

Ph.D. Thesis

**Role of Multivalent Counterions in  
Thermodynamic Properties of Polyelectrolytes**

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## Introduction

Synthetic polyelectrolytes often serve as model substances of biopolyelectrolytes for the reason that natural polyelectrolytes have varying composition (and purity) strongly depending on their origin, so their experimental study can hardly lead to the establishment of rules having general validity. On the other hand, nearly all the thoroughly investigated synthetic polyelectrolytes are very uniform materials: they are usually homopolymers of high charge density carrying 100% carboxylate or sulfonate functional groups. Despite that the crucial role of charge density and degree of polymerization in biological activity was already emphasized in an early work (1952) dealing with synthetic copolymers having similar anticoagulant effect to that of heparin, no systematic further investigation of physicochemical properties of such copolymers has been undertaken. Copolymer polyelectrolytes are rare in the literature anyway, and they are mostly of high charge density ( $50\% \leq$ ), otherwise the copolymer is not soluble in water if the homopolymer of the neutral component (e.g., styrene or methyl acrylate) is insoluble. Charge density is varied, if at all, by changing the pH, i.e., the degree of neutralization, of weak polyacids, what is not feasible in the case of strong polyacids.

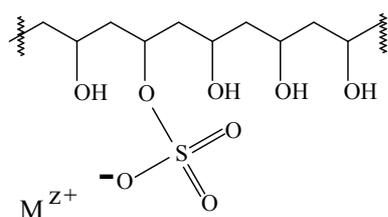
Poly[(vinyl alcohol)-*co*-(vinyl sulfate)] (PVAS) copolymer polyelectrolytes were subjects of several studies at the *Department of Colloid Chemistry* in the last two decades, and they proved to be excellent model substances with well controllable properties. These polyelectrolytes contain non-dissociating hydroxyl and dissociating strong acidic sulfate half ester functional groups (both are water-soluble), so their charge density can be easily varied by the composition (entirely independently of the degree of dissociation). They enable investigation of the transition from entirely separated (isolated) randomly distributed point-like charges to a more or less continuous charge distribution along the chain. The synthesis method also assures that the number average degree of polymerization of each PVAS copolymer is exactly the same as that of the neutral parent polymer, PVA.

Beside charge density of the polyion, valence and chemical nature of the counterions play decisive roles in the properties of polyelectrolytes. Counterion binding is in the center of interest for more than 50 years, however, *thermodynamic* investigation of polyelectrolytes with *trivalent* counterions is restricted to one single study from 1976 (ŠKERJANC et al.) reporting osmotic coefficients (based on osmotic pressure and freezing point depression measurements) of poly(styrenesulfonate), PSS, solutions containing mixtures of  $\text{La}^{3+}$  and  $\text{H}^+$  counterions of different ratios. Unfortunately, the stoichiometric La-salt of PSS could not be studied at all, for preparation of soluble salt was hindered by gel formation.

In a work dealing with thermodynamic properties of solution, the most important quantity is the chemical potential of one of the components, in the present case that of the solvent. The isopiestic method can only be applied for solutions of very high (0.1–7 mol of counterion/kg of water) concentration, while direct osmometry is applicable for the very dilute region (0.0003–0.04 mol of counterion/kg of water). Unfortunately, there exists an intermediate concentration range unavailable by both methods, which makes difficult checking the consistency of the results. Therefore a new, accurate, and, at the same time, relatively simple method, the gel deswelling technique, was applied in this work in order to determine water activity data in our systems. By use of this method, a rather detailed thermodynamic characterization has been already given for several monovalent metal salts of PVAS. Although a few examples demonstrating the effect of the valence of the counterions can also be found in that work, a systematic investigation of multivalent counterions has undoubtedly remained necessary.

