

Aqueous Solutions of Polyelectrolytes: Vapor–Liquid Equilibrium and Some Related Properties

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Abstract This chapter reviews the thermodynamic properties of aqueous solutions of polyelectrolytes, concentrating on properties that are related to phase equilibrium phenomena. The most essential phenomena as well as methods to describe such phenomena are discussed from an applied thermodynamics point of view. Therefore, the experimental findings concentrate on the vapor–liquid phase equilibrium phenomena, and the thermodynamic models are restricted to expressions for the Gibbs energy of aqueous solutions of polyelectrolytes.

Keywords Aqueous solutions · Counterion condensation · Excess Gibbs energy · Osmotic coefficient · Polyelectrolytes · Salt effects · Thermodynamics · Vapor–liquid equilibrium

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Abbreviations

A	Inverse length (in model of Lifson and Katchalsky)
A	Repeating unit (in model of Lammertz et al.)
A_ϕ	Debye-Hückel Parameter
$A_{s,s}$	Second osmotic virial coefficient for interactions between solutes S in water
$A_{s,s,s}$	Third osmotic virial coefficient for interactions between solutes S in water
a	Anion
a	Radius
$a_i^{(k)}$	Activity of species i normalized according to composition scale k
a_w	Activity of water
$a_{i,L}^{(0)}$	Binary interaction parameter between species (groups) i and L
$a_{i,L}^{(1)}$	Binary interaction parameter between species (groups) i and L
$a_{MX}^{(0)}$	Binary interaction parameter between cations M and anions X
$a_{MX}^{(1)}$	Binary interaction parameter between cations M and anions X
$a_{p,p}$	Binary interaction parameter between repeating units
$a_{p,Cl}$	Binary interaction parameter between repeating units and the chloride ion
b	Distance between two electrolyte groups in a polyelectrolyte backbone
b	Numerical value in Pitzer's model ($b = 1.2$)
b^*	Configurational parameter
$b_{i,L,k}$	Ternary interaction parameter between groups i , L and k
BaPSS	Poly(barium styrene sulfonate)
C	Repeating unit that will never dissociate (in model of Lammertz et al.)
c	Cation
c_i	Concentration of species i
c_i	Molarity of species i

CI	Counterion
$c_{k,b}$	Molarity of monomeric groups saturated with counterion k
c_m	Molarity of repeating units
c_P	Concentration of polyelectrolyte P
c_s	Molarity of salt S
\tilde{c}_i	Mass density of solute i
CaPAM	Calcium salt of copolymer of acrylic acid and acrylamide
D	Repeating unit undergoing a chemical reaction (in model of Lammertz et al.)
DMO	Differential membrane osmometry
DS	Degree of substitution
e	Proton charge
EMF	Electromotive force measurement
EQDIA	Equilibrium dialysis
F	Dissociated repeating unit (in model of Lammertz et al.)
F	Free energy
f	Short-range parameter
f^{e1}	Function in the theory of Lifson and Katchalsky
f_i	Functions (in model of Lammertz et al.); $i = 1, 2$
FPD	Freezing point depression
$f(M)$	Molecular mass distribution function
G	Gibbs energy
G_{ji}	Binary interaction parameter (in model of Nagvekar and Danner)
$G_{ji,ki}$	Interaction parameter (in model of Nagvekar and Danner)
g_{ji}	Energy parameter (in model of Nagvekar and Danner)
GDM	Gel deswelling method
h	Length of a polyion
HPAA	Poly(acrylic acid)
HPAMS	Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)
HPAS	Poly(anethole sulfonic acid)
HPES	Poly(ethylene sulfonic acid)
HPMAA	Poly(methacrylic acid)
HPMSS	Poly(methyl styrene sulfonic acid)
HPP	Poly(phosphoric acid)
HPVB	Poly(vinyl benzoic acid)
HPVS	Poly(vinyl sulfuric acid)
HPVSA	Poly(vinyl sulfonic acid)
HPSS	Poly(styrene sulfonic acid)
I	Ionic strength
I_m	Ionic strength (on molality scale)
$I_{m,MX}$	Ionic strength (on molality scale) of an aqueous solution of MX
I_s	Ionic strength (on molarity scale)
ISO	Isopiestic experiments
j	Abbreviation
j	Component
K	Chemical reaction constant (in model of Lammertz et al.)

k	Boltzmann's constant
k	Component
k	Concentration scale
k	Degree of counterion condensation at infinite dilution (in model of Lammertz et al.)
KPA	Poly(potassium acrylate)
KPAM	Potassium salt of copolymer of acrylic acid and acrylamide
l_B	Bjerrum length
LiCMC	Lithium carboxymethylcellulose
M	Cation
M	Molecular mass
M_r	r th moment of distribution function for molecular mass
M_n	Number-averaged molecular mass
M_w	Mass-averaged molecular mass
M_w^*	Relative molecular mass of water divided by 1,000
m_i	Molality of species i
m°	Unit of molality $m^\circ = 1 \text{ mol}/(\text{kg water})$
m_j^*	Modified molality of species j (in model of Pessoa and Maurer)
MgPAM	Magnesium salt of copolymer of acrylic acid and acrylamide
MO	Membrane osmometry
MX	Salt (cations M and anions X)
n	Mole number
N_A	Avogadro's number
$n_{p,diss}$	Number of moles of dissociated repeating units
$n_{freeCl}^{(p)}$	Number of moles of counterions originating from P (in Manning's theory)
$n_{freeCl}^{(s)}$	Number of moles of counterions originating from S (in Manning's theory)
n_T	Total mole number
NaCMC	Sodium carboxymethylcellulose
NaDS	Sodium dextran sulfate
NaPA	Poly(sodium acrylate)
NaPAM	Sodium salt of copolymer of acrylic acid and acrylamide
NaPAMA	poly(sodium acrylamido- <i>co</i> -trimethyl ammonium methyl methacrylate)
NaPAMS	Sodium salt of HPAMS
NaPES	Poly(sodium ethylene sulfate)
NaPMAA	Poly(sodium methacrylate)
NaPP	Poly(sodium phosphate)
NaPSS	Poly(sodium styrene sulfonate)
NaPVAS	Poly(sodium vinyl sulfate)
NH ₄ PA	Poly(ammonium acrylate)
NMR	Nuclear magnetic resonance
P	Polyelectrolyte
P	Polydispersity (M_w/M_n)

p	Pressure
p_w	Vapor pressure of water
PAAm	Poly(allylamino hydrochloride)
PDADMAC	Poly(diallyldimethyl ammonium chloride)
PEI	Poly(ethyleneimine)
PMETAC	Poly(2-(methacryloyloxy) ethyl trimethyl ammonium chloride)
PTMAC	Poly(trimethyl ammonium methyl methacrylate)
PVA	Poly(vinyl alcohol)
PVAm	Poly(vinyl amine)
PVBtMAC	Poly(vinyl benzene trimethyl ammonium chloride)
q	Number of charges
q_{gl}	Surface parameter of the globular form of the polyelectrolyte
q_i	Surface parameter of species i (in model of Lammertz et al.)
q_{max}	Maximum number of charges
q_{st}	Surface parameter of the stretched polyelectrolyte
R	Universal gas constant
R	Radius of a cylindrical cell around a polyion
r	Exponent
r	Distance
r_i	Volume parameter of species i (in model of Lammertz et al.)
T	Temperature
UV/VIS	Ultraviolet/visible light
V	Volume
V_p	Volume in Manning's theory
VO	Vapor pressure osmometry
x_i	Mole fraction of species i
X	Anion or counterion
X_j	Modified mole fraction of component j
X-DP	Salt (with counterion X) of dextran phosphate
X-DS	Salt (with counterion X) of dextran sulfate
z_{Cl}	Absolute valency of counterion
z_j	Absolute valency of ion j
z_j^*	Modified absolute valency of ions j (in model of Pessoa and Maurer)
z_M	Absolute valency of cation M
z_X	Absolute valency of anion X
z_p	Absolute valency of a repeating unit of polyelectrolyte P

Greek Symbols

α	Constant ($\alpha = 2$) in Pitzer's model
α	Total degree of dissociation of the repeating units (in model of Lammertz et al.)

α_{ji}	Nonrandomness parameter (in model of Nagvekar and Danner)
$\alpha_{ji,ki}$	Nonrandomness parameter (in model of Nagvekar and Danner)
β	Dimensionless parameter
Γ	Salt-exclusion parameter
Γ_i	Activity coefficient (on molality scale) of species i (in model of Lammertz et al.)
$\Gamma_{l,Z}$	Activity coefficient (on molality scale) of species l in state Z (in model of Lammertz et al.)
γ	Activity coefficient
γ_{LK}	Dimensionless parameter in the theory of Lifson and Katchalsky
Δ	Difference
ΔT_{FP}	Freezing point depression
ε	Relative permittivity of pure water
ε_0	Permittivity of vacuum
Φ	Osmotic coefficient
Φ_p	Osmotic coefficient (for pressure)
Φ_p^0	Osmotic coefficient (for pressure) at infinite dilution
Φ_T	Osmotic coefficient (for temperature)
$\Phi_s^{(c)}$	Osmotic coefficient (for pressure) on molarity scale due to salt S
$\Phi_{p+s}^{(c)}$	Osmotic coefficient (for pressure) on molarity scale due to salt S and polyion P
φ_p	Volume fraction of the polyelectrolyte
$\phi(r)$	Electrostatic potential that depends on radius r
θ_k	Degree of condensation of a counterion k
θ_z	Ratio in Manning's theory
$\theta_z^{(0)}$	Limit for θ_z in Manning's theory
κ	Inverse radius of the ionic cloud (Debye–Hückel theory)
λ	Charge density parameter
λ_{ij}	Binary interaction parameter (in model of Pessoa and Maurer)
$\lambda_{ij}^{(0)}$	Binary interaction parameter (in model of Pessoa and Maurer)
$\lambda_{ji}^{(1)}$	Binary interaction parameter (in model of Pessoa and Maurer)
μ_i	Chemical potential of component i
Ξ	Volume fraction of polyelectrolyte (in model of Lammertz et al.)
v	Number of repeating units of a polyelectrolyte molecule
v^*	Number of dissociated repeating units of a polyelectrolyte molecule
v_M	Stoichiometric coefficient for cation M in salt MX
v_X	Stoichiometric coefficient for anion X in salt MX
π	Osmotic pressure
Θ_{gl}	Surface fraction of the polyelectrolyte in its globular shape
Θ_L	Surface fraction of group L
Θ_{st}	Surface fraction of the polyelectrolyte in its stretched shape
ρ_i^*	Specific density of pure solvent i
$\bar{\rho}_i^*$	Molar density of pure solvent i

σ_i	Parameter of species i (in model of Pessoa and Maurer)
τ_{ji}	Binary interaction parameter (in model of Nagvekar and Danner)
$\tau_{ji,ki}$	Interaction parameter (in model of Nagvekar and Danner)
v_p^*	Molar volume in Manning's theory
$\bar{v}_{s,pure}$	Molar volume of pure solvent s
$\varpi^{(0)}$	Configurational parameter
$\varpi^{(1)}$	Configurational parameter

Subscripts

A	Repeating unit (in model of Lammertz et al.)
a	Anionic component
c	Cationic component
C	Repeating unit that will never dissociate (in model of Lammertz et al.)
CI	Counterion
Cl	Chloride ion
COI	Coion
cond.	CI contribution due to condensed counterions
D	Repeating unit undergoing a chemical reaction (in model of Lammertz et al.)
F	Dissociated repeating unit (in model of Lammertz et al.)
Free CI	Free counterions
Free COI	Free coions
id.liq.mix.	Ideal liquid mixture
id.mix.	Ideal mixture
H	Hydrogenium ions
K	Potassium ion
k	Contribution
local	Local
LK	Lifson and Katchalsky
M	Cations
m	Solvent component
Ma	Manning's theory
Mg	Magnesium ion
MX	Salt (cations M and anions X)
Na	Sodium ions
p	Polyelectrolyte
Pb	Lead ions
pure liquid	Pure liquid component
pure water	Pure water
rp	Repeating unit of polyelectrolyte

sym	Symmetrical convention
w	Water
$(w + s)$	In an aqueous solution of the salt
$(w + s + p)$	In an aqueous solution of (salt + polyelectrolyte)
X	Ion X

Superscripts

(c)	On molarity scale
Comb.	Combinatorial
E	Excess
el	Contribution from electrostatics
fv	Free volume
id.mix.	Ideal mixture
(k)	Characterizes the concentration scale
LR	Long-range
(m)	On molality scale
ref	Reference state
SLE	Solid–liquid equilibrium
SR	Short-range
vdW	Van der Waals
(x)	On mole fraction scale
∞	Infinite dilution
Δconf	Caused by a difference in the configuration (in model of Lammertz et al.)

1 Introduction

Polyelectrolytes are polymers of a single repeating unit (monomer) that is an electrolyte or of several repeating units (monomers), where at least one of the repeating units is an electrolyte. That electrolyte can dissociate in water and in aqueous solutions resulting in negative or positive charges on the polymer backbone. Polyelectrolytes are very soluble in water, particularly when, in addition to the ionic monomers, the other monomers are also hydrophilic. The large variety of monomers means that there is a huge variety of polyelectrolytes. The number of different repeating units and the number of each of those repeating units determines the primary structure of a polyelectrolyte, i.e., the chemical nature and the molecular mass. However, that information is not sufficient to characterize a polyelectrolyte. As typical of polymers, polyelectrolyte samples reveal a molecular mass distribution (polydispersity). Furthermore, when a polymer consists of

more than a single repeating unit, the secondary structure is important for its properties: the different repeating units might be statistically distributed or arranged in, more or less uniform, blocks. The polymer can be a linear structure or a branching one. It might have a certain shape in space (tertiary structure) that can depend on the surrounding solution. All these parameters influence the properties of an aqueous solution of polymer, but there are more parameters when the polymer has electrolyte groups. These electrolytes can be weak or strong electrolytes, resulting in different degrees of dissociation/protonation. The electrolyte groups of the backbone might be all cationic or all anionic, but they might also be partially cationic and partially anionic. Such polyelectrolytes are called polyampholytes. There is another parameter that has an important influence on the properties of polyelectrolytes in aqueous solutions: the distance between the electrolyte groups in the polymer backbone. When that distance is small, the attractive electrostatic forces between the ionic groups in the backbone and their counterions in the aqueous solutions become so strong that, even if the repeating unit is a strong electrolyte, one observes an ion pairing, i.e., some of the counterions condensate (at least partially) with the ions of the backbone. Therefore, even at high dilution in water such polyelectrolytes are not completely dissociated and the degree of dissociation might depend on the composition of the surrounding aqueous phase. The large number of parameters that influence the properties of aqueous solutions of polyelectrolytes is reflected in the variety of areas where such solutions are found and applied. Table 1 gives some typical examples of applications. These applications take advantage of the particular thermodynamic properties of aqueous solutions of polyelectrolytes. Therefore, there is a need for methods to describe such properties. In applied thermodynamics, the properties of solutions are described by expressions for the Gibbs energy as a function of temperature, pressure, and composition. From such equations all other thermodynamic state functions can be derived.

There are many well-established models for the Gibbs energy of nonelectrolyte solutions and also several methods to describe conventional polymer solutions. However, the state of the art for modeling thermodynamic properties of aqueous solutions of polyelectrolytes is far less elaborated. This is partly due to the particular features of such solutions but is also caused by insufficiencies in the knowledge of the parameters that characterize a polyelectrolyte, for example, the polydispersity and the different structures (primary, secondary etc.) of the polyelectrolytes. The development and testing of thermodynamic models has always been based on reliable experimental data for solutions for which all components are well characterized. Such characterization is particularly scarce for biopolymers and biopolyelectrolytes. Furthermore, such polymers are generally more complex than synthetic polymers. Therefore, the present contribution is restricted to a discussion of the thermodynamic properties of aqueous solutions of synthetic polyelectrolytes that consist of only two different repeating units that are statistically distributed. Furthermore, it is restricted to systems where sufficient information on the polyelectrolyte's polydispersity is available.

Table 1 Applications of polyelectrolytes

Application	Product	References
Stabilization of colloid systems as dispersing agents	Poly(acrylic acid), gelatin, sodium carboxymethylcellulose	[1–6]
Sludge dewatering, flocculating agents	Acrylamidecopolymers, Poly(diallyldimethyl ammonium chloride)	[7, 8]
Retentions aids in paper industry	Poly(ethyleneimine), cationic starches, poly(diallyldimethyl ammonium chloride)	[9, 10]
Thickeners	Gelatin, Sodium carboxymethylcellulose, pectin, arab gum, carrageenan	[11]
Gelling agents	Gelatin, pectin, carrageenan	[12]
Temporary surface coatings for:		
Textile industry	Poly(acrylic acid) sodium salt, Sodium carboxymethylcellulose, poly(acrylic acid) ammonium salt	[12]
Capsules in pharmaceutical applications	Gelatin, Sodium carboxymethylcellulose, cellulose acetate phthalate, copolymers of methacrylic acid	[12]
Corrosion-protecting coatings	Poly(styrene sulfonic acid), poly(acrylic acid)	[12]
Cosmetic industry	Copolymers of acrylic acid	
Antistatic coatings	Copolymers with styrene sulfonate units, cationic polyelectrolytes	
Adhesives for:		
Food industry	Gelatin	[13]
Paper industry	Sodium carboxymethylcellulose	[14]
Dental material/dental composites	Zinc polycarboxylate, polyacrylic acid-glass cements, poly(methyl methacrylate)	[15, 16]
Controlled release of drugs and responsive delivery systems	Cellulose acetate phthalate, poly(dimethylamino ethyl methacrylate-co-tetraethyleneglycol dimethacrylate) gels	[15, 16]
Polymeric drugs	Poly(<i>N</i> -vinyl pyrrolidone- <i>co</i> -maleic acid), sulfonated polysaccharides	[15, 16]

2 Structure and Characterization of Polyelectrolytes

Polyelectrolytes are primarily characterized by the backbone monomers and the electrolyte and/or proton-accepting groups attached to those monomers. Table 2 gives an overview of some of the most important anionic and cationic synthetic polyelectrolytes. Styrene, the vinyl group, cellulose, and dextran are the most important backbone monomers for hydrocarbonic polyelectrolytes. The most important dissociating groups in synthetic, organic polyelectrolytes are sulfonic, acrylic, benzoic, phosphoric, and sulfuric acid. By dissociation, such polymers become electrically charged species, carrying negative charges. Therefore, such polymers are also called “anionic polyelectrolytes,” whereas “cationic polyelectrolytes” have proton-accepting groups. By protonation, such formerly neutral groups can be positively charged. The most important proton-accepting groups are NR_3^+ and NH_2^+ . Short nomenclatures are often used to abbreviate the chemical

Table 2 Important anionic and cationic polyelectrolytes (cf. Scranton et al. [16])

Polyelectrolyte (Abbreviation)	Repeating unit	Polyelectrolyte (Abbreviation)	Repeating unit
Poly(acrylic acid) (HPAA)	$\left[\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right]_n$	Poly(vinyl sulfuric acid) (HPVAS)	$\left[\text{CH}_2 - \underset{\text{OSO}_3\text{H}}{\text{CH}} \right]_n$
Poly(methacrylic acid) (HPMAA)	$\left[\text{CH}_2 - \underset{\text{COOH}}{\overset{\text{CH}_3}{\text{C}}} \right]_n$	Poly(vinyl sulfonic acid) (HPVS)	$\left[\text{CH}_2 - \underset{\text{SO}_3\text{H}}{\text{CH}} \right]_n$
Poly(styrene carboxylic acid)	$\left[\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right]_n$	Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (HPAMS)	$\left[\text{CH}_2 - \underset{\begin{array}{c} \text{O}=\text{C}-\text{NH}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{SO}_3\text{H} \end{array}}{\overset{\text{CH}_3}{\text{C}}} \right]_n$
Poly(styrene sulfonic acid) (HPSS)	$\left[\text{CH}_2 - \underset{\text{SO}_3\text{H}}{\text{CH}} \right]_n$	Poly(phosphoric acid) (HPP)	$\left[\text{O} - \underset{\text{OH}}{\overset{\text{O}}{\text{P}}} \right]_n$
Poly(vinyl benzoic acid) (HPVB)	$\left[\text{CH}_2 - \underset{\text{CH}_2\text{COOH}}{\text{CH}} \right]_n$	Sodium dextran sulfate (NaDS)	$\left[\text{OCH}_2 - \underset{\begin{array}{c} \text{HO} \quad \text{OSO}_3\text{Na} \end{array}}{\overset{\text{O}}{\text{C}}} - \text{O} \right]_n$
Sodium carboxymethyl-cellulose (NaCMC)	$\text{RO} \left[\underset{\text{OR}}{\overset{\text{ROCH}_2}{\text{C}}} - \underset{\text{OR}}{\overset{\text{OR}}{\text{C}}} - \text{O} - \underset{\text{OR}}{\overset{\text{OR}}{\text{C}}} - \underset{\text{OR}}{\overset{\text{OR}}{\text{C}}} - \text{O} \right]_n \text{R}$ R=H or CH ₂ CO ₂ Na		

Table 2 (continued)

Polyelectrolyte (Abbreviation)	Repeating unit	Polyelectrolyte (Abbreviation)	Repeating unit
Poly(ethyleneimine) (PEI)	$\left[\text{NH}-\text{CH}_2-\text{CH}_2 \right]_n$	Poly(vinyl amine) (PVAm)	$\left[\text{CH}_2-\underset{\text{NH}_2}{\text{CH}} \right]_n$
Poly(trimethyl ammonium methyl methacrylate) (PTMAC)	$\left[\text{CH}_2-\underset{\begin{array}{c} \text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_2-\text{CH}_2-\text{N}^+(\text{CH}_3)_3 \text{Cl}^- \end{array}}{\text{CH}} \right]_n$		
Poly(allylamino hydrochloride) (PAAm)	$\left[\text{CH}_2-\underset{\begin{array}{c} \text{CH}_2 \\ \\ \text{NH}_2 \text{ HCl} \end{array}}{\text{CH}} \right]_n$	Poly(diallyldimethyl ammonium chloride) (PDADMAC)	$\left[\text{CH}_2-\underset{\begin{array}{c} \text{CH}_2 \\ \\ \text{H}_2\text{C}-\text{N}^+(\text{CH}_3)_2 \text{Cl}^- \end{array}}{\text{CH}}-\text{CH}_2 \right]_n$
Poly(vinylbenzene trimethyl ammonium chloride) (PVBTMAC)	$\left[\text{CH}_2-\underset{\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{CH}_2 \\ \\ \text{H}_3\text{C}-\text{N}^+(\text{CH}_3)_3 \text{Cl}^- \end{array}}{\text{CH}} \right]_n$	Poly(2-(methacryloyloxy) ethyl trimethyl ammonium chloride) (PMETAC)	$\left[\text{CH}_2-\underset{\begin{array}{c} \text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{H}_2\text{C} \\ \\ \text{CH}_2 \\ \\ \text{H}_3\text{C}-\text{N}^+(\text{CH}_3)_3 \text{Cl}^- \end{array}}{\text{CH}} \right]_n$

formula. The abbreviation usually consists of two parts: one part stands for the backbone and electrolyte group (cf. Table 2), the other for the (approximate) molecular mass. A polyelectrolyte material rarely consists of one single type of molecule, but of a variety of molecules of different molecular masses.

