylsilyl)-1-propane-sulfonic acid (sodium salt hydrate). For both compounds, the spectrum had a peak at 0 ppm and a triplet at 0.6 ppm both due to the reference. The peak at 2.2 ppm (characteristic of the functional group CH₃) may be due to acetone (used to wash the vials and not totally removed). The peak at 4.7 ppm is due to H₂O, which is present because the compounds (solvent and reference, in particular) absorb water. The spectrum between the frequencies 4 ppm and 2.5 ppm are characteristic of each polyelectrolyte, but cannot be analysed precisely.

PEI C
300 MHz
11-15-94
solvent: d2o
etc. HI

H NMR PEI C

PEI C
300 MHz 11-14-94
solvent: d2o
C1, M1

H NMR PEI C

H NMR PEI PO_3

PEI PO₃
500 MHz 11-15-94
solvent: d₂O
T₁: 1H

H NMR PEI PO₃

TITRATION OF THE POLY ACIDS

EXPERIMENTAL

For both polyelectrolytes, two kinds of powder were provided by LANL. However, because of precipitation problems, only one of each was used in our experiments (the first received for PEI PO3 and the third ("old" received in October's 94) for PEI C).

The titration was done under a blanket of N_2 and with fresh sodium hydroxide (NaOH) which was standardised by potassium acid phthalate (KHP). The time required for stabilisation of pH after each addition of NaOH did not exceed 3 minutes.

We used a glass electrode filled with saturated NaCl solution (Corning); its efficiency is always higher than 92 %.

CALCULATION AND RESULTS

DEFINITIONS

We define pcH as the *proton concentration* and pH as the value determined by the pH-meter i.e. the *proton activity*:

$$\text{pcH} = -\log([H^+]) \qquad \text{pH} = -\log(a_{H^+}) \qquad (1)$$

In order to find the relation between pH and pcH, a titration of an amount of standardised NaOH was performed with a solution of standardised HCl. The ionic strength of the solution, the vessel and the electrode were the same as used in the experiments of characterisation of the polyelectrolytes. After plotting pcH (calculated) vs pH (electrode response), the regression analysis leads to the relation below:

$$\text{pcH} = 1.024 (\pm 0.007) \times \text{pH} - 0.24 (\pm 0.07) \qquad (r^2 = 0.999) \qquad (2)$$

DERIVATIVE METHOD

In order to find the pKa of the polyelectrolytes, the data of the titrations were treated by the derivative method. The derivative dpcH/dV is reported as a function of V, where V is the volume of acid added during the titration. *This takes in account the amount of base added at the beginning of the experiments*, which means that V can have negative values. The first and the last maxima indicate the equivalent volumes of protons, V_{e2} and V_{e1} . The pKa values are found as the pH at $V_{e1}/2$. The peak at about $V = 0$ ml correspond to the amount of base initially introduce in the system. The figure below is an example of the application of this method. The figures of all the titrations are presented at the end of this report.

Example: PEI C (titration 1)

Initial conditions:

NaClO₄: 0.1 M, 20 ml

NaOH: 1.058 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4077 g

The results below have been found for the two polyelectrolytes:

PEI C			PEI PO3		
titration #	pKa ₁	pKa ₂	titration #	pKa ₁	pKa ₂
1	5.0 ± 0.1	9.4 ± 0.1	1	5.4 ± 0.2	8.0 ± 0.1
2	5.01 ± 0.08	9.22 ± 0.06	2	5.77 ± 0.09	8.1 ± 0.2
3	4.85 ± 0.08	9.00 ± 0.05	3	5.0 ± 0.1	7.8 ± 0.1
4	5.3 ± 0.1	9.20 ± 0.06	4	5.35 ± 0.06	7.99 ± 0.04
			5	5.40 ± 0.07	8.09 ± 0.09
average	5.04 ± 0.09	9.21 ± 0.07	average	5.4 ± 0.4	8.0 ± 0.1

pKa values (calculation based on the derivative)

The calculation has been performed with and without the pH/pcH correction (equation (2)). In both cases, the values of pKa were the same. The small ionic strength (≈ 0.1 M) allows the approximation: $pH \approx pcH$.