Therefore, in the present work a detailed thermodynamic study of altogether *sixteen* stoichiometric PVAS polyelectrolytes of four different structural charge densities and six different di- and trivalent transition metal and rare earth metal counterions, Co(II), Ni(II), Cu(II), La(III), Ce(III), and Nd(III), was undertaken.

sample	$DS^*$	$n_{VAS}/n_{VOH}^{**}$	$DS \times DP_n^{***}$	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	La <sup>3+</sup>	Ce <sup>3+</sup>	Nd <sup>3+</sup>
PVAS/0.93	0.93%	1 : 107	9.34	✓		✓		✓	
PVAS/3.40	3.40%	1 : 28.4	34.1	✓		✓		✓	
PVAS/6.43	6.43%	1 : 14.5	64.6	✓	✓	✓		✓	✓
PVAS/16.9	16.9 %	1 : 4.92	170	✓	✓	✓	✓	✓	



\* Degree of sulfatation: fraction of vinyl alcohol (VOH) monomer units esterified by sulfate group (VAS).

\*\* Ratio of ionizable (VAS) and neutral (VOH) monomer units.

\*\*\* Average number of ionizable functional groups per polymer chain.

## Experimental Methods

### Synthesis Methods

**Poly[(vinyl alcohol)-co-(vinyl sulfate)] (PVAS) copolymer polyacids** were synthesized from the neutral homopolymer, poly(vinyl alcohol), PVA, by polymer analogous reaction relying on **equilibrium esterification by sulfuric acid** at low temperature. As parent polymer, the medium molar mass fraction of a previously fully hydrolyzed and partially fractionated commercial product, Poval 420 (Kuraray Co., Ltd., Japan), was used. Number

average degree of polymerization of this PVA fraction was  $DP_n = 1005 \pm 20$  (by osmometry). Excess sulfuric acid was removed by dialysis (35–40 days); recoveries were around 80–86%. Sulfate half ester derivatives of four different compositions were prepared; this way **polyelectrolytes of low and medium structural charge densities** (vinyl sulfate / vinyl alcohol ratio between approximately 1:110 – 1:5) could be obtained.

**Stoichiometric transition metal and rare earth salts of PVAS polyacids** were prepared by **ion exchange dialysis**. The procedure, performed in a closed system, ensures to minimize the amount of ionic contamination (including atmospheric CO<sub>2</sub>) in the polyelectrolyte solutions. Nearly saturated stock solutions of CoSO<sub>4</sub>, NiSO<sub>4</sub>, or CuSO<sub>4</sub> (a.l.t., Reanal, Hungary) such as those of Ce(NO<sub>3</sub>)<sub>3</sub> (p.a., Fluka), La(NO<sub>3</sub>)<sub>3</sub> (p.a., Carlo Erba, Italy) or Nd(NO<sub>3</sub>)<sub>3</sub> (puriss., Riedel-de Hæn) were added, respectively, to 5–10 w/w% NaPVAS solutions to provide **20–40× excess** of metal ions to VAS groups in the polymer. No sign of precipitation was observed. Excess metal ions were removed by dialysis (25–35 days), while addition of metal ion stock solutions was repeated two more times to obtain complete ion exchange. Dialysis was continued until conductivity of double distilled water remained under 1.5 μS (2.5 μS for PVAS/16.9) over a 24 hour period. Solutions were concentrated to 8–9 w/w% by evaporation under reduced pressure at 298–308 K. All the stoichiometric PVAS salts were entirely water-soluble. Recoveries were between 72–92 %.

Completion of the dialysis could be very sensitively detected by spectrophotometric measurement of nitrate ion content ( $\epsilon_{201}=9600$ ), too. The NO<sub>3</sub><sup>-</sup> to Ce(III) ratio was found to be less than 0.5% , which excludes the presence of mixed salts like [Ln(NO<sub>3</sub>)<sub>1-2</sub>]PVAS. In the case of Cu<sup>2+</sup> and Ce<sup>3+</sup>, **stoichiometry of the PVAS salts** was also checked by complexometric titration: deviation from the stoichiometric composition was within ±1.7% even for the highest *DS*.