In principle, a distribution function $f(M)$ has to be used to characterize that material: $f(M) dM$ is the fraction of polymers with a molecular mass between $M - dM/2$ and $M + dM/2$, with the normalization:

$$\int_0^\infty f(M) dM = 1. \quad (1)$$

However, as such distributions are difficult to determine, it is common practice to characterize a polymer sample by the number-average (M_n) and the mass-average (M_w) molecular masses, which are the first members in a series of moments:

$$M_r = \frac{\int_{M=0}^{M_i=\infty} f(M) M^r dM}{\int_{M=0}^{M=\infty} f(M) M^{(r-1)} dM}, \quad (2)$$

with $M_1 = M_n$ and $M_2 = M_w$, or by using one of those average molecular masses and the polydispersity P , which is the ratio of M_w to M_n :

$$P = \frac{M_w}{M_n}. \quad (3)$$

There might be a variety of different counterions in a polyelectrolyte, therefore, the quota of different counterions can be used to further characterize a polyelectrolyte. That quota can undergo some changes, e.g., when a polyelectrolyte is dissolved in an aqueous solution of electrolytes or of other polyelectrolytes. The degree of dissociation of a polyelectrolyte is also often used for characterization. However, from the view of thermodynamics, that property depends on the surroundings and therefore it is more suited for characterizing the state of a polyelectrolyte instead of characterizing the polyelectrolyte itself.

Various experimental methods such as potentiometric titration, conductometry, polarography, electrophoresis, spectroscopy (NMR, UV/VIS), osmometry, light scattering (static and dynamic laser light scattering, X-ray scattering, and neutron scattering), viscometry, sedimentation, and chromatography (e.g., size exclusion chromatography and gel electrophoresis) have been used to characterize polyelectrolytes in aqueous solutions (for a recent review cf. Dautzenberg et al. [12]). Experimental information on the average molecular mass of a polyelectrolyte is mostly derived from laser light scattering, osmometry or viscometry, i.e., from methods that are also used to determine the thermodynamic properties of polyelectrolyte solutions, e.g., the activity of water. The polydispersity of polyelectrolytes is usually determined by size-exclusion chromatography. Potentiometric titration is often used to determine the degree of functionalization and the chemical reaction equilibrium constants for the dissociation/protonation reactions, i.e., properties characterizing the number of anionic groups saturated by hydrogen ions (in an anionic polyelectrolyte) or the number of protonated groups (in a cationic polyelectrolyte). The number of ionic groups in an anionic polyelectrolyte is sometimes determined by atomic absorption spectroscopy. X-ray structural analysis and neutron scattering are typical methods for investigating the structure of polyelectrolytes. From the viewpoint of thermodynamics, a polyelectrolyte should be characterized by all single polymers comprising the polyelectrolyte sample, the number of functional groups (ionic as well as neutral groups), the state of the ionic groups (e.g., number and nature of dissociable counterions of anionic groups as well as the number of protonated cationic groups), the secondary structure, and the concentration of any single polyelectrolyte in the sample. However, that information is almost never available. In most cases, the chemical nature of such polyelectrolyte samples is only characterized by the backbone monomers and the kind of

ionic groups, as well as an estimate of the ratio of electrolyte groups to backbone monomers. The accessible information on the counterions is often limited to the chemical nature and a more or less rough estimate for the ratio of different counterions, e.g., the ratio of hydrogen counterions to sodium counterions of an anionic polyelectrolyte. Very often, the degree of polymerization is given only as an estimate of either the number-averaged or the mass-averaged molecular mass, but detailed information on the polydispersity is missing. Thus, the characterization of the polyelectrolyte is often far from satisfactory (at least from the viewpoint of thermodynamics) and, consequently, reported thermodynamic data are often of very limited use, e.g., for testing and developing of models for describing and predicting the thermodynamic properties of such solutions.

3 Experimental Data for the Vapor–Liquid Equilibrium of Aqueous Polyelectrolyte Solutions

Because polyelectrolytes are nonvolatile, the most important thermodynamic property for vapor + liquid phase equilibrium considerations is the vapor pressure of water p_w above the aqueous solution. Instead of the vapor pressure, some directly related other properties are used, e.g., the activity of water a_w , the osmotic pressure π , and the osmotic coefficient Φ . These properties are defined and discussed in Sect. 4. Membrane osmometry, vapor pressure osmometry, and isopiestic experiments are common methods for measuring the osmotic pressure and/or the osmotic coefficient. A few authors also reported experimental results for the activity coefficient γ_{Cl} of the counterions (usually determined using ion-selective electrodes) and for the freezing-point depression of water ΔT_{FP} . The activity coefficient is the ratio of activity to concentration:

$$\gamma_{\text{Cl}}^{(k)} = \frac{a_{\text{Cl}}^{(k)}}{k}, \quad (4)$$

where k in the denominator is used to express a certain concentration scale (e.g., mole fraction x , molarity c or molality m). Superscript (k) indicates that the activity coefficient and the activity are defined using a certain reference state, which depends on the selection of the scale used to express the composition of the solution. Some authors report experimental data for the freezing point depression of an aqueous solution:

$$\Delta T = T^{\text{SLE}} - T_{\text{purewater}}^{\text{SLE}}, \quad (5)$$

and convert that data to an osmotic coefficient $\Phi_T^{(k)}$ by:

$$\Phi_T^{(k)} = \frac{\Delta T}{\Delta T_{\text{id.liq.mix}}^{(k)}}, \quad (6)$$

where $\Delta T_{\text{id.liq.mix}}^{(k)}$ is the freezing point depression of an ideal aqueous solution of the polyelectrolyte. Subscript T to the osmotic coefficient Φ indicates that the osmotic coefficient is here defined with the freezing point depression. Superscript (k) is again used to indicate that the definition of *the ideal mixture* depends on the chosen concentration scale. However, it also depends on an assumption about the dissociation of the polyelectrolyte. It is common practice to assume that in an ideal mixture the polyon is completely dissociated.

3.1 Aqueous Solutions of a Single Polyelectrolyte

Tables 3–6 give a survey of literature data for the vapor–liquid equilibrium of aqueous solutions of a single polyelectrolyte with various counterions. Abbreviations (shown in Table 2) are used to characterize the polyelectrolyte and the experimental procedures (MO membrane osmometry; DMO differential membrane osmometry; VO vapor pressure osmometry; ISO isopiestic experiments; EMF electromotive force measurements including also measurements with ion-selective electrodes as well as titration; FPD freezing point depression; GDM gel deswelling investigations). Table 3 gives a survey for aqueous solutions of poly(styrene sulfonic acid).

Table 3 Survey of literature data for thermodynamic properties of aqueous solutions of polyelectrolytes with styrenesulfonic acid as the backbone monomer (without any other salt)

Molecular mass ($\times 10^{-5}$)	Counterion	Counterion molality	Method	Exp. prop.	References
0.4 and 5	Na^+ ; H^+	0.01–1.4	VO	Φ_p	[17]
		0.8–7.54	ISO	Φ_p	
5	H^+ , Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , N^+R_1 ; [$\text{R}_1 \equiv (\text{CH}_3)_4$, $(\text{C}_2\text{H}_5)_4$, $(\text{C}_4\text{H}_9)_4$]	0.05–1.1	DMO	Φ_p	[18]
0.4–5.2	Na^+ , H^+ , Ca^{++} , Cu^{++} , Cd^{++}	10^{-3} – 10^{-2}	MO	Φ_p	[19]
0.4–5.2	Cu^{++} , Na^+	10^{-3} – 10^{-2}	MO	Φ_p	[20]
0.2–1.0	Na^+ , Tl^+ , Cd^{++} , Ca^{++}	5×10^{-4} – 10^{-2}	MO, EMF	Φ_p ; γ_{Cl}	[21]
0.4	Li^+ , Na^+ , K^+ , Cs^+	6×10^{-3} –0.3	FPD	Φ_T	[22]
0.4	Cd^{++} , Mg^{++}	6×10^{-3} –0.15	FPD	Φ_T	[23]
4.6	H^+ , Li^+ , Na^+ , K^+ , Ca^{++} , Ba^{++} , NH_4^+ , N^+R_1 ; [$\text{R}_1 \equiv \text{C}_3\text{H}_7$, $(\text{C}_2\text{H}_5)_4$, $(\text{CH}_3)_4$, $\text{CH}_2\text{C}_6\text{H}_5$]	0.04–3.3	ISO	Φ_p	[24]
5	Na^+	0.7–1.44	MO, VO	π	[25]
4.3	Na^+	4×10^{-4} –0.37	MO	π	[26]
5	Na^+	0.4–2.7	ISO	π	[27]
1.3	Na^+	5×10^{-4} – 4×10^{-3}	ISO	a_w	[28]

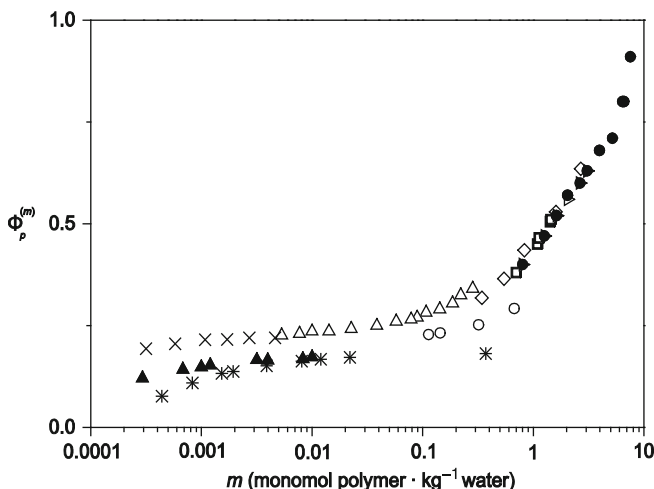


Fig. 1 Osmotic coefficient of aqueous solutions of NaPSS of varying molecular mass (M) at 25°C (unless otherwise indicated): *open triangles* 4×10^4 (0°C) [22]; *times* 4×10^4 [19]; *right-pointing triangle* 4×10^4 [17]; *star* 4.3×10^5 [26]; *closed circles* 5×10^5 [17]; *open diamonds* 5×10^5 [27]; *open squares* 5×10^5 (35°C) [25]; *open circles* 5×10^5 (no temperature given) [18]; *closed triangles* 5×10^5 [19]

Figure 1 shows some typical experimental results for the osmotic coefficient of aqueous solutions of poly(sodium styrene sulfonate) (NaPSS). The osmotic coefficient $\Phi_p^{(m)}$ is plotted versus the concentration of the polyelectrolyte (expressed as the molality of the “repeating units” or “monomer groups”). The figure reveals that the osmotic coefficient of a diluted aqueous solution of a polyelectrolyte is well below unity even at very small concentrations, e.g., at monomer-group molalities below about 0.001 mol/kg. It also reveals that, at low polymer concentrations, the influence of the concentration of the polyelectrolyte on the osmotic coefficient is rather small (e.g., when the monomer-group molality is increased from about 0.0002 to about 0.1 mol/kg, the osmotic coefficient of an aqueous solution of high molecular weight NaPSS increases only from about 0.2 to about 0.25), whereas at higher concentrations the osmotic coefficient increases strongly with increasing polymer concentration (e.g., from about 0.4 to about 0.8, when the monomer-group molality is increased from about 1 to 10 mol/kg). Furthermore, experimental results from different sources often do not agree with each other, but it seems that most experimental results confirm that there is only a very small influence of the molecular mass (M) of the polyelectrolyte on the osmotic coefficient.

Table 4 gives a similar survey for other polyelectrolytes. Figure 2 shows the influence of the backbone monomer of the polyelectrolyte on the osmotic coefficient. At constant polyelectrolyte concentration (again expressed as the molality of the repeating units), the osmotic coefficients might differ by, for example, a factor of five. For example, at 25°C, the osmotic coefficient of a 1 mol/kg aqueous solution of monomer groups of poly(sodium ethylene sulfate) (NaPES) is about 0.22, whereas

Table 4 Survey of literature data for thermodynamic properties of aqueous solutions of a single polyelectrolyte at around 300 K (without any other salt)

Polymer	Molecular mass/ ($\times 10^{-5}$)	Counterion	Counterion molality	Method	Exp. prop.	References
HPMSS	1.5	$\text{Na}^+, \text{H}^+, \text{Ag}^+, \text{Ti}^+, \text{Zn}^{++}, \text{Cd}^{++}, \text{Pb}^{++}$	4×10^{-4} –0.1	EMF	γ_{Cl}	[29] [30]
HPAA	2.6	Na^+/H^+	0.28–0.77	MO, VO	π	[25]
HPAA	0.012	Na^+	0.1–3.1	ISO	Φ_p	[31]
HPAA	0.46	$\text{Na}^+/\text{H}^+, \text{N}^+ (n\text{-C}_4\text{H}_9)_4/\text{H}^+, \text{Li}^+, \text{K}^+, \text{N}^+\text{R}_1; [\text{R}_1 \equiv (\text{C}_2\text{H}_5)_4, (\text{CH}_3)_4, (n\text{-C}_3\text{H}_7)_4]$	0.2–4.5	ISO	Φ_p	[32]
HPAA	1.2	Na^+	4×10^{-3} –0.23	EMF	γ_{Cl}	[33]
HPAA	1.2	Na^+	1.7×10^{-3} –0.25	EMF	γ_{Cl}	[34]
CMC	2.5	$\text{Na}^+, \text{Li}^+, \text{K}^+, \text{N}^+\text{R}_1; [\text{R}_1 \equiv (\text{C}_2\text{H}_5)_4, (\text{CH}_3)_4, (n\text{-C}_4\text{H}_9)_4]$	0.16–2	ISO	Φ_p	[32]
PMETAC	1.7	Cl^-	0.38–1.1	MO, VO	π, Φ_p	[25]
PAAm	0.5	Cl^-	0.44–1.9	MO, VO	π, Φ_p	[25]
HPVB		Na^+	0.32–0.77	MO, VO	π, Φ_p	[25]
HPVAS	2.5	$\text{Na}^+, \text{Li}^+, \text{K}^+, \text{Ca}^{++}, \text{Ba}^{++}$	0.11–2.5	ISO	Φ_p	[35]
HPP	0.61	Na^+	0.13–2.3	ISO	Φ_p	[36]
HPES	1	$\text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{N}^+\text{R}_1; [\text{R}_1 \equiv (\text{C}_2\text{H}_5)_4, (\text{CH}_3)_4, (n\text{-C}_3\text{H}_7)_4, (n\text{-C}_4\text{H}_9)_4, (\text{CH}_3)_3\text{CH}_2\text{C}_6\text{H}_5]$	0.19–6.1	ISO	Φ_p	[37]
PVA/ HPVAS	1.7	$\text{Co}, \text{Ni}, \text{Cu}^{++}$	5×10^{-4} –0.12	GDM	a_w	[38]
PVA/ HPVAS	0.7–0.9	$\text{Na}^+, \text{Cu}^{++}, \text{Li}^+, \text{La}, \text{Cs}^+, \text{Mg}^{++}$	5×10^{-4} –0.2	GDM	a_w	[39]
HPAS	0.1	$\text{Na}^+, \text{Li}^+, \text{Cs}^+$	1×10^{-3} –0.3	VO/ MO	Φ_p	[40]
HPAA	0.03; 0.07	$\text{Na}^+, \text{NH}_4^+$	7×10^{-4} – 4×10^{-3}	ISO	a_w	[41]
HPMAA	0.06; 0.14	Na^+	7×10^{-4} – 3×10^{-3}	ISO	a_w	[41]
HPES	0.02; 0.07	Na^+	4×10^{-4} – 5×10^{-3}	ISO	a_w	[41]

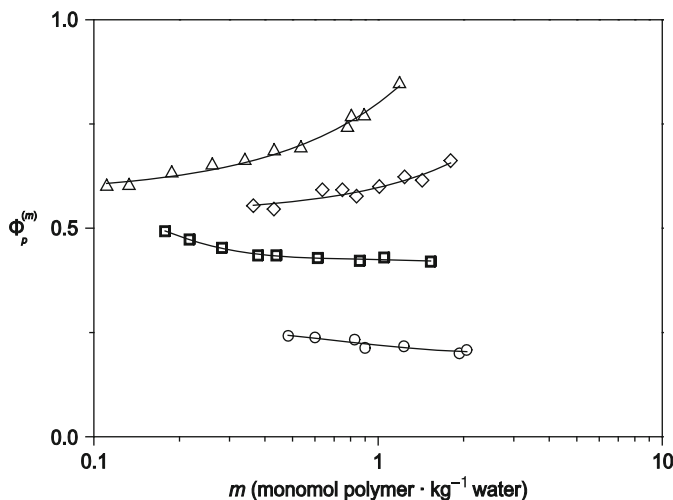


Fig. 2 Osmotic coefficient of aqueous solutions of a polyelectrolyte from isopiestic measurements at 25°C [32, 35–37]: *open triangles* NaPVAS, $M = 2.5 \times 10^5$; *open diamonds* NaCMC, $M = 2.5 \times 10^5$, DS = 0.95; *open squares* NaPP, $M = 6.1 \times 10^4$; *open circles* NaPES, $M = 1 \times 10^5$. DS degree of substitution (carboxymethyl groups per glucose unit)

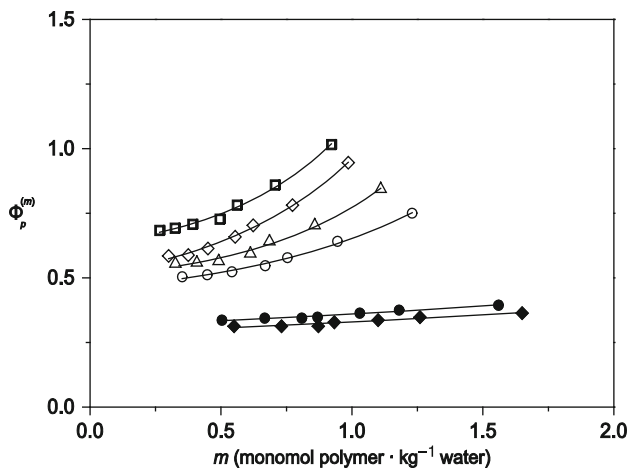


Fig. 3 Influence of counterion on the osmotic coefficient of aqueous solutions of poly(acrylates) at 25°C from isopiestic measurements (Asai et al. [32]): *open squares* $-N(n-C_4H_9)_4$; *open diamonds* $-N(n-C_3H_7)_4$; *open triangles* $-N(n-C_2H_5)_4$; *open circles* $-N(n-CH_3)_4$; *closed circles* $-Li$; *closed diamonds* $-K$

it is about 0.44 when ethylene sulfate is replaced by phosphate (i.e., for NaPP), and is 0.6 and 0.8 for sodium carboxymethylcellulose (NaCMC) and poly(sodium vinyl sulfate) (NaPVAS), respectively.