The very wide peaks found for both compounds, in the titrations indicate most likely that the values we found are the average of a distribution of pKa values: $\overline{pKa_1}$ and $\overline{pKa_2}$ (which is expected for polyelectrolytes).

	$\frac{[HL]}{[L] \cdot [H]}$	$\frac{[H_2L]}{[HL] \cdot [H]}$	$\frac{[H_3L]}{[H_2L] \cdot [H]}$	$\frac{[H_4L]}{[H_3L] \cdot [H]}$	$\frac{[H_5L]}{[H_4L] \cdot [H]}$
IDA	9.34 (±0.02)	2.61 (±0.03)	-	-	-
NTA	9.49 (±0.04)	2.52 (±0.09)	(1.9) (±0.01)	(1.0) (±0.2)	-
EDTA	10.19 (±0.04)	6.13 (±0.03)	2.69 (±0.05)	2.00 (±0.1)	(1.5) (±0.1)

pKa values of IDA, NTA and EDTA,

Experimental conditions: ionic strength = 0.1, temperature = 25°C

(Smith & Martell: Critical Stability Constants, 1989)

The pKa values of the polyelectrolytes can be compared to these of compounds presenting the same functional groups. The values concerning PEI C are compared to the pKa values of IDA, NTA and EDTA (presented in the table above).

The two first ligands, IDA and NTA present one pKa value around 9.4 (due to the bound N-H) and one around 2.5. The absence of pKa value between these two numbers can be attributed to strength of the bound N-H which, because of the proximity of the other bounds, masks another pKa. However, in the case of EDTA, where the bounds are not so close between each other, we observe a pKa value around 6. In the case of PEI C, the molecule is also expanded, so we observe one pKa value around 5. The value at 9.21 is related to the bound N-H. Like IDA, NTA and EDTA, we should expect a value around 2, but our technique used does not permit us to observe such low values.

The pKa values of the polyelectrolyte PEI PO3 are compared to those found in the literature for the imino di (methylenephosphonic) acid (table below).

	$\frac{[HL]}{[L] \cdot [H]}$	$\frac{[H_2L]}{[HL] \cdot [H]}$	$\frac{[H_3L]}{[H_2L] \cdot [H]}$	$\frac{[H_4L]}{[H_3L] \cdot [H]}$	$\frac{[H_5L]}{[H_4L] \cdot [H]}$
Imino (methylenephosphonic) acid	10.79	6.08	5.04	(0.9)	-

pKa values of Iminodiphosphonic acid,

Experimental conditions: ionic strength = 0.1, temperature = 25°C

(Smith & Martell: Critical Stability Constants, 1989)

Since the molecule of PEI PO3 is bonded polymerically compared to the monomer iminodiphosphonic acid, we can expect higher pKa values. In effect, the first value found for PEI PO3 is 5.4 compared to 5.04 for the iminodiphosphonic acid. The increase is more important for the second pKa: 8.0 for PEI PO3 and only 6.08 for the iminodiphosphonic acid. Consequently, we should find in the case of PEI PO3 a third pKa value superior to 10.79. But our technique used does not allow us to find such high values.

CAPACITY IN PROTONS

The capacity in protons of the polyelectrolytes is determined as the number of equivalents present in the volume $Ve_2 - Ve_1$, where Ve_1 and Ve_2 are respectively the first and the second equivalent volume.

The results we have found are presented in the table below.