**Double distilled water** was produced in a Muldestor SE quartz still (Wagner+Munz, Munich) and had a specific conductivity of 0.8–1 μS cm<sup>-1</sup>.

## **Methods**

**Determination of Water Activity.** Thermodynamic activity of water in the polyelectrolyte solutions was measured by the **gel deswelling method**, which enables determination of thermodynamic activity of the solvent in polymer solutions even in a concentration range (0.001–0.1 mol of counterion / kg of water) that is too low for the isopiestic method but at the same time too high for the direct osmometry. The method is based on the phenomenon that

the **degree of swelling** (i.e., the solvent uptake) of a gel highly and explicitly **depends on the thermodynamic activity of the solvent** if it is placed in a mixture from which the solute (because of its size) cannot enter the network.

In the present work, measurements were carried out using **chemically cross-linked poly[(vinyl acetate)-*co*-(vinyl alcohol)] copolymer gels** of the composition 8/10/400. The gel consisted of a copolymer carrying 8 mol% vinyl acetate units, the cross-linking reaction was performed by glutaraldehyde (GDA) in an aqueous solution containing 10 w/w% copolymer, and the ratio of the number of monomer units versus that of GDA molecules was 400. The gel lamina was placed in a **semipermeable tube** (Visking dialysis tubing,  $\varnothing$  14.3 mm, Medicell Int. Ltd., London), and immersed into the polymer solution to ensure **that only the solvent can enter the network**. Masses of the gels swollen in pure double distilled water ( $m_w$ ), in equilibrium with the polymer solution ( $m_e$ ) and after drying ( $m_0$ ) were measured. Reaching (de)swelling equilibrium took 10 days while the temperature was kept at  $298.15 \pm 0.01$  K by a Haake F6 B12 circulating bath. This way, 18 data points could be obtained per  $\sim 3$  weeks.

Being a relative method, gel laminas were **calibrated** using very reliable osmotic pressure data determined for **poly(vinyl pyrrolidone)** (PVP) (Fluka, K 60) solutions. To further improve the reliability of the results, water activities were calculated according to two types of calibration curves. The gels were calibrated in the mass percent region of the PVP solutions between 1–15 w/w% that made **water activity** measurements in the region  $-7 \times 10^{-4} \leq \ln a_1 \leq -4 \times 10^{-6}$  possible.

**Gravimetry.** Polymer content (mass fraction) of the polyelectrolyte solutions and that of the gels was determined by gravimetry. Drying of the solution samples and the gels was performed in a vacuum oven (Binder VD 23) at  $343.0 \pm 0.5$  K for about 4–7 days (until constant mass). Before drying, approximately stoichiometric amounts of a dilute NaOH solution were added to the PVAS solution samples to avoid acid-catalyzed degradation of the copolymers caused by heating.

**Conductometry.** Composition (amount of acidic functional groups) of the synthesized copolymers was determined by conductometric titration at  $298.0 \pm 0.5$  K. Also, dialysis was followed by conductometry in each case, and it was continued until conductivity of the washing water reached that of double distilled water. Conductivity measurements were carried out by an OK-102/1 conductivity meter (Radelkis, Hungary) connected with an OK-0902P (Radelkis) conductivity cell having a cell constant of  $1 \text{ cm}^{-1}$ .

**Potentiometry.** Potentiometric titration of PVAS polyacids was performed by a slope-controlled automatic titrator developed at the *Department of Analytical Chemistry* (ELTE). It consisted of an OP-208/1 pH-meter (Radelkis, Hungary) and a Schott T80 piston burette as well as of a PC.

**Dilatometry.** Densities of PVAS polyelectrolyte solutions were determined in 10 cm<sup>3</sup> picnometers (BLAUBRAND) at 298.15 ± 0.01 K in the polyelectrolyte concentration region 1–10 w/w%.