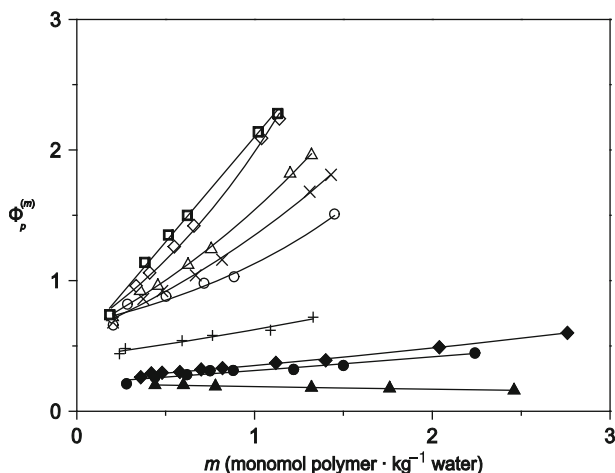


Fig. 4 Influence of counterion on the osmotic coefficient of aqueous solutions of poly(ethylene sulfonates) at 25°C from isopiestic measurements by Ise and Asai [37]: *open squares* $-\text{N}(\text{n-C}_4\text{H}_9)_4$; *open diamonds* $-\text{N}(\text{n-C}_3\text{H}_7)_4$; *open triangles* $-\text{N}(\text{n-C}_2\text{H}_5)_4$; *times* $-\text{N}(\text{n-CH}_3)_4$; *open circles* $\text{N}(\text{CH}_3)_3\text{CH}_2\text{C}_6\text{H}_5$; *+*, $-\text{NH}_4$; *filled diamonds* $-\text{H}$; *closed circles* $-\text{Li}$; *closed triangles* $-\text{K}$

Figures 3 and 4 show some typical examples of the influence of the nature of the counterion of a polyelectrolyte on the osmotic coefficient. The osmotic coefficient is typically very small for inorganic counterions, but it can be increased by a factor of about 10 by organic counterions, for the same temperature and polyelectrolyte monomer-group molality. Figure 4 shows that the osmotic coefficient of an aqueous solution of a poly (ethylene sulfonate) increases in the counterion series K^+ , Li^+ , H^+ , NH_4^+ , $\text{N}^+(\text{CH}_3)_3\text{CH}_2\text{C}_6\text{H}_5$, $\text{N}^+(\text{CH}_3)_4$, $\text{N}^+(\text{C}_2\text{H}_5)_4$, $\text{N}^+(\text{n-C}_3\text{H}_7)_4$, and $\text{N}^+(\text{n-C}_4\text{H}_9)_4$.

3.2 Aqueous Solutions of a Single Polyelectrolyte and a Low Molecular Weight Strong Electrolyte

There have been many investigations on the influence of a low molecular weight strong electrolyte on the thermodynamic properties of an aqueous solution of a polyelectrolyte. A survey on literature data is given in Table 5. The experimental methods already mentioned above are also common for investigating aqueous solutions of both a polyelectrolyte and a salt. However, also equilibrium dialysis (EQDIA) and EMF-measurements with ion-selective electrodes have been used in such experimental investigations. In EQDIA, an aqueous polyelectrolyte solution and an aqueous solution of a low molecular weight salt are separated by a membrane that is permeable to water as well as to the ions of the salt and the counterions of the polyelectrolyte. In phase equilibrium, the concentration of the free ions in the coexisting phases are

Table 5 Survey of literature data for thermodynamic properties of aqueous solutions of a single polyelectrolyte at around 300 K (with an added salt)

Polymer	Polymer conc. (g/dm ³)	Salt	Salt conc. (mol/dm ³)	Method	Experimental properties	References
NaPSS	2.5–31	NaCl	0.01–0.1	MO	π	[42]
NaPSS	0.5–7.5	NaCl	0.005–0.5	MO	π	[26]
NaPSS	68–556	NaCl	0.056–0.91	ISO	Φ_p	[27]
BaPSS	2–52	LiCl, NaCl, KCl	0.001–1		Solubility	[43]
NaPSS	0.2–21	NaCl, Na ₂ SO ₄ , NaCNS	1.7×10^{-4} –0.1	EMF, EQDIA	Γ	[44, 45]
NaPSS	0.08	Pb(NO ₃) ₂ , HNO ₃ , NaNO ₃	0.01–0.02	EQDIA	$\theta_H, \theta_{Na}, \theta_{Pb}$	[46]
NaPSS	<0.8	NaNO ₃	0.005–3.7	EQDIA	θ_{Na}, θ_H	[47]
NaPA	3.7–623	NaCl	0.046–3	ISO	Φ_p	[48]
NaPA	0.09–9.1	NaCl, Na ₂ SO ₄	1.7×10^{-4} –0.1	EMF, EQDIA	Γ, Φ_p	[45]
KPA	5	KCl	0–0.1	EMF, VO	θ_K, γ_{Cl}	[49]
NaPMAA	0.08–49	NaBr	0.001–0.3	DMO	Φ_p	[50]
NaCMC	1–6	NaCl, LiCl, NH ₄ Cl, CaCl ₂ , Mg Cl ₂	0.005–1	MO	π, Φ_p	[51]
NaCMC	0.01; 0.025	NaCl	0.1–5.7	EMF	γ_{Cl}	[52]
CaPAM	0.87	CaCl ₂	0.002–0.02	EMF	γ_{Cl}	[53]
NaPAM	0.19–1.3	NaBr	4×10^{-4} – 4×10^{-2}	EMF	γ_{Cl}	[54]
NaPAM, KPAM, MgPAM	0.22–1.67	NaNO ₃ , KNO ₃ , Mg(NO ₃) ₂	3×10^{-4} –0.05	EQDIA, EMF	$\gamma_{Cl}, \theta_{Na}, \theta_K, \theta_{Mg}$	[55]
X-DP,X-DS; X = (Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ , Rb ⁺ , Mg ⁺⁺ , Ca ⁺⁺ , Cd ⁺⁺)	0.5–1.0	LiCl, NaCl, KCl, CsCl, RbCl, MgCl ₂ , CaCl ₂ , Cd(NO ₃) ₂	$c_p/c_s = 0$ –12	EMF	γ_{Cl}, θ_X	[56]
PEI	5.2	KCl	0.001–0.1	EMF, VO	θ_{Cl}, γ_{Cl}	[49]
PVBTMAC	90–670	NaCl	0.05–0.85	ISO	Φ_p	[27]
PAAM	0.09–9.4	NaCl, Na ₂ SO ₄	1.7×10^{-4} –0.1	EMF, EQDIA	Γ	[44]
PMETAC	0.2–21	NaCl, Na ₂ SO ₄	1.7×10^{-4} –0.1	EMF, EQDIA	Γ	[44]
NaPA, NH ₄ PA, NaPMAA, NaPES, NaPSS	0–40	NaCl	0–0.3	ISO	a_w	[28]

determined, e.g., by titration or by ion chromatography. The results are often reported as the “degree of condensation” θ_k of a counterion k or the “salt-exclusion parameter” Γ . θ_k is the degree of electrolyte groups in the polymer that are neutralized by ionic species k :

$$\theta_k = \frac{c_{k,b}}{vc_p}, \quad (7)$$

where $c_{k,b}$ is the molarity of monomeric electrolyte groups saturated with counterion k , v is the number of repeating units, and c_p is the molarity of the polyelectrolyte. The salt-exclusion parameter Γ is the ratio of the difference in the molarity c_s of the counterion on both sides of the membrane to the molarity of (monomer) electrolyte groups of the polyelectrolyte c_p in the aqueous phase:

$$\Gamma = \frac{c_{s,(w+s)} - c_{s,(w+s+p)}}{c_p}. \quad (8)$$

When ion-selective electrodes have been used, the activity coefficient of the counterions is sometimes presented as a function of the “charge density parameter” λ (from the theory of Lifson and Katchalsky):

$$\lambda = \frac{e^2}{4\pi\epsilon\epsilon_0kTb}, \quad (9)$$

where e , ϵ_0 , ϵ , k and b are the proton charge, permittivity of vacuum, relative permittivity of pure water, Boltzmann’s constant, and the distance between two electrolyte groups in a polyelectrolyte backbone, respectively.

Figure 5 shows some typical results for the osmotic pressure π of aqueous solutions of NaPSS and NaCl. At high ionic strength, the slope of the ratio of osmotic pressure to the (monomer) molarity c_p does not depend on the concentration of the polyelectrolyte. That slope increases with decreasing ionic strength and – at constant, but lower ionic strength – with increasing polymer concentration. In such experiments, the ionic strength is adjusted by the amount of dissolved NaCl; a high ionic strength causes a condensation of sodium ions to the polyelectrolyte backbone. The osmotic pressure is primarily caused by the added salt, and small amounts of the polyelectrolyte cause a change in the osmotic pressure very similar to that observed in an ideal solution. The strong increase of the osmotic pressure with decreasing ionic strength, but constant polymer concentration, is at least partially due to the increasing degree of dissociation of electrolyte groups of the polymer.

When a low molecular weight salt MX is dissolved in an aqueous solution of an anionic polyelectrolyte of counterions Cl , both cations (Cl and M) compete for the anionic groups in the polymer. Such competition could result in a change in the degree of dissociation of the ionic groups, i.e., the ratio of charged to neutral repeating units in the backbone. Some examples are shown in Fig. 6. When the lead ion concentration is increased in an aqueous solution of 0.001 mol/dm^3

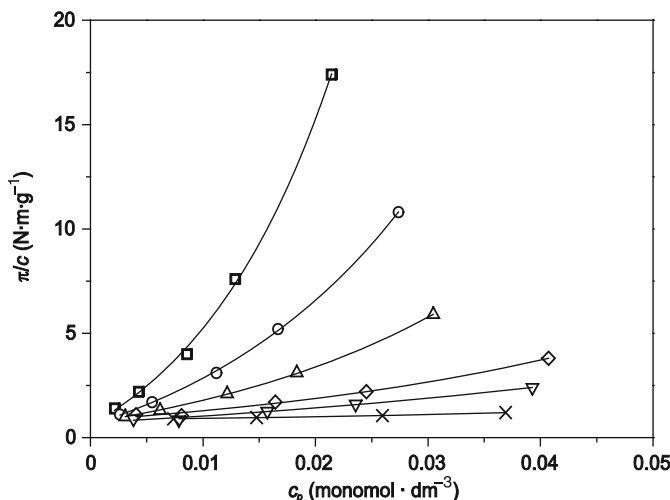


Fig. 5 Reduced osmotic pressure vs. polymer concentration for NaPSS at 25°C in aqueous NaCl solutions of various ionic strength I : open squares $I = 0.005$ mol/dm³; open circles $I = 0.01$ mol/dm³; open triangles $I = 0.02$ mol/dm³; open diamonds $I = 0.05$ mol/dm³; open inverted triangles $I = 0.1$ mol/dm³; crosses 0.5 mol/dm³ [26]

sulfonic acid groups at constant ionic strength [fixed by a mixture of NaNO₃ + Pb(NO₃)₂], the relative amount of sulfonic acid groups neutralized by lead ions (θ_{Pb}) also increases and, consequently, the relative amount of sulfonic acid groups neutralized by sodium ions (θ_{Na}) decreases. However, the decrease of θ_{Na} is not completely compensated by the increase of θ_{Pb} and, therefore, the relative amount of dissociated sulfonic groups increases. θ_{Pb} decreases and θ_{Na} increases when the ionic strength is increased at constant lead concentration. The sum ($\theta_{\text{Pb}} + \theta_{\text{Na}}$) also increases because at the higher ionic strength more ionic species compete for the charged repeating units of the backbone. When, at constant ionic strength, sodium nitrate is replaced by nitric acid, θ_{Pb} increases and θ_{Na} decreases and the sum ($\theta_{\text{Pb}} + \theta_{\text{Na}}$) reveals a small change.

There are also many reports on the application of low angle static light scattering, particularly laser light scattering, in investigations of aqueous polyelectrolyte solutions. Light scattering experiments are common for determining the mass-averaged molecular mass of a polymer, but the technique has also been applied to the determination of osmotic virial coefficients in aqueous solutions.

Osmotic virial coefficients are commonly used to express the osmotic pressure π as a function of solute concentrations. For an aqueous solution of a single solute the osmotic virial equation is:

$$\frac{\pi}{RT} = \frac{\tilde{c}_s}{M_n} + \tilde{c}_s^2 A_{s,s} + \tilde{c}_s^3 A_{s,s,s} + \dots, \quad (10)$$

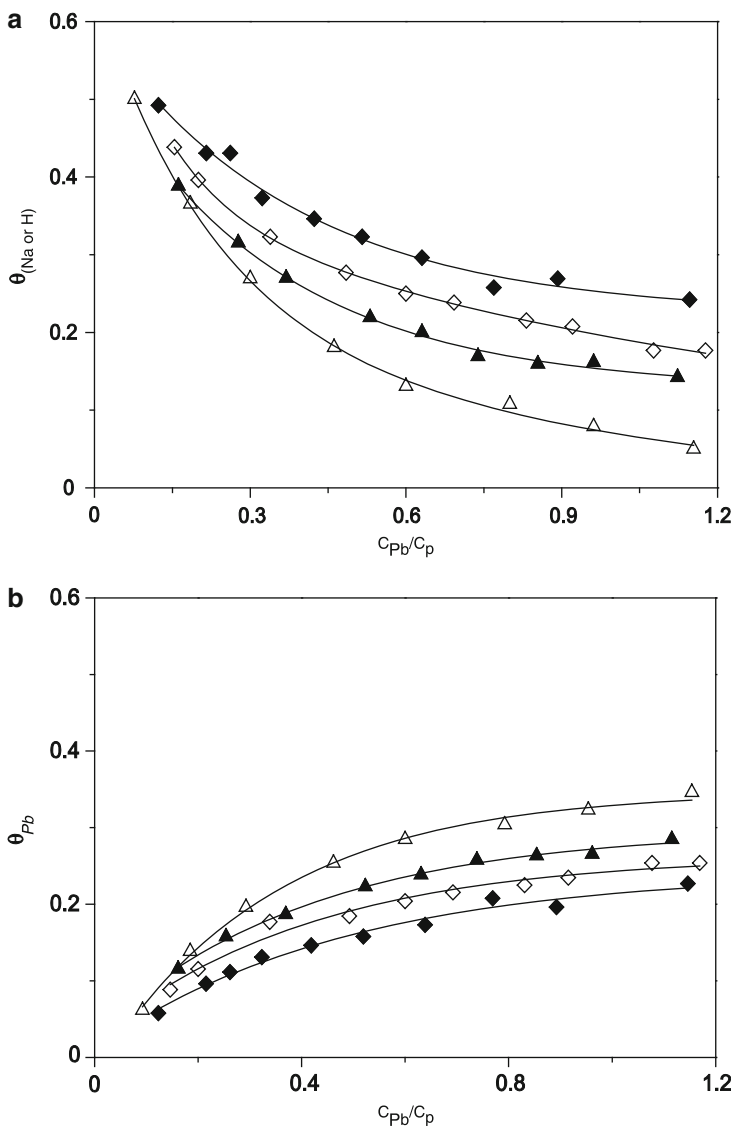


Fig. 6 (a) Degree of condensation of univalent counterions vs. molar concentration c_{Pb} of divalent Pb ions in NaPSS at 25°C, $M = 3.54 \times 10^5$, $c_{\text{sulfonated groups}} = 0.001$ mol/dm³. Closed diamonds PSS/Pb/Na, $I = 0.02$ mol/dm³; open diamonds PSS/Pb/H, $I = 0.02$ mol/dm³; closed triangles PSS/Pb/Na, $I = 0.01$ mol/dm³; open triangles PSS/Pb/H, $I = 0.01$ mol/dm³ [46]. (b) Degree of condensation of divalent counterions vs. molar concentration c_{Pb} of divalent Pb-ions in NaPSS at 25°C, $M = 3.54 \times 10^5$, $c_{\text{sulfonated groups}} = 0.001$ mol/dm³. Closed diamonds PSS/Pb/Na, $I = 0.02$ mol/dm³; open diamonds PSS/Pb/H, $I = 0.02$ mol/dm³; closed triangles PSS/Pb/Na, $I = 0.01$ mol/dm³; open triangles PSS/Pb/H, $I = 0.01$ mol/dm³ [46]

where \tilde{c}_s is the mass density of solute s and $A_{s,s}$ and $A_{s,s,s}$ are the second and third osmotic virial coefficients, respectively, of solute s in the solvent. In nearly all light scattering experiments of aqueous solutions of a polyelectrolyte, the solvent was not only pure water but an aqueous solution of a salt, and the experimental results were interpreted using (10). Then, the evaluated data for the osmotic virial coefficients depend on the nature and the concentration of that salt. Table 6 gives a survey of literature sources for the second osmotic virial coefficients of a single polyelectrolyte in an aqueous solution from light scattering experiments. The second osmotic virial coefficient is determined by extrapolating experimental results to infinite dilution. Light scattering is particularly suited for the investigation of such highly diluted mixtures.

However, even when the polymer contains no ionic groups the extrapolation might be rather difficult (e.g., Hasse et al. [70], Kany et al. [71, 72]). Figure 7 shows a typical example of the influences of the molecular mass and the concentration of a salt on the second osmotic virial coefficient of a polyelectrolyte in water. The second osmotic virial coefficient increases considerably with decreasing salt concentration. The influence of the molecular mass is less distinct and often hidden by the scattering of the experimental data, particularly if that data is from different literature sources. In an aqueous solution of a strong electrolyte, the second osmotic virial coefficient of polyelectrolytes with different backbone monomers can vary by about one order of magnitude.