PEI C		PEI PO3	
titration #	capacity in meq/g	titration #	capacity in meq/g
1	7.1 ± 0.02	1	6.4 ± 0.6
2	6.4 ± 0.4	2	6.3 ± 0.3
3	6.3 ± 0.4	3	7.1 ± 0.5
4	6.2 ± 0.5	4	6.4 ± 0.2
		5	6.6 ± 0.3
average	6.3 ± 0.4	average	6.6 ± 0.4

Capacity in protons of PEI C and PEI PO3

THE DEGREE OF IONISATION

pKa (or pK_i) values can be also found from the degree of ionisation.

The degree of ionisation is determined by the equation (3):

- with:
- * $[H^+]$ is the concentration in protons (10^{-pH}),
 - * C_t is the concentration of titrable groups,
 - * C_{OH} is the concentration of NaOH added in the titration vessel,
 - * C_H is the concentration of HCl added in the titration vessel,
 - * K_w is the ionic product of water in 0.1 M $NaClO_4$ solution.

$$\alpha = \frac{[H^+] - \frac{K_w}{[H^+]} + C_{OH} + C_H}{C_t} \quad (3)$$

The model used is based on a modified equation of Tanford (1963):

- with:
- * α is the degree of ionisation of the polymeric material,
 - * n is the term responsible for electrostatic interactions.

$$pH - \log\left(\frac{\alpha}{1-\alpha}\right) = \overline{pK_i} + n \cdot \alpha \quad (4)$$

For chemical homogeneous polymers the values of $\overline{pK_i}$ are close to the pK of the repetitive monomeric unit (intrinsic constant). If the polyelectrolyte has irregular and chemically heterogeneous structures, it is likely that the $\overline{pK_i}$ represents a statistical weight average of the intrinsic constant.

The value of $\overline{pK_i}$ is obtained by extrapolating $\{pH - \log(\alpha/1-\alpha)\}$ to $\alpha = 0$. If the curve $\{pH - \log(\alpha/1-\alpha)\}$ vs α presents several parts of straight line, several pK will be found.

Here is an example of the application of this model:

Example: PEI PO3 (titration 1)

Initial conditions:

$NaClO_4$: 0.1 M, 20 ml

NaOH: 0.9314 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4981 g

The single straight line allows calculation of only one pK_i value. We could except the line to be resolvable in two straight lines, which would give a second pK_i value. However our technique do not permit reaching such values. This is also true in the case of the compound PEI C.

The table below presents the values found for the different titrations:

PEI C				PEI PO3			
titration #	slope	pK_i	r^2	titration #	slope	pK_i	r^2
1	4.6 ± 0.1	8.14 ± 0.07	0.988	1	6.29 ± 0.07	6.72 ± 0.04	0.997
2	3.57 ± 0.04	8.21 ± 0.02	0.998	2	5.56 ± 0.06	7.09 ± 0.03	0.997
3	3.58 ± 0.05	7.72 ± 0.02	0.998	3	6.38 ± 0.09	6.33 ± 0.05	0.995
4	3.45 ± 0.02	8.11 ± 0.01	0.999	4	6.41 ± 0.09	7.08 ± 0.05	0.995
-	-	-	-	5	6.4 ± 0.1	6.55 ± 0.05	0.995
average	3.53 ± 0.04	8.05 ± 0.03	-		6.37 ± 0.09	6.75 ± 0.04	-

pK_a intrinsic values (calculation based on the degree of ionisation)

The results presented above show that in this study, the degree of ionisation is not a satisfactory method to analyse the pK_a values. Other calculation methods have been applied to our results, but none have given satisfactory results in obtaining two values of pK_a . To obtain both highest and lowest pK_a values of PEI C and PEI PO3, an other technique than a simple titration must be envisaged, such as proton NMR. In this case, we would study the variation of the chemical shift of the protons with the pH (Rizkalla and Choppin, 1982).

SOLVENT EXTRACTION

Experiments using solvent extraction were performed to measure the complexation constants of the polyelectrolytes with a cation (europium).