**Viscometry.** Relative viscosities of solutions of PVAS polyacid and its alkali metal salts were determined in a modified Fitz–Simmons-type (basically Ubbelohde-type) capillary viscometer at 298.15 ± 0.01 K. Efflux time of the water was 128.9 ± 0.2 s.

**Spectrophotometry.** UV-VIS absorption spectra of solutions of transition metal and rare earth metal PVAS polyelectrolytes were measured by a Perkin–Elmer Lambda 2S spectrophotometer.

## **New Scientific Results**

**1. Alkali metal ions are bound by PVAS with good approximation almost to the same extent as H<sup>+</sup>.** Viscometric titration of HPVAS polyacid by NaOH does not show the typical behavior observed for weak polyacids (e.g., PAA), i.e., the steep increase of reduced viscosity due to the increasing charge on the polyelectrolyte chain. Comparison of reduced viscosities of HPVAS polyacid and its stoichiometric alkali metal salts revealed that practically no difference exists between H<sup>+</sup> and Na<sup>+</sup>, while a maximum 4% increase can be observed in the reduced viscosities in the order H<sup>+</sup> ≈/≤ Na<sup>+</sup> < K<sup>+</sup> < Cs<sup>+</sup> < Li<sup>+</sup>. This tendency corresponds to literature results for another strong polyacid, poly(vinyl sulfonate), PVS, except for K<sup>+</sup> that, against expectations, is not bound more than H<sup>+</sup> by PVAS.

**2. Application of the usual formula used for weak acids to calculate average degree of dissociation of ionizable groups on the polymer chain is not correct in the case of partially neutralized PVAS polyacids.** Slopes of the Henderson–Hasselbach and equivalent empirical linear relationships between pK, pH and degree of dissociation suggest that PVAS has increasing acidity with increasing degree of neutralization. The *n* value that is obtained from the slopes (and which is commonly used to characterize acid-base properties of polyacids) correspond to *n* = 0.5, a value that has never been obtained so far. Taking into consideration that Na<sup>+</sup> ions compete with H<sup>+</sup> ions exactly to the same extent for the free

ionized sulfate groups along the polymer chain, a constant average degree of dissociation is proposed for the polyanion, which equals that of the pure polyacid at the beginning of the titration. This modification corrects the too high apparent acidity of PVAS and result in a nearly constant pK. The literature titration curve of PVS suggests that, maybe not so pronounced but, the same problem holds in the case of PVS and probably other strong polyacids (e.g., PSS), as well.

**3. Partial molar volume of the VAS monomer unit in the copolymer is indifferent to chemical nature, valence, or molar mass of the counterion in the investigated samples.**

The determined values for Co(II)-, Ni(II)-, and Cu(II)- as well as for Ce(III)-PVAS salts all agree very well with results previously found for NaPVAS salts (41 cm<sup>3</sup>/mol). Accordingly, solution densities in the 1–10 w/w% region and also density of the polyelectrolyte component are linear functions of *DS* of the copolymer chains but do not depend on the nature of the counterions.

**4. The water activity lowering effect of trivalent lanthanide salts of PVAS is unusually small for polyelectrolytes and it is comparable with that of neutral polymers.** Despite the even smaller effect than that of NaPVAS of the lowest *DS* ever investigated (*DS* = 0.64%), also trivalent salts of copolymers of different composition can be clearly distinguished. Water activity is lowered in the order of the vinyl sulfate content of the polyelectrolytes, except for the one above the critical charge density (*DS* = 16.9%).

**5. Combination of previous equations into one linear relationship allows direct obtainment of degrees of dissociation at infinite dilution,  $\alpha_0$ , from intercepts of reduced osmotic pressure curves of polyelectrolyte solutions ( $\Pi/c$  method):**

$$\left( \frac{\Pi}{c_{m,2}} \right)_{c_{m,2} \rightarrow 0} = \frac{RT}{M_n} \times (\alpha_0 N_{ci} + 1)$$

The equation also reveals that uncertainty of  $\alpha_0$  is bigger in the case of lower *DS* and higher counterion valence, i.e., for higher  $M_n/N_{ci}$ .