Table 6 Survey of literature data for the second osmotic virial coefficients of a single electrolyte in an aqueous solution from light scattering investigations

Polymer	Polymer concentration \tilde{c}_p (g/dm ³)	Salt	Salt concentration c_s (mol/dm ³)	References
NaPSS	0.5–3	NaCl	0.005–4.2	[57]
Na/HPSS	< 0.8	Na/H/NO ₃	0.005–3.7	[47]
NaPSS; Pb/HPSS	0.4–3	NaNO ₃ , HNO ₃ , Pb(NO ₃) ₂	0.005–2	[58]
KPSS		KCl	0.1	[59]
NaPA	0.1–2	NaCl	0.01–1	[59]
HPAA	0.1–3	NaCl	0.01–1	[60, 61]
		NaBr	1.5	
		CaCl	0.1	
NaCMC	0.1–4	NaCl	0.001–0.5	[62]
NaCMC	0.2–0.8	NaCl	0.005–0.5	[63]
NaPAMS	–	NaCl	0.01–5	[64]
NaPAMA	–	NaCl	1	[65]
PDADMAC	–	NaCl	0.5	[66]
PDADMAC	–	NaCl	1	[67]
PAAm	1.87	NaCl	0.05–3	[68]
PTMAC	–	NaCl	1	[65]
PTMAC	–	NaCl	0.1–4	[69]

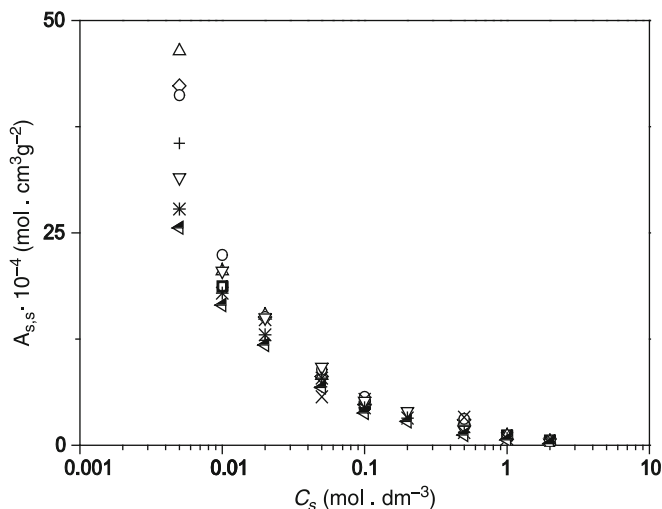


Fig. 7 Second osmotic virial coefficient of sodium poly(styrene sulfonate) of varying molecular mass (M) vs. the concentration of added NaCl: *squares* (23.4×10^5); *diamonds* (22.8×10^5); *triangles* (15.5×10^5); *circles* (10×10^5); *crosses* (3.9×10^5); *plus* (3.2×10^5) data from Takahashi et al., 25°C [57]; *half-closed triangles* (12.2×10^5); *stars* (7.3×10^5); *inverted triangles* (3.2×10^5) data from Nordmeier, 20°C [58]

4 Gibbs Energy of Aqueous Solutions of Polyelectrolytes

For several reasons, it is rather difficult to develop a reliable method for describing (i.e., correlating and predicting) the thermodynamic properties of aqueous solutions of polyelectrolytes. The thermodynamics of polymer solutions in nonaqueous systems as well as of aqueous electrolyte solutions are still major areas of research and, consequently, the situation is less satisfactory for aqueous solutions of polyelectrolytes, for which the dissociation reactions have to be taken into account. This section reviews the most important features of some methods of modeling the Gibbs energy of aqueous polyelectrolyte solutions. The Gibbs energy of an aqueous solution is the sum of contributions from all (solute plus solvent) species i :

$$G = \sum_i n_i \mu_i, \quad (11)$$

where n_i and μ_i are the number of moles and the chemical potential of component i (i.e., of the solvent and the solutes), respectively. It is common to split the Gibbs energy into two parts, a contribution from ideal mixing and an excess contribution:

$$G = G^{\text{id.mix.}} + G^E. \quad (12)$$

As the Gibbs energy is the sum of contributions from all components, $G^{\text{id.mix.}}$ and G^E are also sums of contributions by all components:

$$G^{\text{id.mix.}} = \sum_i n_i \mu_i^{\text{id.mix.}}, \quad (13)$$

$$G^E = \sum_i n_i \mu_i^E \quad (14)$$

or

$$G = \sum_i n_i (\mu_i^{\text{ref}} + RT \ln a_i). \quad (15)$$

Therefore, the following relation holds:

$$\mu_i = \mu_i^{\text{id.mix.}} + \mu_i^E = \mu_i^{\text{ref}} + RT \ln a_i. \quad (16)$$

By definition, component i experiences in an ideal mixture the same intermolecular forces as in the reference state and therefore all differences between $\mu_i^{\text{id.mix.}}$ and μ_i^{ref} are caused by differences in the concentration (i.e., dilution) only:

$$\mu_i^{\text{id.mix.}} = \mu_i^{\text{ref}} + RT \ln a_i^{\text{id.mix.}}. \quad (17)$$

Consequently, the activity of component i in an ideal mixture, $a_i^{\text{id.mix.}}$, is known from the composition of the real solution. However, the actual expression for $a_i^{\text{id.mix.}}$ depends on the choice of reference states and the concentration scale applied. The reference state for the solvent (in this case water) is usually the pure liquid at the temperature and pressure of the mixture:

$$\mu_s^{\text{ref}} = \mu_{s, \text{ pure liquid}}(T, p). \quad (18)$$

However, various reference states are used for a dissolved component. One common reference state is a hypothetical solution of that component in water at a concentration of 1 mol/kg water (i.e., a one molal solution) where the solute experiences interactions only with water, i.e., as if infinitely diluted in water. With that reference state, it is also common practice to replace the activity of a solute species i by the product of molality m_i and activity coefficient $\gamma_i^{(m)}$:

$$a_i^{(m)} = m_i \gamma_i^{(m)}, \quad (19)$$

where superscript (m) indicates both the reference state and the concentration scale. The activity coefficient of a solute species i becomes unity in an ideal solution and,

consequently (as follows from the Gibbs–Duhem equation), the activity of the solvent (represented by subscript s) in an ideal mixture is:

$$\ln a_{s,\text{id.mix.}}^{(m)} = -\frac{1000}{M_s} \sum_{i \neq s} m_i, \quad (20)$$

where i represents any (but only) solute species.

Another common reference state for a solute is a hypothetical solution of one mole of that solute in one liter of water (i.e., a one molar solution) where the solute experiences interactions only with water, i.e., as if infinitely diluted in water. With that reference state, it is also common practice to replace the activity of a solute species i by the product of molarity c_i and activity coefficient $\gamma_i^{(c)}$:

$$a_i^{(c)} = c_i \gamma_i^{(c)}, \quad (21)$$

where superscript (c) indicates both the reference state and the concentration scale.

The activity coefficient of a solute species i becomes unity in an ideal solution and, consequently (following again from the Gibbs–Duhem equation), the activity of the solvent s is:

$$\ln a_{s,\text{id.mix.}}^{(c)} = -\frac{1}{\bar{\rho}_s^*} \sum_{i \neq s} c_i, \quad (22)$$

where $\bar{\rho}_s^*$ is the molar density of water (in moles per liter).

As usual, the following relations also hold for the excess part of the chemical potential of a solute i and a solvent s :

$$\mu_i^E = RT \ln \left(\frac{a_i}{a_{i,\text{id.mix.}}} \right), \quad (23)$$

$$\mu_s^E = RT \ln \left(\frac{a_s}{a_{s,\text{id.mix.}}} \right). \quad (24)$$

One has to keep in mind that the excess parts of the chemical potentials depend on the selection of the reference state for a solute component, as both the activity of a solute component and the activity of the solvent in an ideal mixture depend on the reference states of the solutes. The activity coefficients of a solute on molality scale, $\gamma_i^{(m)}$, and on molarity scale, $\gamma_i^{(c)}$, are related by:

$$\gamma_i^{(c)} = \gamma_i^{(m)} \frac{m_i}{c_i} \rho_s^*, \quad (25)$$

where ρ_s^* is the specific density of the pure solvent in kg/dm³.

Most methods assume that there are several contributions to the excess Gibbs energy:

$$G^E = \sum_k G_k^E, \quad (26)$$

where k represents such a contribution. More details on such contributions are given below.

For describing the thermodynamic properties of aqueous electrolyte solutions one often uses the osmotic pressure π :

$$\pi = -\frac{RT}{\bar{v}_{s,\text{pure}}} \ln a_s, \quad (27)$$

where $\bar{v}_{s,\text{pure}}$ is the molar volume of the pure solvent and the osmotic coefficient Φ_p :

$$\Phi_p = \frac{\pi}{\pi_{\text{id.mix.}}} = \frac{\ln a_s}{\ln a_{s,\text{id.mix.}}} \quad (28)$$

The numerical value of the osmotic coefficient depends on the selection of the reference state of the solutes, whereas the number for the osmotic pressure does not depend on that reference state.

5 Thermodynamic Models

The fundamentals of the thermodynamic modeling of aqueous solutions of polyelectrolytes were established by Lifson and Katchalsky [73, 74]. Their model was extended by various authors. For example, Dolar and Peterlin [75] extended it to polyelectrolytes with two different counterions. One of the most important extensions was presented by Manning in a series of papers. The new fundamental idea introduced by Manning is the so-called counterion condensation concept. That theory was further extended by Manning [76–78] and others. Manning’s theory of counterion condensation was adopted in more recent work, where his results were applied in a more or less straightforward manner. Manning’s concept has been supported by molecular dynamic simulations of polyelectrolyte solutions, showing the changes in the polymer backbone configuration and the counter ion condensation, e.g., by Stevens and Kremer [79]. There are other examples for the solution of the Poisson–Boltzmann equation, which use other hypotheses about the boundary conditions for which the equation is solved. The examples are more or less related to the work cited before. The model by Feng et al. [80], who considered the presence of salts in the aqueous solution, is an interesting example. There are other interesting examples of extensions, such as those presented by Ospeck and

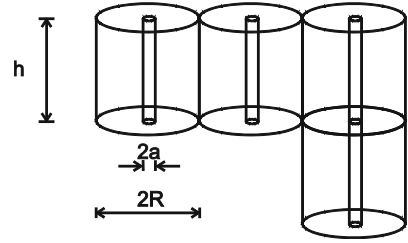
Fraden [81], who solved the Poisson–Boltzmann equation for a system of two cylinders confined between two plates, and by Dahmert and Huster [82, 83], who solved the Poisson–Boltzmann equation for a plate-like polyelectrolyte immersed in a salt solution. Rödenbeck et al. [84] solved the same equation using the approximation of elementary cells around a symmetrically charged central body. The use of cavity-correlation functions was investigated by Jiang et al. [85, 86]. However, using the Poisson–Boltzmann equation for such systems has also attracted some criticism. For example, Blaul et al. [87] compared results derived using the Poisson–Boltzmann equation with experimentally determined osmotic pressure data, and concluded that the difference between the predicted and the experimental behavior is due to some deficiencies of the model, for example, an insufficient treatment of ion–ion correlations. Deserno et al. [88] found that the cell model systematically overestimates the osmotic coefficient. Colby et al. [89] showed that, in the semidilute range of concentrations, the hypotheses used to solve the equations are no longer valid. Diehl et al. [90] mentioned that short-range interactions between the polymer backbones might not be negligible. Many other investigations, for example, by Monte Carlo simulations (Chang and Yethiraj [91]), by molecular dynamic simulations (Antypov and Holm [92]) and by field-theoretical methodologies (Baeurle et al. [93]) were conducted to achieve a better understanding of the behavior of polyelectrolyte solutions. Such investigations are important from a more theoretical point of view. However, it is very difficult either to apply them directly or to use their results in a more indirect way for engineering calculations. That statement particularly holds for aqueous solutions containing a polyelectrolyte and other compounds such as salts and/or neutral polymers. The difficulties are related to computational issues (which may still be an impediment), as well as to the absence of sufficient information. Therefore, despite the large amount of theoretical work, there is still a great need for simplified models that can be applied to the description of phase equilibrium in polyelectrolyte aqueous solutions at medium and high polyelectrolyte concentrations. A similar statement holds for the so-called scaling-law approach (cf. [94–100]).

This contribution is therefore restricted to the models introduced by Lifson and Katchalsky as well as by Manning on one side, and to the extensions and modifications of these models by Danner et al. [101, 102] and by members of our own research group as they seem to have the most potential for applications in chemical engineering.

5.1 *Cell Model of Lifson and Katchalsky*

The model of Lifson and Katchalsky [74] is an extension of the Debye–Hückel theory of highly diluted aqueous solutions of strong (low molecular weight) electrolytes to polyelectrolyte solutions. Lifson and Katchalsky start from the idea that an aqueous solution of a polyelectrolyte reveals a microscopic structure. That structure is caused by two competing effects: the electric charges on the backbone

Fig. 8 Cell model of Lifson and Katchalsky [74] showing radii a and R



monomers (that tend to stretch the polyelectrolyte) and the tendency of the polyelectrolyte to increase its entropy by forming globular or entangled coils (at low or high polymer concentrations, respectively). As shown in Fig. 8, the polyelectrolyte backbone is modeled as a stretched cylinder of radius a and length h . That cylinder is surrounded by another cylindrical cell (radius R and length h). The electrical charge on the backbone is approximated by a uniform charge on the surface of the inner cylinder. The counterions are dissolved in the cylindrical space between radii a and R , where they form an ionic cloud. The radius R depends on the concentration of the polyelectrolyte. It is low in highly concentrated solutions and increases with decreasing concentration to reach infinity in an infinitely diluted solution. The electrostatics in that cloud are described by the Poisson–Boltzmann equation. In a manner analogous to the Debye–Hückel theory, the electrostatic potential caused by the interactions between the stretched backbone on one side and the surrounding counterions on the other side is calculated by solving the Poisson–Boltzmann differential equation. The electrostatic potential $\varphi(r)$ in the cylindrical space between the radii a and R ($a \leq r \leq R$) is:

$$\varphi(r) = \frac{kT}{e} \ln \left\{ \frac{2\lambda}{\beta^2} \frac{r^2}{(R^2 - a^2)} \sinh^2[\beta \ln(Ar)] \right\}, \quad (29)$$

where λ is a (dimensionless) charge density parameter that describes the charge density on the polyelectrolyte's backbone. When the repeating unit is a 1:1 electrolyte, that parameter becomes:

$$\lambda = \frac{l_B}{b}, \quad (30)$$

where l_B is the Bjerrum length:

$$l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 kT}, \quad (31)$$

which characterizes the solvent through its relative dielectric constant ϵ . Parameters b , e , and ϵ_0 are the length of that repeating unit, the elementary charge, and the permittivity of vacuum, respectively. The two other parameters A (which is an

inverse length) and β (which is dimensionless) are determined from the condition of electroneutrality in the cylindrical cell of radius R and from the condition that at $r = R$, the electrostatic potential $\varphi(r)$ has to reach an extreme (for symmetry reasons). As long as the charge density parameter λ is “small” parameter β is a real number (between zero and one), whereas it is an imaginary number (between zero and $1.0i$) for “large” charge densities. The distinction between “small” and “large” depends on the polyelectrolyte concentration. When β becomes imaginary, β has to be replaced by $|\beta|$ in (29). Consequently there are two different regions where the remaining parameters (A and β) have to be determined:

When β is real:

$$\lambda = \frac{1 - \beta^2}{1 + \beta \coth(\beta \gamma_{LK})}, \quad (32)$$

$$1 + \beta \coth[\beta \ln(AR)] = 0. \quad (33)$$

When β is imaginary:

$$\lambda = \frac{1 + |\beta|^2}{1 + |\beta| \cot(|\beta| \gamma_{LK})}, \quad (34)$$

$$\beta \ln A + |\beta| \ln R + \arctan|\beta| = 0, \quad (35)$$

where γ_{LK} is another dimensionless parameter:

$$\gamma_{LK} = \ln \frac{R}{a} \quad (36)$$

that is related to the volume fraction ϕ_p of the polyelectrolyte in the aqueous solution:

$$\phi_p = \ln \left(\frac{a}{R} \right)^2. \quad (37)$$

Unfortunately, there is no analytical solution to determine A and β . But at infinite dilution (i.e., when $\gamma_{LK} \rightarrow \infty$) one finds from (32) and (33):

$$\beta = 1.0 - \lambda \quad \text{for } \lambda \leq 1 \quad \text{and} \quad \beta = 0.0 \quad \text{for } \lambda > 1. \quad (38)$$

Figure 9 shows the results for $\beta(\lambda, \gamma_{LK})$ as calculated from (33) to (35).

Lifson and Katchalsky [74] determined the influence of the electrostatic potential $\varphi(r)$ on the thermodynamic properties of an aqueous solution of a single polyelectrolyte through an expression for the change of the Helmholtz energy ΔF_{LK} that is due to the presence of the electrostatic potential by:

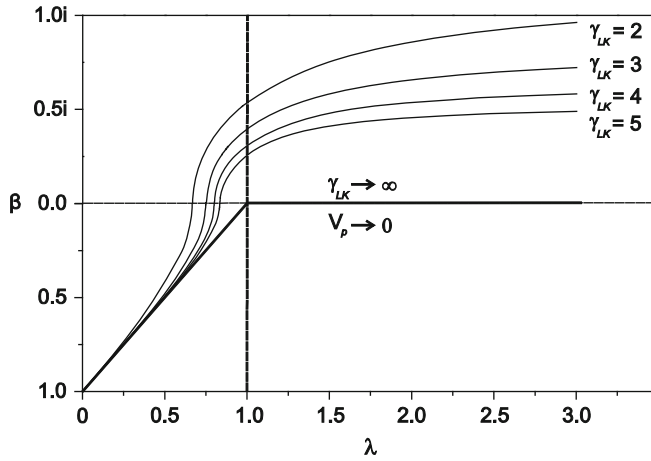


Fig. 9 Theory of Lifson and Katchalsky: Integration constant β as a function of the charge density parameter λ for several parameters γ_{LK}

$$\Delta F_{LK} = c_p V R T f^{\text{el}} \quad (39)$$

with:

$$f^{\text{el}} = \frac{v}{\lambda} \left[\lambda \ln \frac{((\exp \gamma_{LK})^2 - 1)((1 - \lambda)^2 - \beta^2)}{2\lambda} - \lambda - (1 + \beta^2)\gamma_{LK} - \ln \frac{(1 - \lambda)^2 - \beta^2}{1 - \beta^2} \right], \quad (40)$$

where c_p is the molarity of the polyelectrolyte in the solution, and V is the volume of the solution (i.e., $c_p V$ is the number of moles of polyelectrolyte in the solution) and v is the number of repeating units of the polyelectrolyte.

The osmotic pressure π is split into two contributions:

$$\pi = \pi_{\text{id.mix.}} + \Delta\pi^{\text{el}}, \quad (41)$$

where the osmotic pressure of the ideal mixture $\pi_{\text{id.mix.}}$ is calculated assuming that the polyelectrolyte is completely dissociated. When the repeating unit is a 1:1 electrolyte that contribution is:

$$\pi_{\text{id.mix.}} = (1 + v)c_p R T. \quad (42)$$

The second contribution $\Delta\pi^{\text{el}}$ is caused by the electrostatic potential. It is calculated from the contribution of the electrostatic forces to the Helmholtz energy:

$$\Delta\pi^{\text{el}} = - \left(\frac{\partial F^{\text{el}}}{\partial V} \right)_{T, \text{composition}}. \quad (43)$$

The final result for the osmotic coefficient $\Phi_p^{(c)}$ (on molarity scale) is:

$$\Phi_p^{(c)} = \frac{1 - \beta^2}{2\lambda} \quad \text{for } \lambda \leq 1 \quad (44)$$

and:

$$\Phi_p^{(c)} = \frac{1 + \beta^2}{2\lambda} \quad \text{for } \lambda > 1. \quad (45)$$

Figure 10 shows the osmotic coefficient of an aqueous solution of a single polyelectrolyte as a function of the molarity of the repeating units $c_m = \nu c_p$ and the charge density parameter λ . In a highly diluted aqueous solution (i.e., when $\gamma_{LK} \rightarrow \infty$), the final result is:

$$\Phi_p^{(c)} = 1 - \frac{\lambda}{2} \quad \text{for } \lambda \leq 1, \quad (46)$$

$$\Phi_p^{(c)} = \frac{1}{2\lambda} \quad \text{for } \lambda > 1. \quad (47)$$

For the calculation of the osmotic pressure of an aqueous solution of a single polyelectrolyte where the repeating unit is a 1:1 electrolyte one needs:

- For the polyelectrolyte: the radius of the hard polymer rod a , the length of the polymer rod h (or the length of a cylindrical monomer b and the number of such monomers in a polyelectrolyte molecule ν)

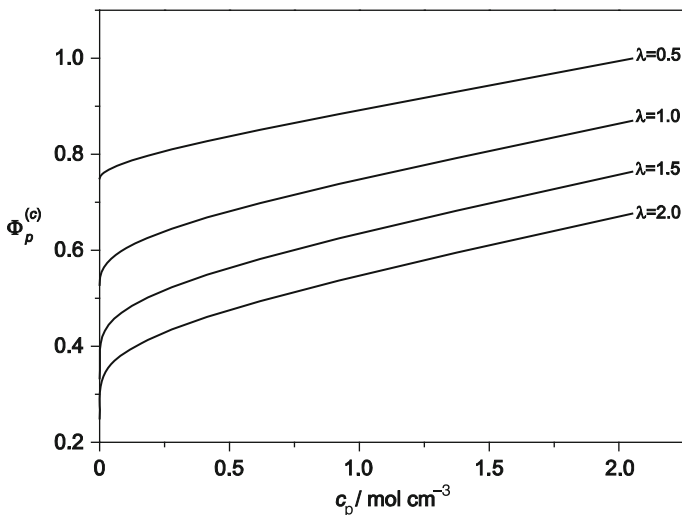


Fig. 10 Theory of Lifson and Katchalsky: Osmotic coefficient of an aqueous solution of a single polyelectrolyte as a function of the charge density parameter λ