EXPERIMENTAL

The extractant used was HDEHP (10^{-4} M) in toluene and the aqueous phase contained NaClO_4 (0.1 M), acetic acid (used as a buffer: 10^{-2} M), Eu ($5.4 \cdot 10^{-10}$ M) in HClO_4 10^{-3} M and a variable amount of polyelectrolyte.

All the solutions, organic or inorganic, were filtered (pore size: $\varnothing$ 0.2 μm for the aqueous solution and $\varnothing$ 0.45 μm for the organic solutions). The experiments were performed in glass vials created to minimise sorption of the metal ions (Caceci and Choppin., 1982).

The vials were shaken and after equilibration and phase separation, the activity of the aqueous and organic phases was counted (Torres, 1982).

A kinetic study showed that the equilibrium between the two phases is reached in less than 1 minute for PEI C, but with PEIPO3, much longer times are required (several hours). Accordingly, all the experiments were equilibrated for 24H.

The pH of the buffered experiments was 4.7 ± 0.1 .

The plots of the distribution coefficient (D) as a function of the initial polyelectrolyte concentration are shown below. D is calculated as the ratio between the total concentration of all the metal species in the organic phase and in the aqueous phase:

$$D = \frac{\sum[\text{Eu}]_{\text{organic}}}{\sum[\text{Eu}]_{\text{aqueous}}} \quad (5)$$

Plot of the distribution coefficient as a function of the initial polyelectrolyte concentration, case of PEI C

Plot of the distribution coefficient as a function of the initial polyelectrolyte concentration, case of PEI PO3

CALCULATIONS AND RESULTS

Since acetic acid was used as a buffer, the calculation of β must take in account the complexes formed between the acetate ion and the metal (Eu).

The equation of D becomes:

$$D = \frac{\sum [\text{Eu}]_{\text{organic}}}{\left([\text{Eu}] \cdot \left\{ 1 + \sum_{i=1}^n \beta_i^B [\text{Ac}]^i \right\} \cdot \left\{ 1 + \sum_{i=1}^m \beta_i^{\text{L apparent}} [\text{PEI}]^i \right\} \right)} \quad (6)$$

where $\beta_i^X = [\text{Eu X}]/[\text{Eu}] \cdot [\text{X}]^i$, X can be B (buffer) or L (ligand)

$$\beta_i^{\text{L apparent}} = \beta_i^{\text{L}} / (1 + \beta_i^B [\text{Ac}])$$

$$\beta_i^B = \beta_{\text{Eu/Ac}} = 10^2$$

If D_0 is the distribution coefficient of Eu in the absence of polyelectrolyte, the equation becomes (Caceci and Choppin, 1983):

$$D_0/D = 1 + \sum_{i=1}^m \beta_i^{\text{L apparent}} [\text{PEI}]^i \quad (7)$$

The graph presenting $D_0/D-1$ vs $[\text{PEI}]$ should give a straight line (slope = $\beta_i^{\text{L apparent}}$) in the case of the formation of one complex, or a curve if more complexes are involved. In our case, we obtained in all experiments a linear relation, which permitted us to determine the first complexation constant. The figures, for both case, are presented below.

Determination of the stability constant PEI C/Eu (solvent extraction)

ION EXCHANGE

In order to find the stability constants between the polyelectrolytes and Eu by an other technique, the ion-exchange method was used.

EXPERIMENTAL

The resin (DOWEX 50W-X12, 100-200 Mesh) is prepared by washing alternatively with methanol, water, HCl (6 M) and water (the treatment was done on a fritted-disc funnel using water suction to speed the washing process). To convert the resin to the Na^+ form, NaOH (1 M) was used. The resin was washed with water to remove the excess base, and with HClO_4 adjusted to pH 3.9 with NaOH. Finally the resin was washed with the same buffer solution used during the experiments (NaClO_4 (0.1 M), CH_3COOH (0.01 M)) and then with water, before oven drying at 80°C for 4 hours.