**6. The previously found distance between reduced osmotic pressure curves of Mg- and BaPVAS of the same *DS* is not caused by the considerable difference in the chemical nature of the counterions but rather by the difference between their molar masses.** Reduced osmotic pressure data points of Co-, Ni-, and CuPVAS of the same *DS* cannot be

distinguished from each other, although curves of Mg- and BaPVAS were found previously to run completely separated. Present findings (and also the coincidence of the osmotic coefficient curves of Mg- and BaPVAS/8.1) suggest that it is not the chemical nature of the counterion what appears in the reduced osmotic pressure curves. The molar masses of Mg and Ba are so different that they cause considerable deviation in the  $M_n$  of their PVAS salts, as well.  $M_n$  of Ni- and CuPVAS/16.9 differs only by 0.6% (and this value is even smaller for lower  $DS$ ), whereas it reaches 8.5% in the case of Mg- and BaPVAS/8.1. So, the reduced osmotic pressure curve very sensitively detects, besides dissociation, the molar mass differences of the counterions, as well, therefore it must be regarded with special caution.

**7. Reduced osmotic pressure curves of most of the investigated di- and trivalent PVAS salts bear an inflection.** Curves of NaPVAS polyelectrolytes were found previously to have opposite curvatures to those of neutral polymers at low concentrations: their curves were convex from above (have very high positive curvatures), and the usual concave shape was not observable at all. Multivalent salts of PVAS also have increasing curvature with dilution in the diluted region, however, at the same time, they show the other form at high concentration. Usual experimental methods cannot span the whole concentration region needed for this observation: direct osmometry shows osmotic coefficient curves of Na- and HPSS to be definitely convex at very low concentrations, while isopiestic and freezing point depression measurements result in concave curves at higher concentrations. A clear inflection is observable in the case of Li- and tetraalkylammonium salts of PVS, as well.

**8. Combination of former equations has led to a simple linear relationship describing the concentration dependence of degree of dissociation,  $\alpha$  ( $\chi$  method).**

$$\alpha = \varphi_2 \times (\chi_{lin} - \chi_{1,2}) \times \frac{V_{2,\alpha=0}}{V_1} \times \frac{1}{N_{ci}}$$

where  $\chi_{1,2}$  is the experimentally determined solvent–segment interaction parameter, while  $\chi_{lin}$  is the fitted straight line at high polymer concentration, where no dissociation is supposed.  $\alpha$  is directly proportional to the difference between  $\chi_{lin}$  and  $\chi_{1,2}$  and to the volume fraction of the polyelectrolyte in the solution. Other terms are constant for a polyelectrolyte of given composition and counterion.

**9. Degrees of dissociation at zero concentration take values between 21–62% and 8–36% in the case of di- and trivalent counterions, respectively.** Values calculated by the  $\Pi/c$

method and the  $\chi$  method agree very well with each other.  $\alpha_0$ -s are increasing with decreasing *DS*.

**10. Quantitative binding of the counterions is reached uniformly above the polyelectrolyte molality  $\sim 1 \times 10^{-3}$  mol of polymer chains/kg of water in the case of all counterions and copolymers of all *DS* investigated.** This finding apparently contradicts Manning's calculations, namely that the limiting charge fraction of the polyelectrolyte chains should remain constant up to counterion concentrations  $\sim 0.1$ M. The same might hold for our systems only in the case if the  $\chi_{1,2}$  parameter of PVA was used as  $\chi_{\text{lin}}$  in all calculations of  $\alpha$ . However, it would not be correct since the same  $\chi_{1,2}$  cannot be valid for PVA and PVAS at the same time, as any changes in chemical structure very sensitively appear in  $\chi_{1,2}$ .