- The concentration of the polyelectrolyte in the aqueous phase (or the radius R of a cylindrical cell surrounding each polyelectrolyte molecule)
- The relative dielectric constant of water ϵ

The equations only hold for an aqueous solution of a single polyelectrolyte that consists of monovalent repeating units (1:1 electrolytes). There are publications on extensions. For example, Dolar and coworkers treated polyelectrolytes with two counterions (Dolar and Peterlin, [75], Dolar and Kozak, [103]), and Katchalsky [104] extended the theory to aqueous solutions of a polyelectrolyte and a low molecular weight salt. Katchalsky just superimposed the contributions from the polyelectrolyte with those from the added salt. The osmotic pressure of an aqueous solution of a single polyelectrolyte then becomes:

$$\pi = \pi_p + \Delta\pi^{\text{el}} + \Delta\pi_s. \quad (48)$$

The first term on the right-hand side, π_p , is the contribution for an ideal aqueous solution (on molarity scale) of the undissociated polyelectrolyte:

$$\pi_p = c_p RT. \quad (49)$$

The second term, $\Delta\pi^{\text{el}}$, results from the dissociation of the polyelectrolyte. It is expressed by combining (42), (45) and (47). When β is real:

$$\Delta\pi^{\text{el}} = \frac{1 - \beta^2}{2\lambda} v c_p RT \quad (50)$$

and when β is imaginary:

$$\Delta\pi^{\text{el}} = \frac{1 + \beta^2}{2\lambda} v c_p RT. \quad (51)$$

The third term, $\Delta\pi_s$, is approximated by the osmotic pressure of an aqueous solution of the single, low molecular weight strong electrolyte S , that consists of v_M cations M and v_X anions X :

$$\Delta\pi_s = (v_M + v_X) c_s RT \Phi_s^{(c)}, \quad (52)$$

where c_s and $\Phi_s^{(c)}$ are the molarity of the strong electrolyte S and the osmotic coefficient (on molarity scale) of an aqueous solution of the single strong electrolyte S . Then, the osmotic coefficient of an aqueous solution of a polyelectrolyte P (of monovalent repeating units) and a low molecular weight strong electrolyte S becomes:

$$\Phi_{p+s}^{(c)} = \frac{\pi_p + \Delta\pi^{\text{el}} + \Delta\pi_s}{\pi_{\text{id.mixture}}} = \frac{c_p + \Phi_p^{(c)} v c_p + (v_M + v_X) c_s \Phi_s^{(c)}}{c_p + v c_p + (v_M + v_X) c_s}. \quad (53)$$

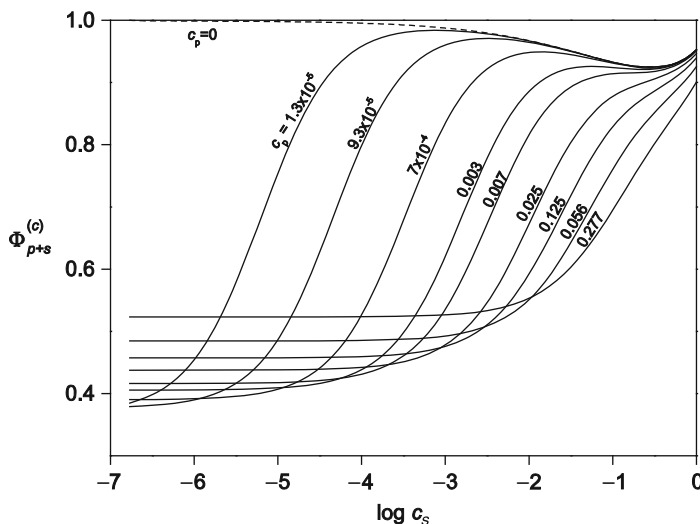


Fig. 11 Osmotic coefficient of an aqueous solution of a polyelectrolyte (charge density parameter $\lambda = 1.5$) and NaCl (salt molarity c_s) at 25°C for several values for the molarity c_p of the polyelectrolyte (the data for the polyelectrolyte-free solution are taken from [105])

As commonly $v \gg 1$ that equation can be simplified to:

$$\Phi_{p+s}^{(c)} = \frac{\Phi_p^{(c)} v c_p + (v_M + v_X) c_s \Phi_s^{(c)}}{v c_p + (v_M + v_X) c_s}. \quad (54)$$

Figure 11 shows a typical example for the osmotic coefficient of an aqueous solution of a polyelectrolyte and NaCl calculated with (54).

An extension to multisolute aqueous solutions with a polyelectrolyte, nonelectrolyte solutes, and low molecular weight salts might start from (48) using (49) together with (50) and (51) for the contributions of the polyelectrolyte, but replacing (52) by the osmotic pressure of an aqueous solution of the polyelectrolyte-free solutions, i.e., an aqueous solution of the low molecular weight salts and the other nonelectrolyte solutes. However, such an extension always suffers from neglecting the interactions between the other solutes and the polyelectrolyte.

5.2 Counterion Condensation Theory of Manning

Manning [76–78] modified and extended the Lifson–Katchalsky model to include the effects caused by the presence of strong, low molecular weight electrolytes in the aqueous polyelectrolyte solution. The polyelectrolyte is described as a linear

chain of N monomers that contain an electrolyte group. Dissociation results in ionic groups on the polymer backbone, resulting in a charged polymeric backbone and counterions. The electric charge is considered to be evenly distributed over the whole backbone and the dissociated counterions are considered as point charges in the solvent of relative dielectric constant ε . Similarly to Lifson and Katchalsky, Manning also assumes that the number of repeating units in the polyelectrolyte chain is very large and, therefore, chain-end effects are neglected. The excess Gibbs energy results from interactions between the charged chain and all other ions (counterions as well as ions from some added low molecular weight strong electrolytes) in the surrounding solution. The properties of that surrounding electrolyte solution are approximated by the Debye–Hückel theory. Manning assumes that some counterions might form ion pairs with some monomers of the backbone. These ion pairs are not really fixed to the backbone but can move in a certain volume around the backbone, i.e., these “condensed counterions” have an additional mobility that increases the entropy of the system. Manning neglects all interactions between all backbone groups of the polyelectrolyte molecule.

In the following description, the molarity scale is used. The reference states are:

- For the solvent: the pure liquid
- For the polyion: the completely dissociated polyion that experiences no electrostatic interactions, but otherwise behaves like at infinite dilution in water
- For an added salt: the completely dissociated salt that also experiences interactions as if at infinite dilution in water.

As an example, we discuss here an aqueous solution of one polyelectrolyte P and one strong electrolyte S ($=M_{v_M}X_{v_X}$), where P and S share a common counterion X . Some of the counterions that originate from the polyelectrolyte are assumed to be located in a small volume V_p around the polyelectrolyte backbone (the phenomenon is called “counterion condensation”). The polyelectrolyte, “condensed” counterions, “free” counterions, free coions, and water contribute to the Gibbs energy of the solution:

$$G = G_p + G_{\text{cond.Cl}} + G_{\text{free.Cl}} + G_{\text{free.COI}} + G_w. \quad (55)$$

Each contribution consists of a contribution from the reference state and a contribution from mixing:

$$G_i = n_i(\mu_i^{\text{ref}} + RT \ln a_i). \quad (56)$$

The reference state for a solute is always based on the molarity scale (at unit molarity in water but with interactions as if infinitely diluted in water) whereas for water the reference state is pure liquid water. The contributions are described below.

5.2.1 Contribution from the Polymer

Manning assumed that there are only contributions from electrostatic interactions. He approximated these contributions from the cylindrical version of the Debye–Hückel theory:

$$G_p = n_p \mu_p^{\text{ref}} + G_p^{E,\text{el}} \quad (57)$$

with

$$G_p^{E,\text{el}}/(RT) = -n_p v (1 - z_{\text{Cl}} \theta_z)^2 \lambda \ln[1 - \exp(-\kappa b)]. \quad (58)$$

n_p and v are the number of moles of the polyion and the number of dissociable repeating units in that polyion, respectively (i.e., $n_p v$ is the total mole number of dissociable electrolytic groups in the backbone). z_{Cl} is the (absolute) valency of the counterions of the polyelectrolyte. $z_{\text{Cl}} \theta_z$ is the ratio of charges carried by those counterions that are “condensed” to the backbone to the maximum number of charges on that backbone. That ratio is also called the “neutralization fraction of the polyion”. Thus $(1 - z_{\text{Cl}} \theta_z)$ is the ratio of the actual number of charges q to the maximum number q_{max} of charges on the backbone of the polyelectrolyte.

$$\frac{q}{q_{\text{max}}} = (1 - z_{\text{Cl}} \theta_z). \quad (59)$$

Consequently, the number of moles of dissociated repeating units, $n_{p,\text{diss}}$ is:

$$n_{p,\text{diss}} = n_p v (1 - z_{\text{Cl}} \theta_z). \quad (60)$$

λ is the charge density parameter [cf. (30)]. When the charge density is small (i.e., the distance b between two dissociable groups is large so that $\lambda < 1$) the polyelectrolyte is completely dissociated. Thus, the first part on the right-hand side of (58) [i.e., $n_p v (1 - z_{\text{Cl}} \theta_z)^2 \lambda$] is the number of moles of dissociated polymer groups times the charge density parameter. Parameter κ is the inverse of the radius of the ionic cloud in the aqueous solution, as introduced in the Debye–Hückel theory:

$$\kappa^2 = 2N_A \frac{e^2}{\epsilon \epsilon_0 kT} I_S = 8\pi N_A I_S l_B, \quad (61)$$

where I_S is the ionic strength of the aqueous solution on the molarity scale.

When a single polyelectrolyte and a single low molecular weight salt $M_{v_M} X_{v_X}$ are dissolved in water, that ionic strength is:

$$I_S = \frac{1}{2} [(v_M z_M^2 + v_X z_X^2) c_s + z_{\text{Cl}} z_p (1 - z_{\text{Cl}} \theta_z) v c_p], \quad (62)$$

where z_M , z_X , and z_p are the charge numbers of cations M , anions X and the monomer electrolyte group, respectively and c_s and c_p are the molarity of the low molecular weight salt and of the polyelectrolyte, respectively. Thus, the last term on the right-hand side of (58) describes the influence of the ionic cloud of the solution on the Gibbs excess energy of the polyelectrolyte.

5.2.2 Contribution from Condensed Counterions

Those counterions that do not dissociate from the polyion are treated as a further solute:

$$G_{\text{cond.CI}} = n_{\text{cond.CI}} \mu_{\text{cond.CI}}^{\text{ref}} + \Delta G_{\text{cond.CI}}. \quad (63)$$

$\Delta G_{\text{cond.CI}}$ results from a transfer of the condensed counterions from the real solution (i.e., at molarity c_{CI}) to a volume V_p near the polyelectrolyte. In that volume, the concentration of the counterions differs from the concentration in the surrounding aqueous solution as that volume contains all condensed counterions, i.e., $n_p \theta_z z_p$ counterions. The molarity of the counterions in that volume is the “local” molarity $c_{\text{CI,local}}$:

$$c_{\text{CI,local}} = \frac{n_{\text{cond.CI}}}{V_p} = \frac{n_p v \theta_z z_p}{V_p}. \quad (64)$$

V_p is the (unknown) volume of the *condensate*. The change of the Gibbs energy encountered in that transfer is approximated by the corresponding change of the entropy:

$$\Delta G_{\text{cond.CI}}/(RT) = n_{\text{cond.CI}} \ln \left(\frac{c_{\text{CI,local}}}{c_{\text{CI}}} \right) \quad (65)$$

resulting in:

$$\Delta G_{\text{cond.CI}}/(RT) = n_p v z_p \theta_z \ln \left(\frac{\theta_z z_p}{v_p^* c_{\text{CI}}} \right), \quad (66)$$

where v_p^* is an unknown molar volume:

$$v_p^* = \frac{V_p}{n_p v}. \quad (67)$$

That molar volume v_p^* is estimated by Manning in the following way. As a decrease in the degree of dissociation (i.e., an increase of θ_z) results in an increase

of $G_p^{E,el}$ and a decrease of $\Delta G_{\text{cond.Cl}}$, Manning assumed that the condensation process reaches an equilibrium when the sum ($G_p^{E,el} + \Delta G_{\text{cond.Cl}}$) reaches a minimum:

$$\left(\frac{\partial (G_p^{E,el} + \Delta G_{\text{cond.Cl}})}{\partial \theta_z} \right) = 0. \quad (68)$$

This equation is evaluated for the aqueous solution of the single polyion, also assuming that the influence of θ_z on the ionic strength can be neglected. The molar volume v_p^* is calculated from:

$$1 + \ln \left(\frac{\theta_z z_p}{v_p^* c_{\text{Cl}}} \right) + 2 \frac{z_{\text{Cl}}}{z_p} \lambda (1 - z_{\text{Cl}} \theta_z) \ln[1 - \exp(-\kappa b)] = 0. \quad (69)$$

For low concentrations of the polyelectrolyte (i.e., when $c_{\text{Cl}} \rightarrow 0$) that equation can only be fulfilled when:

$$\theta_z^{(0)} = \lim_{c_{\text{Cl}} \rightarrow 0} \theta_z = \frac{1}{z_{\text{Cl}}} \left(1 - \frac{z_p}{z_{\text{Cl}} \lambda} \right). \quad (70)$$

As $\theta_z^{(0)} z_{\text{Cl}}$ is the ratio of the number of actual charges on the polyelectrolyte backbone to the maximum number of charges on that backbone, i.e., $0 \leq (\theta_z^{(0)} z_{\text{Cl}}) \leq 1$, then $\theta_z^{(0)} z_{\text{Cl}}$ is positive as long as $z_p/(z_{\text{Cl}} \lambda) < 1$. The polyelectrolyte is completely dissociated when $z_p/(z_{\text{Cl}} \lambda) = 1$, i.e., $\theta_z^{(0)} z_{\text{Cl}} = 0$. $\theta_z^{(0)}$ cannot be negative even if $z_p/(z_{\text{Cl}} \lambda) > 1$. Therefore, two cases have to be distinguished:

Case A:

$$z_p/(z_{\text{Cl}} \lambda) \leq 1, \quad \theta_z^{(0)} = \frac{1}{z_{\text{Cl}}} \left(1 - \frac{z_p}{z_{\text{Cl}} \lambda} \right). \quad (71)$$

Case B:

$$z_p/(z_{\text{Cl}} \lambda) > 1, \quad \theta_z^{(0)} = 0. \quad (72)$$

v_p^* is calculated from (69) by replacing θ_z by $\theta_z^{(0)}$, which is taken from (71). As for the case when $\theta_z^{(0)} = 0$, no counterion condensation occurs and therefore there is no contribution from condensed counterions to the Gibbs energy.

The result for the molar volume v_p^* is:

$$v_p^* = 4\pi N_A z_p^2 b^3 \left(\frac{z_{\text{Cl}} \lambda}{z_p} - 1 \right) \exp(1). \quad (73)$$

5.2.3 Contribution from Free Counterions

The aqueous phase contains “free” (or “dissolved”) counterions. These ions are either dissociated from the polyelectrolyte or result from the dissolution of the salt S . Their contribution to the Gibbs energy of the solution is:

$$G_{\text{freeCI}} = n_{\text{freeCI}} \mu_{\text{freeCI}}^{\text{ref}} + \Delta G_{\text{freeCI}}, \quad (74)$$

$$\Delta G_{\text{freeCI}}/(RT) = \left[n_{\text{freeCI}}^{(p)} + n_{\text{freeCI}}^{(s)} \right] \ln \left\{ c_{\text{freeCI}} \gamma_{\text{CI}}^{(c)} \right\}. \quad (75)$$

The mole number $n_{\text{freeCI}}^{(p)}$ of the counterions that originate from the polyelectrolyte is:

$$n_{\text{freeCI}}^{(p)} = \frac{n_p v (1 - z_{\text{CI}} \theta_z)}{z_{\text{CI}}} z_p \quad (76)$$

and the mole number of the same counterionic species from the added salt is:

$$n_{\text{freeCI}}^{(s)} = n_s v_{\text{CI}}, \quad (77)$$

where n_s and v_{CI} (either v_M or v_X) are the mole number of the dissolved salt S and the stoichiometric coefficient of the counterion of S , respectively. The molarity c_{freeCI} of the counterions in the aqueous solution surrounding the polyelectrolyte is:

$$c_{\text{freeCI}} = (n_{\text{freeCI}}^{(p)} + n_{\text{freeCI}}^{(s)})/V \quad (78)$$

or:

$$c_{\text{freeCI}} = \frac{z_p v (1 - z_{\text{CI}} \theta_z)}{z_{\text{CI}}} c_p + v_{\text{CI}} c_s. \quad (79)$$

Therefore:

$$\begin{aligned} \Delta G_{\text{freeCI}}/(RT) &= \left[v_{\text{CI}} n_s + \frac{z_p}{z_{\text{CI}}} (1 - z_{\text{CI}} \theta_z) v n_p \right] \\ &\quad \times \ln \left\{ \gamma_{\text{CI}}^{(c)} \left[v_{\text{CI}} c_s + \frac{z_p v}{z_{\text{CI}}} (1 - z_{\text{CI}} \theta_z) c_p \right] \right\}. \end{aligned} \quad (80)$$

$\gamma_{\text{CI}}^{(c)}$ is the activity coefficient of the counterions in the aqueous solution of ionic strength I_S (on molarity scale) [cf. (62)]. That activity coefficient might be set to unity or be approximated by the Debye–Hückel theory.

5.2.4 Contribution from Coions

When a neutral salt S is dissolved in the aqueous polyelectrolyte solution there is also a contribution to the Gibbs energy of the aqueous solution by the other ions, here called coions. When v_{COI} is the stoichiometric coefficient of that coion in S , following the same ideas as explained before for the free counterions, that contribution is:

$$G_{\text{freeCOI}} = n_{\text{freeCOI}} \mu_{\text{freeCOI}}^{\text{ref}} + \Delta G_{\text{freeCOI}}, \quad (81)$$

where:

$$\Delta G_{\text{freeCOI}}/(RT) = v_{\text{COI}} n_s \ln \left(v_{\text{COI}} c_s \gamma_{\text{COI}}^{(c)} \right). \quad (82)$$

The activity coefficient $\gamma_{\text{COI}}^{(c)}$ of the coions (on molarity scale) is treated in the same way as the activity coefficient $\gamma_{\text{CI}}^{(c)}$ of the counterions (i.e., it is either set to unity or expressed through the Debye–Hückel expression).

5.2.5 Contribution from Water

The final contribution to the Gibbs energy results from the presence of water (subscript w):

$$G_w = n_w \mu_w^{\text{ref}} + n_w RT \ln a_w. \quad (83)$$

The activity of water is approximated by using the osmotic coefficient $\Phi_p^{(c)}$ on the molarity scale:

$$\Phi_p^{(c)} = \frac{\ln a_w}{\ln a_{w,\text{id.mix}}^{(c)}} = - \frac{\ln a_w}{(c_{\text{CI}} + c_{\text{COI}})/\bar{\rho}_w^*}. \quad (84)$$

where $\bar{\rho}_w^*$ is the molar density of water in the aqueous solution in moles per liter:

$$\ln a_w = -\Phi_p^{(c)} \left[(v_{\text{CI}} + v_{\text{COI}}) n_s + \frac{z_p}{z_{\text{CI}}} (1 - z_{\text{CI}} \theta_z) v n_p \right]. \quad (85)$$

The osmotic coefficient $\Phi_p^{(c)}$ is again either set to unity (that is the common approach) or taken from the Debye–Hückel theory for an aqueous solution containing n_s moles of salt S and $n_{\text{freeCI}}^{(p)}$ moles of counterions dissociated from the polyelectrolyte.