The solution of radioelement was the same used for solvent extractant (Eu of $5.4 \cdot 10^{-10}$ M in HClO_4 10^{-3} M). All the solutions were filtrated ($\varnothing$ 0.2 μm for the aqueous solution). The experiments were performed in treated glass vials (Caceci and Choppin., 1982).

The experiments consisted of shaking during 24 hours the vials containing 10 ml of the solution: Eu ($5 \cdot 10^{-11}$ M), polyelectrolyte, resin (~ 0.1 g) in the buffer solution described previously. After separation of the phases (liquid / resin), an aliquot of the aqueous phase in each vial was counted (activity A_f), and compared to a reference (Eu ($5 \cdot 10^{-11}$ M) in the buffer solution: activity A_0).

CALCULATION AND RESULTS

The analysis of the ion-exchange data followed that of the solvent extraction. Instead of analysing the coefficient "D", the value of "Kd", the distribution coefficient was used. This is expressed as:

$$K_d = \frac{\text{activity} / \text{g resin}}{\text{activity} / \text{ml solution}} \quad K_d = \frac{\text{activity} / \text{g resin}}{\text{activity} / \text{ml solution}} \quad (8)$$

A_0 and A_f are respectively the activity of the solution before and after contact with the resin, the distribution coefficient can be written as below:

$$K_d = \left(\frac{A_0}{A_f} - 1 \right) \cdot \left(\frac{V}{g} \right) \quad (9)$$

where V is the volume of the aqueous phase and g the mass of dry resin.

The plots of K_d as a function of the concentration of polyelectrolyte are presented below.

Plot of Kd as a function of the concentration of polyelectrolyte, case of PEI C

Plot of Kd as a function of the concentration of polyelectrolyte, case of PEI PO3

The calculation are basically the same in the ion exchange and solvent extraction methods (Torres, 1982). The stability constant is found as the slope of the straight line on the graph " $(K_{d0}/K_d - 1)$ vs $[PEI]$ ". These figures are presented below.

Determination of the stability constant PEI C/Eu (ion exchange)

Determination of the stability constant PEI PO3/Eu (ion exchange)

The value of stability constants found are presented in the table below:

PEI C	PEI PO3
pH = 4.7 ± 0.1 , $\alpha \approx 0.0005$	pH = 4.7 ± 0.1 , $\alpha \approx 0.01$
$\beta_{101} = 10^{6.84} (\pm 11 \%)$	$\beta_{101} = 10^{8.35} (\pm 35 \%)$

Values of the stability constant between the polyelectrolytes and Eu.
Ion exchange method

We note that the results from the ion exchange method are *very similar to those from the solvent extraction method*.

In the case of the ion exchange method, the possibility of interactions between polyelectrolyte and resin needs to be checked. If the polyelectrolyte is sorbed onto the resin, some of the activity that is lost from the aqueous phase would not be directly bound to the resin, but rather to the polyelectrolyte sorbed on the resin (Torres, 1982). For this reason, polyelectrolyte concentrations is determined spectrophotometrically, at the end of the experiments.

SPECTROPHOTOMETRIC MEASUREMENTS

The spectrophotometric measurements were performed on an OLIS 4100C Spectrophotometer. In order to find the appropriated wavelength, a spectrum of a solution of each polyelectrolyte was performed, between 0 and 1000 nm. Both are presented below.

PEI C

[PEI C] = 20 mg/l

absorbance at 203.5 nm

PEI PO3

[PEI PO3] = 20 mg/l

absorbance:
between 190 and 200 nm

Both compounds have an absorbance at a wavelength close to 200 nm: 203 nm for PEI C and between 190 and 200 nm for PEI PO3. So, for our investigations, we worked between 0 nm and

300 nm. However, since we were working near the limits of detection, the measurements could not be very precise. In particular, we could not determine a precise wavelength for PEI PO3.