**11. The average number of released trivalent counterions is approaching to a constant value of  $\sim 4.5$  per polymer chain with increasing *DS* at infinite dilution. The charge number of the polyion approaches to  $\sim 13.5$ .** Such a limit is not reached in the case of divalent counterions in the *DS* range investigated. The plateau indicates some type of condensation of the trivalent counterions that restricts the charge density parameter along the chain to  $\xi \leq 0.0375$  and maintains an average charge distance of  $b \geq 19$  nm. These values significantly differ from the values predicted by the Manning-theory for counterion condensation of trivalent counterions ( $\xi = 0.333$  and  $b = 2.2$  nm). However, supposition of a contraction ratio of 1:9 compared to the rod-like model leads to the charge density parameter fulfilling the condition for counterion condensation according to the theory for LnPVAS/6.43–16.9. The rod-like model is surely not valid for the investigated LnPVAS polyelectrolytes (and probably in general for all polyelectrolytes with low structural charge density). Solvent–segment interaction, characterized by the  $\chi$  parameter, strongly affects chain dimensions in solution: a higher  $\chi_{\text{lin}}$ , just as in the case of LnPVAS, means a more compact conformation of the polymer chain.

**12. Osmotic coefficient of stoichiometric LaPVAS/16.9 affirms the value ( $\Phi \approx 0.1$ ) that was predicted for the stoichiometric LaPSS at  $1 \times 10^{-3}$  counterion molality by ŠKERJANC et al. based on measurements performed on (H,La)PSS mixed salts.** Different ways of calculation of  $\Phi$ , both regarding and neglecting changes in degree of dissociation, are also discussed.

## List of Publications

### Publications Forming the Basis of the Present Ph.D. Thesis

#### Papers

1. **The Role of Linear Charge Density and Counterion Quality in Thermodynamic Properties of Strong Acid Type Polyelectrolytes: Divalent Transition Metal Cations**  
Judit Horváth, Miklós Nagy  
*Langmuir* **2006**, 22, 10963–10971. IF = 3.705 (2005)
2. **Thermodynamic Characterization of Rare Earth Salts of Strong Polyacid Copolymers**  
Judit Horváth, Miklós Nagy  
*J. Phys. Chem. B* **2007**, 111, 5140–5148. IF = 4.033 (2005)

#### Lectures

- I. **Effect of Multivalent Counterions on the Thermodynamic Properties of Poli[(Vinyl Alcohol)-co-(Vinyl Sulfate)] Copolymers** (in Hungarian)  
Meeting of the Colloid Chemistry and Material Science Working Committee of the Hungarian Academy of Sciences at Mátrafüred, Hungary, 26<sup>th</sup> April 2002
- II. **The Role of Multivalent Counterions in Thermodynamic Properties of Aqueous Polyelectrolyte Solutions** (in Hungarian)  
Award Ceremony of the 'Dr. Wolfram Ervin Foundation'  
Professors' Club, Eötvös Loránd University, Budapest, 25<sup>th</sup> November 2005

### Publications in Connection with the Topic of the Present Ph.D. Thesis

#### Papers

3. **Interaction of poly(vinyl alcohol) with the Belousov-Zhabotinsky reaction mixture**  
Judit Horváth, Zsuzsanna Nagy-Ungvárai, Stefan C. Müller  
*Phys. Chem. Chem. Phys.* **2001**, 3, 218-223. IF = 1.787 Indep. Cit.: 3

#### Lectures

- III. **Herstellung einer Gelmatrix für die Belousov-Zhabotinsky Reaktion** (in German)  
Meeting of the Department of Biophysics, Institute of Experimental Physics, Faculty of Science, Otto-von-Guericke Universität, Magdeburg, Germany 1999
- IV. **Fixing of the Ce Catalytor Used in the Belousov-Zhabotinsky Reaction in Gel Systems** (in Hungarian)  
Meeting of the Reaction Kinetics and Photochemistry Working Committee of the Hungarian Academy of Sciences at Balatonalmádi, Hungary, 29<sup>th</sup> April 1999