For highly diluted solutions, the results of Manning's theory agree with the results of Lifson and Katchalsky [cf. (46) and (47)]. For example, Manning [106] gives for the osmotic coefficient of an aqueous solution of a single polyion where the counterions have the (absolute) charge number z_{Cl} :

$$\lim_{c_p \rightarrow 0} \Phi_p^{(c)} = 1 - \frac{\lambda}{2} z_p z_{\text{Cl}} \quad \text{for } \lambda z_p z_{\text{Cl}} \leq 1 \quad (86)$$

and:

$$\lim_{c_p \rightarrow 0} \Phi_p^{(c)} = \frac{1}{2\lambda z_p z_{\text{Cl}}} \quad \text{for } \lambda z_p z_{\text{Cl}} > 1. \quad (87)$$

Manning [106] gives for the limiting activity coefficient of the counterions in such an aqueous solution:

$$\lim_{c_p \rightarrow 0} \ln \gamma_{\text{Cl}}^{(c)} = -\frac{\lambda}{2} z_p z_{\text{Cl}} \quad \text{for } \lambda z_p z_{\text{Cl}} \leq 1 \quad (88)$$

and:

$$\lim_{c_p \rightarrow 0} \ln \gamma_{\text{Cl}}^{(c)} = -\frac{1}{2} - \ln(\lambda z_p z_{\text{Cl}}) \quad \text{for } \lambda z_p z_{\text{Cl}} > 1. \quad (89)$$

The equations (88) and (89) are only appropriate when a single polyelectrolyte is dissolved in an aqueous solution of a single salt and a single polyelectrolyte with a common counterion. Manning has also given extensions for cases in which several low molecular weight salts are dissolved and when those salts and the polyelectrolyte have no common ions [78].

5.3 Modifications of Manning's Theory

There have been some efforts (for example, by Nordmeier [107] and by Hao und Harvey [108]) to modify Manning's model. Here, only the modification by Hao and Harvey will be discussed. Hao and Harvey applied statistical thermodynamics for a linear lattice to derive an improved expression for the "neutralization fraction of the polyion" θ_z that can be used to avoid the approximation $\theta_z = \theta_z^{(0)}$. For an aqueous solution of a single salt and a single polyion (both having a common ion – the counterion), that result is:

$$\theta_z = \frac{1}{z_{\text{Cl}}} \left(1 - \frac{z_p}{z_{\text{Cl}} \lambda} \right) - \ln(f) \left[\frac{\ln(jc_{\text{Cl}})^{-1}}{z_{\text{Cl}}^2 \lambda} + \frac{\ln(jc_{\text{Cl}})^{-2}}{(z_{\text{Cl}} \lambda - 1)(z_{\text{Cl}}^2 \lambda - z_{\text{Cl}} \lambda + 1)} \right], \quad (90)$$

where j stands for:

$$j = 4\pi N_A b^2 l_B (z_{\text{Cl}}^2 v_{\text{Cl}} + z_{\text{COI}}^2 v_{\text{COI}}) \quad (91)$$

and f is a “short-range” parameter. Hao and Harvey did not use the concept of a volume V_p where the condensed counterions are located, but introduced a binding constant to describe the counterion condensation phenomenon. They expressed that binding constant using an adjustable, dimensionless (positive) parameter f . For $f = 1$, (90) reduces to Manning’s approximation ($\theta_z = \theta_z^{(0)}$), whereas for $f \neq 1$ the correction term on the right-hand side of (90) does not vanish.

5.4 NRTL Model of Nagvekar and Danner

Nagvekar and Danner [101] tried to overcome the limitations of the theoretical expression by combining Manning’s result for highly diluted aqueous solutions of a polyion with the semiempirical electrolyte–NRTL (nonrandom two liquid) equation of Chen and Evans [109]. Their expression for the Gibbs energy of an aqueous solution of a polyion consists of three parts. The first part describes the ideal mixture, the two other parts describe the excess Gibbs energy G^E , which results from short-range (superscript SR) as well as from long-range (superscript LR) electrostatic interactions:

$$G = \sum_{\text{all components } j} n_j \mu_{j,\text{id.mix.}} + G^{E,\text{SR}} + G^{E,\text{LR}}. \quad (92)$$

The chemical potential of a component j in an ideal mixture $\mu_{j,\text{id.mix.}}$ is defined on the mole fraction scale using the unsymmetrical convention, i.e., the reference state for the solvent (water) is the pure liquid solvent. For any solute species, the reference state is a hypothetical pure liquid where the species experience interactions as if at infinite dilution in water.

As the activity coefficient $\gamma_j^{(x)}$ of component j is:

$$RT \ln \gamma_j^{(x)} = \left(\frac{\partial G^E}{\partial n_j} \right)_{n_{k \neq j,p,T}}, \quad (93)$$

$\gamma_j^{(x)}$ is a product of a short-range and a long-range contribution:

$$\gamma_j^{(x)} = \gamma_j^{\text{SR},(x)} \gamma_j^{\text{LR},(x)}. \quad (94)$$

Danner et al. express the short-range contribution using a modification of the electrolyte–NRTL equation of Chen and Evans [109] and take the long-range contribution from Manning’s model (for the case of infinite dilution of a

polyelectrolyte in water). For example, they treat an aqueous solution of a single polyelectrolyte as a three-component mixture consisting of the solvent, the counterion, and the polyion backbone that is approximated by its charged repeating units. As the electrolyte-NRTL model is a “local composition” model, such a solution is described by cells. There are as many types of cells as there are different species in the mixture. Each cell type consists of a single species surrounded by its nearest neighbors. There are three different cells in an aqueous solution of a single polyion, i.e., with a water molecule, a counterion, or a repeating unit, in the center. The cell with water as the central species might be surrounded by other water molecules, counterions, and repeating units of the polyion. The nearest neighborhood of a cell with a central counterion also contains water and repeating units of the polyion, but it is assumed that there are no further counterions. The nearest neighborhood of a cell with a central repeating unit consists of two further repeating units (its neighbors in the polyion), counterions, and water molecules. In contrast to Chen and Evans, Danner and coworkers [101, 102] do not assume that the criterion of electroneutrality is fulfilled in each cell. Because the electrolyte-NRTL model is commonly given for a symmetrical convention, whereas polyelectrolyte systems are normalized according to the unsymmetrical convention, Danner et al. use the following expression for $G^{E,SR}$ of a multicomponent solution:

$$\frac{G^{E,SR}}{n_T RT} = \frac{G^{E,SR,sym}}{n_T RT} - \sum_{\text{all solutes } j} x_j \ln \gamma_j^{SR,(x),\infty}, \quad (95)$$

where $G^{E,SR,sym}$ is the excess Gibbs energy in the symmetrical convention, n_T is the total mole number of the solution:

$$n_T = \sum_{\text{all components } j} n_j \quad j = w, a, c \quad (96)$$

and $\gamma_j^{SR,(x),\infty}$ is the contribution of the short-range interactions to the activity coefficient of solute j (i.e., either a cation c or anion a , in the symmetrical convention, on the mole fraction scale at infinite dilution in water).

$$\gamma_j^{SR,(x),\infty} = \lim_{n_k \rightarrow 0} \gamma_j^{SR,(x)}, \quad (97)$$

where subscript k stands for all solutes and:

$$RT \ln \gamma_j^{SR,(x)} = \left(\frac{\partial G^{E,SR,sym}}{\partial n_j} \right)_{n_{k \neq j,p,T}}. \quad (98)$$

The mole fraction of species in a shell of nearest neighbors around a central species is expressed using a Boltzmann term as a weighting factor. Danner et al. give the following expression for the contributions of short-range forces to the

excess Gibbs energy of a multisolute and multisolvent mixture in the symmetrical convention:

$$\begin{aligned} \frac{G^{E,SR,sym}}{n_T RT} = & \sum_s X_s \frac{\sum_j X_j G_{js} \tau_{js}}{\sum_k X_k G_{ks}} + \sum_c X_c \sum_a \frac{X_a}{\sum_{a'} X_{a'}} \frac{\sum_{j \neq c} X_j G_{jc,ac} \tau_{jc,ac}}{\sum_{k \neq c} X_k G_{kc,ac}} \\ & + \sum_a X_a \sum_c \frac{X_c}{\sum_{c'} X_{c'}} \frac{\sum_{j \neq a} X_j G_{ja,ca} \tau_{ja,ca}}{\sum_{k \neq a} X_k G_{ka,ca}}, \end{aligned} \quad (99)$$

where subscript s refers to a solvent component, and subscripts c and a refer to anionic and cationic species, respectively, regardless of their source (either from a polyion or from an added salt). Subscripts j and k stand for any of the species in the mixture and primes are used to distinguish different species of the same type. The composition of the mixture is described by “modified mole fractions” X_j :

$$X_j = x_j z_j, \quad (100)$$

where x_j is the mole fraction of species j and z_j is (for a charged species) its (absolute) charge number, and for any uncharged species $z_i = 1$

There are two types of interaction parameters that are distinguished by the number of subscripts: G_{ji} and τ_{ji} on one side and $G_{ji,ki}$ and $\tau_{ji,ki}$ on the other side, which are expressed using binary parameters g_{ji} for interactions between species j and i and by binary and ternary nonrandomness parameters α_{ji} and $\alpha_{ji,ki}$:

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (101)$$

with:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \quad (102)$$

and:

$$G_{ji,ki} = \exp(-\alpha_{ji,ki} \tau_{ji,ki}) \quad (103)$$

with:

$$\tau_{ji,ki} = \frac{g_{ji} - g_{ki}}{RT}. \quad (104)$$

Danner et al. used Manning’s results for the long-range contribution to the activity coefficient of the counterions in an aqueous solution of a single polyion:

$$\ln \gamma_{Cl}^{LR,(c)} = -\frac{\lambda}{2} z_p z_{Cl} \quad \text{for } \lambda z_p z_{Cl} \leq 1 \quad (105)$$

and

$$\ln \gamma_{\text{CI}}^{\text{LR},(c)} = -\frac{1}{2} - \ln(\lambda z_p z_{\text{CI}}) \quad \text{for } \lambda z_p z_{\text{CI}} > 1, \quad (106)$$

where λ is a charge density parameter [see (30) and (31)] and z_p and z_{CI} are the (absolute) numbers of elementary charges on a dissociated repeating unit and on the counterion, respectively. The osmotic coefficient on the molarity scale is:

$$\Phi_p^{(c)} = \frac{\ln a_w}{\ln a_{w,\text{id.mix}}^{(c)}} = \frac{\ln(x_w \gamma_w^{\text{LR},(x)} \gamma_w^{\text{SR},(x)})}{\ln a_{w,\text{id.mix}}^{(c)}} = \frac{\ln(x_w \gamma_w^{\text{LR},(x)})}{\ln a_{w,\text{id.mix}}^{(c)}} + \frac{\ln \gamma_w^{\text{SR},(x)}}{\ln a_{w,\text{id.mix}}^{(c)}}, \quad (107)$$

where, as in (22):

$$\ln a_{w,\text{id.mix}}^{(c)} = -\frac{1}{\bar{\rho}_w^*} \sum_{i \neq w} c_i. \quad (108)$$

The long-range contribution is described using Manning's results and one obtains for the osmotic coefficient (on the molarity scale):

$$\Phi_p^{(c)} = \lim_{c_p \rightarrow 0} \Phi_{p,\text{Ma}}^{(c)} - \bar{\rho}_w^* \frac{\ln \gamma_w^{\text{SR},(x)}}{\sum_{\text{all solutes } j} c_j}. \quad (109)$$

$$\Phi_p^{(c)} = \lim_{c_p \rightarrow 0} \Phi_{p,\text{Ma}}^{(c)} - \bar{\rho}_w^* \frac{\ln \gamma_w^{\text{SR},(x)}}{c_p (1 + \frac{z_p}{z_{\text{CI}}} v)}, \quad (110)$$

where

$$\lim_{c_p \rightarrow 0} \Phi_{p,\text{Ma}}^{(c)} = 1 - \frac{\lambda}{2} z_p z_{\text{CI}} \quad \text{for } \lambda z_p z_{\text{CI}} \leq 1 \quad (111)$$

and

$$\lim_{c_p \rightarrow 0} \Phi_{p,\text{Ma}}^{(c)} = \frac{1}{2\lambda z_p z_{\text{CI}}} \quad \text{for } \lambda z_p z_{\text{CI}} > 1. \quad (112)$$

As above, c_p and v are the molarity of the polyion and the number of repeating units of that polyion. The short-range part of the activity coefficient of water is calculated using (98).

The model needs numerical values for interaction parameters and nonrandomness parameters. Danner et al. mention that the nonrandomness parameters α_{ji} and

$\alpha_{ji,ki}$ were arbitrarily set to 0.20, except when the central species in the cell is a repeating unit and its nearest neighbors are also repeating units. Then, the nonrandomness parameter was set to 0.33. They finally adjusted four interaction parameters to experimental results for the osmotic coefficient of an aqueous solution of a single polyelectrolyte. However, no parameters have been published and all comparisons were given only in graphical form. But, the method is obviously suited for a good correlation of experimental data for the osmotic coefficient of aqueous solutions of a single polyelectrolyte.

Danner et al. did not report results from their method to describe the influence of an added salt on the osmotic coefficient of aqueous solutions that contain a single polyion.

5.5 Pessoa's Modification of the Pitzer Model

Pessoa and Maurer [110] assume that a polyion might not completely dissociate in an aqueous solution and that the degree of dissociation is independent of the composition of the aqueous solution. They propose the use of experimental data for the osmotic coefficient of an aqueous solution of the single polyelectrolyte at infinite dilution to determine that degree. On the molality scale the osmotic coefficient is:

$$\Phi_p^{(m)} = \frac{\pi}{\pi_{\text{id.mix}}^{(m)}} = \frac{\ln a_w}{\ln a_{w,\text{id.mix}}^{(m)}}, \quad (113)$$

where

$$\ln a_{w,\text{id.mix}}^{(m)} = -M_w^* \sum_{\text{all solutes } j} \frac{m_j}{m^\circ}. \quad (114)$$

M_w^* is the relative molecular mass of water divided by 1,000 (i.e., $M_w^* = 0.01806$), m_j is the molality of species j and $m^\circ = 1 \text{ mol/(kg water)}$.

The ideal solution is defined so that all counterions are completely dissociated:

$$m_{\text{Cl}} = \nu m_p \frac{z_p}{z_{\text{Cl}}}, \quad (115)$$

where m_p is the molality of the polyion. The activity of water in an ideal aqueous solution of a single polyelectrolyte is:

$$\ln a_{w,\text{id.mix}}^{(m)} = -M_w^* \left(1 + \nu^* \frac{z_p}{z_{\text{Cl}}} \right) \frac{m_p}{m^\circ}. \quad (116)$$

Taking into account that, in a real solution, the polyion is not completely dissociated, the equation gives at high dilution in water:

$$\ln a_w^{(m)} = -M_w^* \left(1 + v^* \frac{z_p}{z_{Cl}} \right) \frac{m_p}{m^0}. \quad (117)$$

The ratio v^*/v is the degree of dissociation of the repeating units of the polyion. Combining (116) and (117) results in:

$$\lim_{m_p \rightarrow 0} \Phi_p^{(m)} = \Phi_p^{0,(m)} = \frac{1 + v^* \frac{z_p}{z_{Cl}}}{1 + v \frac{z_p}{z_{Cl}}}. \quad (118)$$

When the repeating unit is a 1:1 electrolyte and the number of repeating units is large, the limiting value of the osmotic coefficients equals the degree of dissociation:

$$\Phi_p^{0,(m)} = \frac{v^*}{v}. \quad (119)$$

A real aqueous solution of a single polyion is considered to be a mixture of water, (partially dissociated) polymer chains, and the dissolved counterions. In an ideal mixture all solutes only experience interaction with water, whereas in a real solution there are also interactions between the solutes. The deviations that are caused by these interactions are taken into account through an expression for the excess Gibbs energy. Pessoa and Maurer [110] started from Pitzer's equation [105, 111] for the excess Gibbs energy of aqueous solutions of low molecular weight strong electrolytes. That method was extended previously to describe the Gibbs energy of aqueous solutions that contain both a strong electrolyte and a neutral polymer [112–114]. As in the work by Danner et al. [101, 102], the Gibbs energy of an aqueous solution is split into a contribution from ideal mixing and contributions from long-range and short-range interactions. The contributions are expressed using the unsymmetrical convention. However, Pitzer's equation applies the molality scale to express the composition of the aqueous solution:

$$G = \sum_{\text{all components } j} n_j \mu_{j,\text{id.mix.}} + G^{E,\text{SR}} + G^{E,\text{LR}}. \quad (120)$$

For a solute component j , the chemical potential in an ideal mixture $\mu_{j,\text{id.mix.}}$ is:

$$\mu_{j,\text{id.mix.}} = \mu_j^{\text{ref.},(m)} + RT \ln \frac{m_j}{m^0}, \quad (121)$$

where $\mu_j^{\text{ref.},(m)}$ is the chemical potential of solute j in an one molal aqueous solution (i.e., $m_j = m^0 = 1 \text{ mol}/(\text{kg water})$). In that reference state, the solute experiences similar interaction as in infinite dilution in water. For the solvent (i.e., water) the reference state is the pure liquid solvent and the difference between the chemical

potential in the real mixture and that of the pure liquid is expressed via the activity of water:

$$\mu_w = \mu_{w,\text{pure}} + RT \ln a_w^{(m)}. \quad (122)$$

Pitzer uses a modification of the limiting law by Debye and Hückel to account for long-range interactions that are caused by Coulomb forces:

$$\frac{G^{E,\text{LR}}}{n_w M_w^* RT} = -A_\varphi \frac{4I_m}{b} \ln(1 + b\sqrt{I_m}). \quad (123)$$

A_φ is the Debye-Hückel parameter (at 298.2 K $A_\varphi = 0.3914$), I_m is the ionic strength (on molality scale), and b is a numerical value ($b = 1.2$). This expression is very well suited to describe the activity coefficient of ions at high dilutions, but cannot directly be applied to polyelectrolyte solutions because the Debye-Hückel term was developed for punctual electric charges (such as small mobile ions). It is not valid for highly charged polymer backbones. Pessoa and Maurer [110] replaced the contribution of the polyion in the expression for the ionic strength:

$$I_m = \frac{1}{2} \sum_j \frac{m_j^*}{m^o} (z_j^*)^2, \quad (124)$$

where for all solute species (with the exception of the polyion) $m_j^* = m_j$ and $z_j^* = z_j$, whereas for a polyion ($j \equiv p$) $m_p^* = v^* m_p$ and $z_p^* = z_p$, i.e., for the calculation of the ionic strength the polyelectrolyte is replaced by its dissociated repeating units. The activity coefficient of a solute caused by the long-range interactions is:

$$\ln \gamma_i^{\text{LR},(m)} = -A_\varphi \sigma_i z_i^2 \left(\frac{2}{b} \ln(1 + b\sqrt{I_m}) + \frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} \right), \quad (125)$$

where $\sigma_i = 1$ for all solutes, with the exception of the polymer where $\sigma_i = v^*$.

The long-range contribution to the activity coefficient of the solvent is:

$$\ln \gamma_w^{\text{LR},(m)} = 2A_\varphi M_w^* \frac{I_m^{3/2}}{1 + b\sqrt{I_m}}. \quad (126)$$

The short-range contributions are described with a virial-type equation for the excess Gibbs energy that was adapted from Pitzer [105]. It is applied here neglecting ternary and higher interactions between solute species:

$$\frac{\underline{G}^{E,\text{SR}}}{n_w M_w^* RT} = \sum_{i \neq w} \sum_{j \neq w} \lambda_{ij}(I_m) \frac{m_i^*}{m^o} \frac{m_j^*}{m^o}, \quad (127)$$

where n_w is the number of moles of water and $\lambda_{ij}(I_m)$ is an osmotic virial coefficient for interactions between solute species i and j that depends on the ionic strength I_m through:

$$\lambda_{ij}(I_m) = \lambda_{ij}^{(0)} + \lambda_{ij}^{(1)} \frac{2}{\alpha^2 I_m} \left(1 - (1 + \alpha \sqrt{I_m}) \exp(-\alpha \sqrt{I_m}) \right). \quad (128)$$

Equation (127) applies the same definition for the molality m_i^* of a solute species i as (124) for the ionic strength. $\lambda_{ij}^{(0)}$ and $\lambda_{ji}^{(1)}$ are binary parameters for interactions between the solutes, for example, between a repeating unit of the polyion and a dissolved counterion. No distinction is made – as far as the interaction parameters are concerned – between neutral and dissociated repeating units. The binary parameters are symmetrical ($\lambda_{ij}^{(0)} = \lambda_{ji}^{(0)}$ and $\lambda_{ij}^{(1)} = \lambda_{ji}^{(1)}$) and α is a constant ($\alpha = 2$). For a solute species, the contribution of the short-range interactions to the activity coefficient is:

$$\begin{aligned} \ln \gamma_i^{\text{SR},(m)} &= 2\sigma_i \sum_{j \neq w} \lambda_{ij}(I_m) \frac{m_j^*}{m^\circ} + -\sigma_i z_i^2 M_w^* \\ &\times \sum_{j \neq w} \sum_{k \neq w} \lambda_{ij}^{(1)} \frac{1}{\alpha^2 I_m^2} \left(1 - \left(1 + \alpha \sqrt{I_m} + \frac{\alpha^2 I_m}{2} \right) \exp(-\alpha \sqrt{I_m}) \right) \frac{m_j^*}{m^\circ} \frac{m_k^*}{m^\circ} \end{aligned} \quad (129)$$

and for the solvent:

$$\ln \gamma_w^{\text{SR},(m)} = -M_w^* \left(\sum_{i \neq w} \sum_{j \neq w} \left(\lambda_{ij}^{(0)} + \lambda_{ij}^{(1)} \exp(-\alpha \sqrt{I_m}) \right) \frac{m_i^*}{m^\circ} \frac{m_j^*}{m^\circ} \right). \quad (130)$$

The final equation for the activity of a solute i and of the solvent (water) is obtained by coupling the above expressions through:

$$a_i = m_i \gamma_i^{\text{LR}} \gamma_i^{\text{SR}}. \quad (131)$$

$$a_w = \exp \left(-M_w^* \sum_{i \neq w} \frac{m_i}{m^\circ} \right) \gamma_w^{\text{LR}} \gamma_w^{\text{SR}}, \quad (132)$$

where the sum is over all solute species, i.e., in an aqueous solution of a single electrolyte, i stands for the polyion ($m_i \rightarrow m_p$) and for the counterion ($m_i \rightarrow v^* \frac{z_p}{z_{\text{Cl}}} m_p$).