In order to check if the polyelectrolytes are adsorbed on the resin during the ion exchange experiments, the supernatants were measured by spectroscopy, after separation of the phases. The results are compared to the absorbance of a reference (solution of the polyelectrolyte, before contact with the resin).

The absorbance has been checked for many systems, we report in the figures below one example for each compound.

PEI C

reference:

$$[\text{PEI C}] = 20 \text{ mg/l}$$

ion exchange:

$$[\text{PEI C}]_{\text{initial}} = 20 \text{ mg/l}$$

PEI PO3

reference:

$$[\text{PEI PO3}] = 2.8 \text{ mg/l}$$

ion exchange:

$$[\text{PEI PO3}]_{\text{initial}} = 2.8 \text{ mg/l}$$

As can be seen above, the proximity of the limit of detection does not allow us to provide definite results. Nevertheless, the figures presented above show that in both cases (PEI C and PEI PO3), there seems no real difference between the absorbances of the reference and the supernatant of the ion exchange experiment. Therefore, we conclude that *the polyelectrolytes were not significantly adsorbed on the resin during the ion exchange experiments*, and so the values of complexation constants provided above do not need to be modified.

The augmentation of the absorbance between 210 nm and 240 nm, for the analysis of the supernatants of the ion exchange experiments is due to a contribution of the resin.

CONCLUSION

Titration have been conducted on both compounds synthesised by Los Alamos National Laboratory. In order to find pK_a and capacity values, calculations have been done by the method of derivatives. For the compound PEI-amino carboxylate (PEI C), $pK_{a1} = 5.04$, $pK_{a2} = 9.21$ and the capacity in protons has been estimated to be 6.5 meq/g. For PEI-phosphonic acid (PEI PO₃), $pK_{a1} = 5.4$, $pK_{a2} = 8.0$ and the capacity is 6.6 meq/g. For both compounds, PEI C and PEI PO₃, the pK_a values determined have been compared to the literature (IDA, NTA, EDTA, imino diphosphonic acid).

The complexation constants between both compounds and europium were determined by two methods: solvent extraction and ion exchange. Both methods provided very similar results. The constant, $\log \beta_{101}$, describing the complexation PEI C/Eu is found to be 6.13 and 6.91, respectively with solvent extraction and ion exchange. In the case of PEI PO₃/ Eu, the value of $\log \beta_{101}$ is 8.16 and 8.35, by the same techniques. Similar high values of the complexation constant between europium and macromolecules such as humic acids or fulvic acids are found in the literature (Torres, 1982; Bodoglio, 1991...).

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ANNEX: FIGURES CONCERNING THE TITRATIONS

TITRATION OF THE COMPOUND PEI C

PEI C TITRATION 1

PEI C TITRATION 2

PEI C TITRATION 3

Initial conditions:

NaClO₄: 0.1 M, 20 ml

NaOH: 1.213 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4045 g

PEI C TITRATION 4

Initial conditions:

NaClO₄: 0.1 M, 20 ml

NaOH: 1.017 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4056 g

TITRATION OF THE COMPOUND PEI PO3

PEI PO3 TITRATION 1

Initial conditions:

NaClO₄: 0.1 M, 20 ml

NaOH: 0.9314 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4981 g

PEI PO3 TITRATION 2

Initial conditions:

NaClO₄: 0.1 M, 20 ml

NaOH: 1.201 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.5011 g

PEI PO3 TITRATION 3

Initial conditions:

NaClO₄: 0.1 M, 20 ml

NaOH: 1.143 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4103 g

PEI PO3 TITRATION 4

Initial conditions:

NaClO₄: 0.1 M, 20 ml

NaOH: 1.044 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4401 g

PEI PO3 TITRATION 5

Initial conditions: NaClO₄: 0.1 M, 20 ml

NaOH: 0.956 M, 4 ml

HCl: 0.5 M (titrant)

solid: 0.4129 g