Modeling the osmotic coefficient of an aqueous solution of a single homopolymer polyion (i.e., a polyion that consists of a single repeating unit and a single counterion) requires:

- The osmotic coefficient of an aqueous solution of the polyelectrolyte at infinite dilution $\Phi_p^{0,(m)}$
- The number of repeating units of the polyion v
- The binary interaction parameters $\lambda_{ij}^{(0)}$ and $\lambda_{ij}^{(1)}$

$\Phi_p^{0,(m)}$ is either determined from experimental results for the osmotic coefficient or estimated using the results of Manning's theory (in that case the length of a repeating unit has to be known). For a polyion that consists only of a single repeating unit, the number of repeating units ν is calculated from the number-averaged molecular mass of the polyion and the molecular mass of the repeating unit. It is assumed that binary interaction parameters between species carrying electrical charges of the same sign can be neglected (i.e., they are set to zero). Therefore, there are only two, nonzero binary parameters for interactions between a repeating (subscript p) unit and the counterion $\lambda_{pCl}^{(0)}$ and $\lambda_{pCl}^{(1)}$. These interaction parameters are fitted to some experimental properties such as the osmotic coefficient. Figure 12 shows a typical example for a correlation. The model can be straightforwardly extended to aqueous solutions of a single polyion and a single low molecular weight strong electrolyte (cf. Fig. 13) but also to aqueous solutions of a polyion and a neutral polymer. Such mixtures often form aqueous two-phase systems. Figure 14 gives a typical example.

5.6 VERS-PE Model

Lammertz et al. [116] extended the Virial-Equation with Relative Surface Fractions (VERS) model of Großmann et al. [112–114] for the excess Gibbs energy of aqueous solutions of neutral polymers and low molecular weight electrolytes to the treatment of aqueous solutions that also contain polyions. That extension is

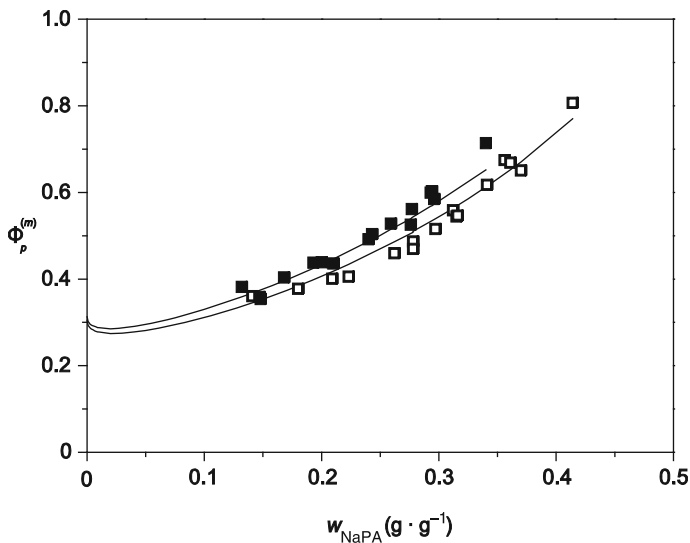


Fig. 12 Osmotic coefficient of aqueous solutions of NaPA at 298.15 K. Experimental data [41]: closed squares NaPA 5; open squares NaPA 15. Lines show the modeling

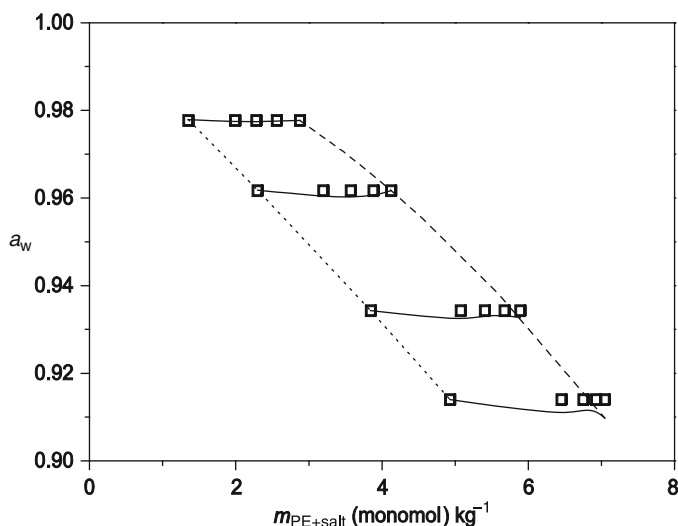


Fig. 13 Activity of water in aqueous solutions of NaPA 5 and NaCl. *Symbols* experimental data [28]; *dashed line* modeling of systems without salt; *dotted line* modeling of systems without polyelectrolyte; *solid lines* correlation results

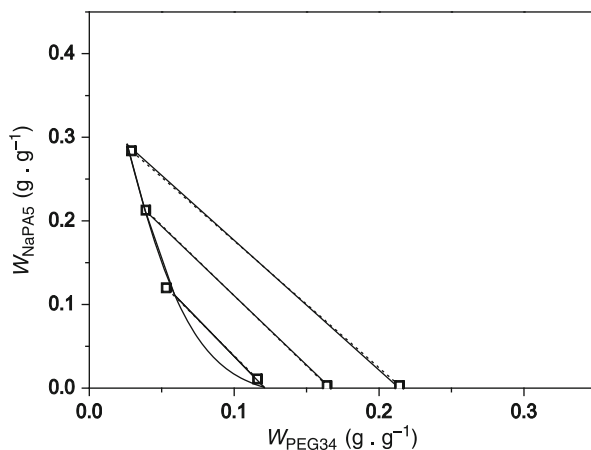


Fig. 14 Liquid-liquid equilibrium of aqueous solutions of NaPA 5 and PEG 34. *Symbols* experimental equilibrium compositions [115]; *dotted lines* experimental tie lines; *solid lines* correlation results

called VERS model for polyelectrolytes (VERS-PE model). Like the model of Pessoa and Maurer, the VERS model is based on Pitzer's equation [105] for the Gibbs excess energy of aqueous solutions of low molecular weight, strong electrolytes. Großmann et al. introduced two modifications to allow for the treatment of neutral polymers: the molality scale was replaced by a surface fraction scale, and

the interactions with a polymer are described via interactions with groups of that polymer, i.e., the polymer was split into groups. The groups commonly consist of the repeating units of the polymer. The extension of the model to polyions also considers the phenomenon of counterion condensation by a chemical reaction equilibrium approach. For convenience, the extension of the model for the excess Gibbs energy to aqueous solutions of polyions is described here first for an aqueous solution of a single polyelectrolyte (designated by subscript p) where only a single counterion might dissociate from a repeating unit and that repeating unit is a 1:1 electrolyte.

The reference state for the chemical potential of the solvent (water) is the pure liquid, whereas for the solute (polyelectrolyte) it is a hypothetical one molal solution of the undissociated polyelectrolyte in water ($m_p = m^\circ = 1 \text{ mol}/(\text{kg water})$), where it experiences interactions with water molecules only, i.e., in that reference state the undissociated polyelectrolyte is infinitely diluted in water ($m_p = 0$ in pure water). The difference between the chemical potential of the polyelectrolyte in the real solution $\mu_p(T, m_p)$ and in its reference state μ_p^{ref} is calculated in five steps:

$$\mu_p - \mu_p^{\text{ref}} = \Delta_{12}\mu_p + \Delta_{23}\mu_p + \Delta_{34}\mu_p + \Delta_{45}\mu_p + \Delta_{56}\mu_p. \quad (133)$$

In the first step (Δ_{12}), only the molality of the polyelectrolyte is changed to its molality m_p in the real solution:

$$\Delta_{12}\mu_p = RT \ln\left(\frac{m_p}{m^\circ}\right). \quad (134)$$

This contribution accounts for the change from the reference state to an ideal dilution (assuming that at state 2 the interactions are the same as in the reference state) and there is still no dissociation.

The second contribution (Δ_{23}) describes the change in the chemical potential due to splitting the polyelectrolyte into its monomers. This change is the sum of two contributions: a free volume contribution (superscript fv) caused by the increase of the number of particles, and a combinatorial contribution (superscript comb) caused by the increase of the number of degrees of freedom:

$$\Delta_{23}\mu_p = \Delta_{23}\mu_p^{\text{fv+comb}}. \quad (135)$$

In state 3, the aqueous polyelectrolyte solution has been replaced by an aqueous solution of the nondissociated repeating units. The repeating units still experience only interactions with water. As one polyelectrolyte molecule consists of v monomer units (characterized by subscript A), the molality of species A, m_A , is:

$$m_A = vm_p \quad (136)$$

and the chemical potential of the polyelectrolyte in state 3 is:

$$\mu_{p,3} = v\left(\mu_A^{\text{ref}} + RT \ln\left(\frac{vm_p}{m^\circ}\right)\right). \quad (137)$$

μ_A^{ref} is the chemical potential of nondissociated repeating units in their reference state. That reference state is defined in the same way as the reference state for a polyelectrolyte.

In the next step (Δ_{34}), all monomer units A are split into two groups. Subscript C designates all repeating units that will never dissociate while subscript D designates repeating units that are assumed to undergo a dissociation reaction. The condition of mass balance requires that for the chemical potential of the polyelectrolyte in state 4 is:

$$\mu_{p,4} = v_{C,4} \cdot \mu_{C,4} + v_{D,4} \cdot \mu_{D,4}. \quad (138)$$

For the sake of simplicity, $v_{C,4}$ and $v_{D,4}$ are expressed through a new property k , that is directly related to the degree of counterion condensation at infinite dilution of the polyelectrolyte in water.

$$k = \frac{v_{C,4}}{v}. \quad (139)$$

The chemical potential of the polyelectrolyte in state 4 is:

$$\begin{aligned} \mu_{p,4} = & vk \left(\mu_C^{\text{ref}} + RT \ln \left(\frac{vk m_p \Gamma_{C,4}}{m^\circ} \right) \right) + v(1-k) \\ & \times \left(\mu_D^{\text{ref}} + RT \ln \left(\frac{v(1-k) m_p \Gamma_{D,4}}{m^\circ} \right) \right). \end{aligned} \quad (140)$$

$\Gamma_{C,4}$ and $\Gamma_{D,4}$ are the activity coefficients (on molality scale) of species C and D , respectively, in state 4. But, as there is at this stage no difference between the natures of groups A , C , and D :

$$\Gamma_{C,4} = \Gamma_{D,4} = \Gamma_{A,4} \quad (141)$$

and

$$\mu_C^{\text{ref}} = \mu_D^{\text{ref}} = \mu_A^{\text{ref}}. \quad (142)$$

Consequently,

$$\mu_{p,4} = v \left(\mu_A^{\text{ref}} + RT \ln \left(\frac{vk^k (1-k)^{(1-k)} m_p \Gamma_{A,4}}{m^\circ} \right) \right). \quad (143)$$

The change of the chemical potential of the polyelectrolyte caused by the transition from step 3 to 4 is:

$$\Delta_{34} \mu_p = vRT \ln \left(k^k (1-k)^{(1-k)} \Gamma_{A,4} \right). \quad (144)$$

In the next step (Δ_{45}), the partial dissociation of species D is achieved (to account for the phenomenon of counterion condensation). The dissociation is expressed by a chemical reaction:



where CI and F stand for the counterion and for the dissociated monomer unit, respectively. The chemical potential of the polyelectrolyte in state 5 is (as only a single counterion dissociates from one monomer unit):

$$\mu_{p,5} = (kv + v_{D,5})\mu_{A,5} + v_{CI,5}\mu_{CI,5} + v_{CI,5}\mu_{F,5}. \quad (145)$$

For convenience, the total degree of dissociation of the repeating units α is introduced:

$$\alpha = \frac{v_{CI,5}}{v} \quad \text{where } 0 < \alpha < (1 - k). \quad (146)$$

As there is no difference between species C and D (all are designated by A): $\mu_{C,5} = \mu_{D,5} = \mu_{A,5}$:

$$\mu_{p,5} = v \cdot (\mu_{A,5} + \alpha(\mu_{CI,5} + \mu_{F,5} - \mu_{D,5})). \quad (147)$$

Because in dissociation equilibrium:

$$\mu_{CI,5} + \mu_{F,5} - \mu_{D,5} = 0 \quad (148)$$

the chemical potential of the polyelectrolyte in state 5 is:

$$\mu_{p,5} = v \left(\mu_A^{\text{ref}} + RT \ln \left(vk^k (1 - k - \alpha)^{(1-k)} \frac{m_p}{m^o} \Gamma_{A,5} \right) \right). \quad (149)$$

When furthermore (as another approximation), the difference between the activity coefficients of the undissociated repeating units in states 4 and 5 is neglected, the change of the chemical potential of the polyelectrolyte caused by the transition from 4 to 5 is:

$$\Delta_{45}\mu_p = v(1 - k)RT \ln \left(1 - \frac{\alpha}{1 - k} \right). \quad (150)$$

The fifth contribution to the chemical potential is to account for the repolymerization of the charged and noncharged monomers. This difference is approximated by reversing the change from state 2 to state 3, but applying a correction term $\Delta_{56}\mu_p^{\Delta_{\text{conf}}}$ that accounts for the difference in the conformation of the polymer chain

from a more globular structure in state 2 (where the polymer is neutral) to a more stretched structure in state 6 (where the polymer backbone is charged):

$$\Delta_{56}\mu_p = -\Delta_{23}\mu_p^{\text{fv+comb}} + \Delta_{56}\mu_p^{\Delta\text{conf}}. \quad (151)$$

It is assumed that the fraction of polyions in a stretched configuration equals the total degree of dissociation α of the repeating units. Furthermore, the difference between the chemical potentials of a polyion in its stretched and its globular structures is approximated using the combinatorial part of the UNIQUAC (universal quasichemical) model of Abrams and Prausnitz [117] for the excess Gibbs energy of nonelectrolyte solutions. In the UNIQUAC model, the shape of a molecule i is described by a volume parameter r_i and a surface parameter q_i . A change in the polyelectrolyte's conformation changes only its surface parameter resulting in:

$$\frac{\Delta_{56}\mu_p}{RT} = 5\alpha \left(\ln \left(\frac{(\Theta_{\text{st}})^{q_{\text{st}}}}{(\Theta_{\text{gl}})^{q_{\text{gl}}}} \Xi^{(q_{\text{gl}}-q_{\text{st}})} \right) + (1 - \Xi)(q_{\text{gl}} - q_{\text{st}}) \right). \quad (152)$$

q_{st} and q_{gl} are the polyelectrolyte's surface parameters in the stretched and the globular configuration, respectively. Similarly, Θ_{st} and Θ_{gl} are the polyelectrolyte's surface fractions in the stretched and the globular configuration, respectively, and Ξ is the volume fraction of the polyelectrolyte in the aqueous solution. The polyelectrolyte's surface fraction is:

$$\Theta_{ab} = \frac{\frac{m_p}{m^o} \cdot q_{ab}}{\frac{m_p}{m^o} \cdot q_{ab} + 55.5 \cdot q_w} \quad \text{for "ab" either "st" or "gl"}, \quad (153)$$

where q_w is the surface parameter of water. The surface parameter of the stretched polyion is calculated using the surface parameter q_{rp} of a repeating unit and the number v of repeating units which form that polyion:

$$q_{\text{st}} = vq_{\text{rp}}. \quad (154)$$

The surface parameter of the globular polyion is smaller than that of the stretched polyion. It is approximated by introducing a configurational parameter b^* (that is close to, but smaller than 0.5):

$$q_{\text{gl}} = v^{2b^*} q_{\text{rp}}. \quad (155)$$

The polyelectrolyte's volume fraction is:

$$\Xi = \frac{v \cdot \frac{m_p}{m^o} \cdot r_{\text{rp}}}{v \cdot \frac{m_p}{m^o} \cdot r_{\text{rp}} + 55.5 r_w}, \quad (156)$$

where r_{rp} and r_w are the volume parameters of a repeating unit of the polyion and of water, respectively.

Summing up the contributions from the five steps gives the chemical potential of the polyion in an aqueous solution. The chemical potential of the polyion on the molality scale is also given by:

$$\mu_p = \mu_p^{\text{ref}} + RT \ln \left(\frac{m_p}{m^\circ} \gamma_p^{(m)} \right) \quad (157)$$

and the activity coefficient is:

$$\begin{aligned} \ln \gamma_p^{(m)} = & v \ln \left(k^k (1 - k - \alpha)^{(1-k)} \Gamma_{A,5} \right) \\ & + 5\alpha \left(\ln \left(\frac{(\Theta_{\text{st}})^{q_{\text{st}}}}{(\Theta_{\text{gl}})^{q_{\text{gl}}}} \Xi^{(q_{\text{gl}} - q_{\text{st}})} \right) + (1 - \Xi)(q_{\text{gl}} - q_{\text{st}}) \right). \end{aligned} \quad (158)$$

The model requires pure-component surface (q_{rp} and q_w) and size (r_{rp} and r_w) parameters for the monomer unit and for water, the degree of counterion dissociation in infinite dilution (k), the total degree of dissociation of the repeating units (α), the configurational parameter (b^*), and interaction parameters (in the expressions for the activity coefficients in state 5 where the solution is a mixture of water, undissociated as well as dissociated repeating units and counterions).

Surface and size parameters are either available in the literature or are calculated following the proposals by Bondi [118]. The degree of counterion dissociation in infinite dilution is estimated from experimental data for the limiting osmotic coefficient of an aqueous solution of the polyion. Following the ideas outlined in the description of the Pessoa and Maurer model above, one finds when the repeating unit is a 1:1 electrolyte:

$$\Phi_p^{0,(m)} = \frac{1 + kv}{1 + v} \approx k. \quad (159)$$

The activity coefficients in state 5 ($\Gamma_{i,5}$, where i is any solute that is present in state 4, i.e., the neutral repeating unit A , the dissociated repeating unit F and the counterion CI) are calculated using the VERS model of Großmann et al. [112–114]. The activity coefficient Γ_i is assumed to consist of contributions from van der Waals-like interactions Γ_i^{vdW} and electrostatic interactions Γ_i^{el} :

$$\Gamma_i = \Gamma_i^{\text{vdW}} \Gamma_i^{\text{el}}. \quad (160)$$

The electrostatic contribution is expressed in a similar way as the long-range contribution in the model of Pessoa and Maurer [cf. (125)] from the Debye–Hückel parameter A_φ , the charge number z_i of groups/species i and the ionic strength I_m (on molality scale):

$$\ln \Gamma_i^{\text{el}} = -A_\varphi z_i^2 \frac{1}{2} \frac{1 - k}{\alpha v} \left(\frac{2}{1.2} \ln(1 + 1.2\sqrt{I_m}) + \frac{\sqrt{I_m}}{1 + 1.2\sqrt{I_m}} \right). \quad (161)$$

The ionic strength is:

$$I_m = \frac{1}{2} \sum_{k=CI,F} \frac{m_k}{m^\circ} z_k^2. \quad (162)$$

The contribution from short-range interactions to the activity coefficient of solute species (i.e., groups) i , Γ_i^{vdW} , is taken from the VERS model:

$$\begin{aligned} \ln \Gamma_i^{\text{vdW}} = & \frac{2}{M_w^*} \frac{q_i}{q_w} \sum_{\text{all groups } L} \frac{\Theta_L}{\Theta_w} \left(a_{i,L}^{(0)} + a_{i,L}^{(1)} \cdot f_1(I_m) \right) \\ & - \left(\frac{z_i}{M_w^*} \right)^2 f_2(I_m) \sum_{\text{all groups } L} \sum_{\text{all groups } k} \frac{\Theta_L}{\Theta_w} \frac{\Theta_k}{\Theta_w} a_{L,K}^{(1)} \\ & + \frac{3}{(M_w^*)^2} \frac{q_i}{q_w} \sum_{\text{all groups } L} \sum_{\text{all groups } k} \frac{\Theta_L}{\Theta_w} \frac{\Theta_k}{\Theta_w} b_{i,L,K} \end{aligned} \quad (163)$$

with:

$$f_1(I_m) = \frac{1}{2I_m} \left[1 - (1 + 2\sqrt{I_m}) \exp\{-2\sqrt{I_m}\} \right] \quad \text{and} \quad (164)$$

$$f_2(I_m) = \frac{1}{4I_m^2} \left[1 - (1 + 2\sqrt{I_m} + 2I_m) \exp\{-2\sqrt{I_m}\} \right] \quad (165)$$

The sum in (163) is over all solute species, i.e., nondissociated repeating units C , nondissociated repeating units D , dissociated repeating units F and counterions CI . M_w^* is the relative molar mass of water divided by 1,000 ($M_w^* = 0.018016$). Subscript w stands for water and q_i is the surface parameter of species i . The surface fraction of a group L is abbreviated by Θ_L . As the mixture consists of species C , D , F , CI and water, the following relative surface ratios are required:

$$\frac{\Theta_C}{\Theta_w} = M_w^* v k \frac{m_p q_{\text{TP}}}{m^\circ q_w}, \quad (166)$$

$$\frac{\Theta_D}{\Theta_w} = M_w^* v (1 - k - \alpha) \frac{m_p q_{\text{TP}}}{m^\circ q_w}, \quad (167)$$

$$\frac{\Theta_F}{\Theta_w} = M_w^* v \alpha \frac{m_p q_{\text{TP}}}{m^\circ q_w}, \quad (168)$$

$$\frac{\Theta_{CI}}{\Theta_w} = M_w^* v \alpha \frac{m_p q_{CI}}{m^\circ q_w}. \quad (169)$$

$a_{i,L}^{(0)}$ and $a_{i,L}^{(1)}$ denote binary interaction parameters between species (groups) i and L . These interaction parameters are symmetric, i.e., $a_{i,L}^{(0)} = a_{L,i}^{(0)}$ and $a_{i,L}^{(1)} = a_{L,i}^{(1)}$. They form a set of adjustable model parameters. The degree of dissociation α is calculated assuming chemical equilibrium between monomers D and its dissociation products F and CI in state 5:

$$K = \frac{m_{CI}m_F}{m_D m^\circ} \frac{\Gamma_{CI}\Gamma_F}{\Gamma_D} = \frac{v\alpha^2}{1-k-\alpha} \frac{m_p}{m^\circ} \frac{\Gamma_{CI}^{\text{vdW}}\Gamma_F^{\text{vdW}}}{\Gamma_D^{\text{vdW}}} \Gamma_{CI}^{\text{el}}\Gamma_F^{\text{el}}, \quad (170)$$

where all molalities are those in state 5. Chemical reaction equilibrium constant K is one of the adjustable parameters of the model.

When there is also an additional single 1:1 salt MX in the aqueous solution, (162) (for the ionic strength) and (163) (for the van der Waals contribution to the group activity coefficient) have to be extended; the sums must also include the ions M and X . The extension requires the relative surface ratios for M and X :

$$\frac{\Theta_M}{\Theta_w} = M_w^* \frac{m_{MX}q_M}{m^\circ q_w}, \quad (171)$$

$$\frac{\Theta_X}{\Theta_w} = M_w^* \frac{m_{MX}q_X}{m^\circ q_w}. \quad (172)$$

Furthermore, as well as the chemical potential of the polyelectrolyte, the chemical potential of MX is also required (for the calculation of the activity of water, see below). That chemical potential is given by the sum of the chemical potentials of cations M and anions X :

$$\mu_{MX} = \mu_M + \mu_X = \mu_M^{\text{ref}} + \mu_X^{\text{ref}} + RT \ln \left(\frac{m_M \Gamma_M}{m^\circ} \frac{m_X \Gamma_X}{m^\circ} \right). \quad (173)$$

Finally, the activity of water a_w is calculated from the chemical potentials of the solutes (either a single polyelectrolyte or a binary solute mixture of a polyelectrolyte and a low molecular weight salt) by applying the Gibbs–Duhem equation:

$$d\mu_w = d(\mu_w - \mu_w^{\text{pure liquid}}) = -M_w^* \sum_{i \neq w} \frac{m_i}{m^\circ} \cdot d\mu_i. \quad (174)$$

Integration at constant temperature for an aqueous solution containing a polyelectrolyte P and a salt MX results in:

$$\Delta\mu_w = RT \ln a_w = -M_w^* \int_{\text{water}}^{\text{mix}} \frac{m_p}{m^\circ} d\mu_p - M_w^* \int_{\text{water}}^{\text{mix}} \frac{m_{MX}}{m^\circ} \cdot d\mu_{MX}. \quad (175)$$

The right-hand side is solved in two steps. In the first step, the integration is carried out starting from pure water to a polyelectrolyte-free but salt-containing solution:

$$\frac{\Delta\mu_{w,1}}{2RTM_w^*} = -\frac{m_{MX}}{m^o} + A_\varphi \frac{I_{m,MX}^{1.5}}{1 + 1.2\sqrt{I_{m,MX}}} - \left(\frac{m_{MX}}{m^o}\right)^2 \left[a_{MX}^{(0)} + a_{MX}^{(1)} \exp(-2\sqrt{I_{m,MX}}) \right], \quad (176)$$

where $a_{MX}^{(0)}$ and $a_{MX}^{(1)}$ are binary interaction parameters between ions M and X^- and $I_{m,MX}$ is the ionic strength (on molality scale) of the polyelectrolyte-free aqueous solution of MX .

In the second step, the molality of the salt is fixed at m_{MX} and the molality of the polyelectrolyte increases from zero to m_p :

$$\Delta\mu_{w,2} = -M_w^* \left[\int_{m_p=0}^{m_p} m_p \frac{\partial\mu_p}{\partial m_p} d\left(\frac{m_p}{m^o}\right) \right]_{m_{MX}} - M_w^* \frac{m_{MX}}{m^o} [\mu_{MX}(m_{MX}, m_p) - \mu_{MX}(m_{MX}, m_p = 0)], \quad (177)$$

where

$$\left[\int_{m_p=0}^{m_p} m_p \frac{\partial\mu_p}{\partial m_p} d\left(\frac{m_p}{m^o}\right) \right]_{m_{MX}} = RT \left[\frac{m_p}{m^o} + \int_{m_p=0}^{m_p} m_p \left(\frac{\partial \ln \gamma_p^{(m)}}{\partial m_p} \right)_{m_{MX}} d\left(\frac{m_p}{m^o}\right) \right]. \quad (178)$$

The integral is solved numerically using (158) for the activity coefficient of the polyelectrolyte.

The final equation for the activity of water in an aqueous solution of a strong electrolyte MX and a polyelectrolyte P (where both MX and the repeating unit of the polyion are 1:1 electrolytes) is:

$$\begin{aligned} \frac{1}{M_w^*} \ln a_w = & -2 \frac{m_{MX}}{m^o} - \frac{m_p}{m^o} + 2 \cdot A_\varphi \frac{I_{m,MX}^{1.5}}{1 + 1.2\sqrt{I_{m,MX}}} \\ & - 2 \left(\frac{m_{MX}}{m^o}\right)^2 \left[a_{MX}^{(0)} + a_{MX}^{(1)} \exp(-2\sqrt{I_{m,MX}}) \right] \\ & - \frac{m_{MX}}{m^o RT} [\mu_{MX}(m_{MX}, m_p) - \mu_{MX}(m_{MX}, m_p = 0)] \\ & - \left[\int_{m_p=0}^{m_p} m_p \left(\frac{\partial \ln \gamma_p^{(m)}}{\partial m_p} \right)_{m_{MX}} d\left(\frac{m_p}{m^o}\right) \right]. \end{aligned} \quad (179)$$

It is worth mentioning that the chemical potential $\mu_{MX}(m_{MX}, m_p)$ is calculated from (173) where the activity coefficients of both ions M and X are calculated for an aqueous solution in which the polyelectrolyte is cut into its repeating units and the species [nondissociated repeating units (D), counterions (CI), and dissociated repeating units (F)] are in chemical reaction equilibrium.

For the example treated here (an aqueous solution of a strong electrolyte MX and a polyelectrolyte P where the salt and the repeating unit of the polyion are 1:1 electrolytes) the activity of water in an ideal solution is:

$$\frac{1}{M_W^*} \ln a_{w, id. mix}^{(m)} = -2 \cdot \frac{m_{MX}}{m^o} - (1 + \nu) \cdot \frac{m_p}{m^o} \quad (180)$$

The following parameters must be known when the activity of water (or the osmotic coefficient) of an aqueous solution of a single polyelectrolyte is to be calculated:

The number of monomer units ν is estimated from the number-averaged molecular mass of the polymer and the molecular mass of a repeating unit.

- UNIQUAC surface (q_k) and volume (r_k) parameters of water and the nondissociated repeating units are calculated by the method of Bondi [118]. No distinction is made between those parameters for the dissociated and nondissociated repeating units. The surface parameter of water ($q_w = 1.4$) is also assigned to all counterions.
- The degree of counterion condensation k at infinite dilution in water is determined from experimental data for the osmotic coefficient at infinite dilution (as for $\nu \gg 1$) $\Phi_p^{0, (m)} = 1 - k$.
- The chemical reaction (dissociation) constant K is one of the adjustable parameters of the model. It is assumed that, at constant temperature, K is a constant for a certain repeating unit.
- Parameter b^* that is used to describe the configurational change from a globular to a stretched conformation of the polyelectrolyte is also an adjustable model parameter.
- Binary parameters ($a_{ij}^{(0)}$ and $a_{ij}^{(1)}$) are used for interactions between all solute species in water. As these parameters are symmetric and as there are three solute species, there are 12 such parameters. However, all parameters $a_{ij}^{(1)}$ are neglected, ($a_{ij}^{(1)} = 0$) and all parameters $a_{ij}^{(0)}$ for interactions with the counterion are also neglected ($a_{i, CI}^{(0)} = 0$ for all solutes i). The parameter for interactions between dissociated repeating units is also neglected ($a_{F, F}^{(0)} = 0$). With these assumption, there are only two parameters: one for interactions between nondissociated repeating units (C or A) and one for interactions between these nondissociated monomers and the dissociated repeating units. The distinction between these binary parameters is also neglected, resulting in a single, adjustable binary interaction parameter that characterizes the polyelectrolyte's repeating unit A : $a_{A, A}^{(0)} = a_{A, F}^{(0)} = a_{p, p}$

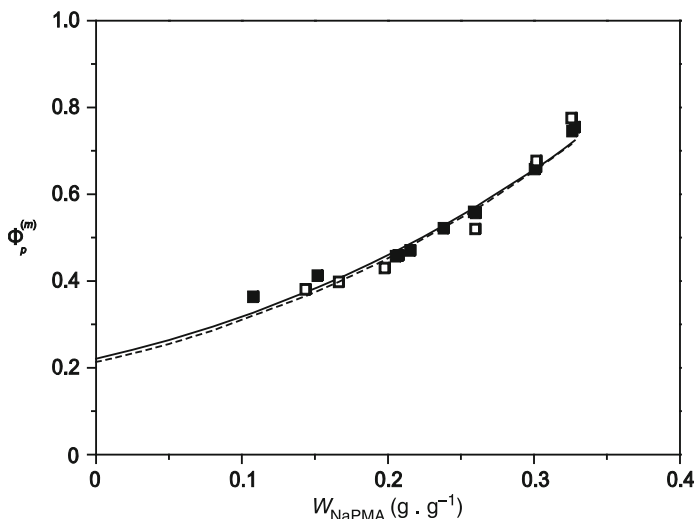


Fig. 15 Osmotic coefficient of aqueous solutions of poly(sodium methacrylate) at 298.2 K with two different molecular masses. Experimental results: *closed squares* NaPMA 6; *open squares* NaPMA 15. Correlation results: *solid line* NaPMA 6; *dashed line* NaPMA 15 [116]

Figure 15 shows a typical example for correlation of experimental results for the osmotic coefficient (on molality scale) of aqueous solutions of poly(sodium methacrylate).

For the calculation of the thermodynamic properties of an aqueous solution of a single polyion that additionally contains a low molecular weight strong electrolyte, some more model parameters are required. The volume and surface parameters of the ions of the strong electrolyte are also approximated by the parameters of water. Therefore, for an aqueous solution of the single salt the model does not differ from Pitzer's model, and for a large number of salts the binary interaction parameters $a_{MX}^{(0)}$ and $a_{MX}^{(1)}$ are available in the literature. All further interaction parameters (i.e., between cations and anions of the salt on one side and groups and counterions from the polyion on the other side) are also set to zero, with the exception of a single parameter. That parameter accounts for interactions between that ion of MX that carries an electrical charge of the opposite sign as the counterion of the polyion on one side, and the neutral group of the polyelectrolyte (i.e., A or C) on the other side. For example, if NaCl is added to an aqueous solution of poly(sodium methacrylate), the only additional interaction parameter is $a_{A,\text{Cl}}^{(0)} (=a_{p,\text{Cl}})$. Because the configuration of the polyion in the aqueous salt-containing solution might differ from that in the salt-free solution, it might be advantageous to consider the influence of the low molecular weight salt on the polyion's configuration parameter b^* . An empirical relation such as:

$$b^* = \varpi^{(0)} + \varpi^{(1)} \frac{m_{MX}}{m^o}, \quad (181)$$

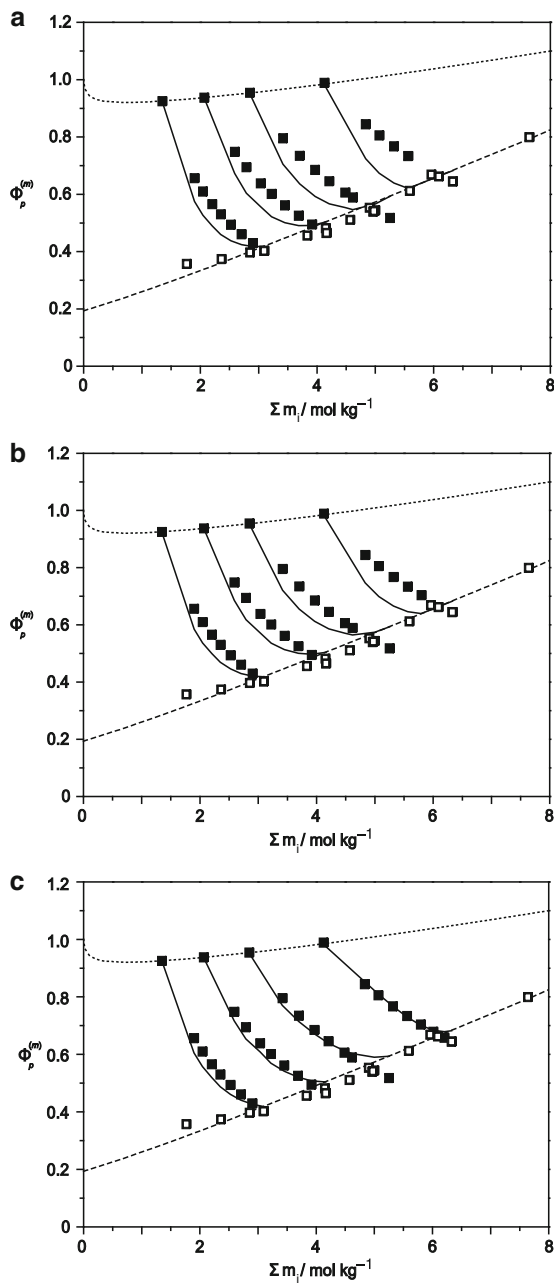


Fig. 16 Osmotic coefficient of aqueous solutions of NaPA 15 and NaCl at 298.2 K. Experimental results are shown with *symbols*. (a) Prediction results. (b) Correlation results setting $\varpi^{(1)} = 0$. (c) correlation results setting $\varpi^{(1)} \neq 0$. *Dashed lines* corresponds to systems without salt; *dotted lines* systems without polyelectrolyte; *solid lines* lines of constant water activity [116]

where $\varpi^{(0)}$ is the configurational parameter for the polyion when it is dissolved in pure water and $\varpi^{(1)}$ is an adjustable parameter, proved to be sufficient to describe that influence.

Predictions from the model for the osmotic coefficient can be made when the binary parameter between nondissociated repeating units and the counterion of the low molecular weight salt, as well as the influence of that salt on the configurational parameter b^* are neglected. Figure 16 shows comparisons between experimental data and calculation results for the osmotic coefficient for aqueous solutions of a sodium poly(acrylate) (NaPA 15) and NaCl. The osmotic coefficient (on molality scale) is plotted versus the “overall solute molality” $\sum \bar{m}_i$ that is defined as:

$$\sum \bar{m}_i = 2m_{MX} + (1 + \nu)m_p. \quad (182)$$

The experimental results for the mixed solute systems are shown for a constant activity of water. The results extend from the polyelectrolyte (i.e., salt-free) system to the (NaCl + water) system. The top diagram of Fig. 16 shows the comparison with prediction results, i.e., the calculations were performed setting $a_{p,Cl} = 0$ and $\varpi^{(1)} = 0$. The middle diagram of Fig. 16 shows the comparison with correlation results when the influence of NaCl on the configurational parameter b^* is neglected (i.e., adjusting only $a_{p,Cl}$). The bottom diagram of Fig. 16 shows that the best agreement is achieved by adjusting both parameters. With those parameter an essential improvement is achieved, in particular at high concentrations (i.e., at low water activities). Figure 17 shows a comparison between the correlation results

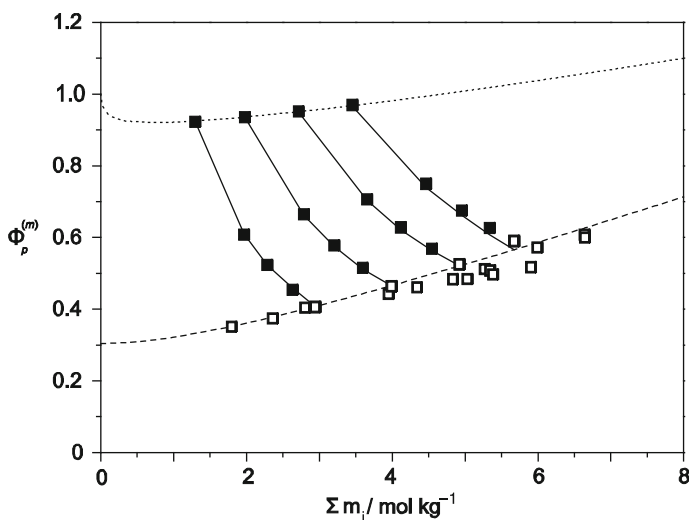


Fig. 17 Osmotic coefficient of aqueous solutions of $\text{NH}_4\text{PA 10}$ and NaCl at 298.2K. Experimental results are shown with *symbols*. *Dashed line* correlation results for system without salt; *dotted line* correlation results for system without polyelectrolyte; *solid lines* lines of constant water activity [116]

and the experimental data for the osmotic coefficient of aqueous solutions of ammonium poly(acrylate) ($\text{NH}_4\text{PA 10}$) and NaCl . For this particular system it was not necessary to consider an influence of NaCl on the configurational parameter. The comparisons reveal that the model is well suited for the correlation of the vapor–liquid equilibrium of aqueous solutions of polyelectrolytes with and without an added low molecular weight salt.

6 Summary

A literature review is given on the liquid–vapor phase equilibrium of aqueous solutions of polyelectrolytes. Experimental findings as well as selected thermodynamic models for the prediction and correlation of such phase equilibria are reviewed. The treatment of the thermodynamic models starts with theories and later focuses on combining the results from such theories with engineering models for the excess Gibbs energy. Such combinations allow for a good correlation of experimental data, for example, the osmotic coefficient (and related properties) of aqueous solutions of a single polyelectrolyte with and without an added salt.

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