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Solubility of highly charged anionic polyelectrolytes in presence of multivalent cations: Specific interaction effect

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Abstract. Studies performed on strong polyelectrolytes and on a weak polyelectrolyte, sodium poly(acrylate), show that their stability in presence of multivalent cations depends on the chemical nature of the charged side groups of the polymer. For sulfonate groups (SO_3^-) or sulfate groups (OSO_3^-) phase separation generally occurs in presence of inorganic cations of valency 3 (as La³⁺) or larger and a resolubilization takes place at high salt concentration. The interactions of the polyelectrolyte with multivalent cations are of electrostatic origin and the phase diagrams are weakly dependent on the chemical nature of the polymer backbone and on the specificity of the counterions. For acrylate groups, (COO⁻), the phase separation was observed with inorganic cations of valency 2 (as Ca²⁺) or larger without resolubilization at high salt concentration. The phase separation is due to a chemical association between cations and acrylate groups of two neighboring monomers of the same chain. This chemical association creates a hydrophobic complex by dehydrating both monomer and cation. With organic trivalent cation, as spermidine ⁺H₃N(CH₂)₄NH⁺₂(CH₂)₃NH⁺₃, where no chemical association occurs with the charged side groups COO⁻ or SO⁻₃ of the polyelectrolyte, similar phase diagrams were observed whatever was the polyelectrolyte with a resolubilization at high trivalent cation concentration.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.20.Qg Structure of associated liquids: electrolytes, molten salts, etc. – 83.70.Hq Heterogeneous liquids: suspensions, dispersions, emulsions, pastes, slurries, foams, block copolymers, etc.

1 Introduction

Anionic polyelectrolytes possess ionizable groups, which dissociate in aqueous media to give negatively charged polymer chains and positively charged counterions. The repulsion between charged monomers tends to expand the polymer chain. The high charge density on the polymer backbone produces a high electrostatic potential around it and a fraction of counterions are consequently located in the immediate vicinity of the polymer chain leading to a phase separation at low salt concentration, if counterions are multivalent. This precipitation of polyelectrolytes by multivalent salt, usually called "salting out", has been studied for long time by several authors [1–13], but still remains poorly understood. The stability of the polyelectrolyte solution depends on the counterion valency and the characteristics of the polymer: nature of backbone (hydrophobic, hydrophilic, rigid, flexible), distance between charged groups, and nature of charged groups (carboxylate, sulfonate, sulfate, phosphate). Two types of phase diagram have been observed [2] namely the H-precipitation type (high critical salt concentration) and the L-precipitation type (low critical salt concentration). The H-precipitation occurs at high salt concentration threshold and weakly depends on the polymer concentration. The L-precipitation type appears at low multivalent salt concentrations, and the salt concentration needed for phase separation is proportional to polyelectrolyte concentration.

The present study addresses the nature of the specific interactions between highly charged polyelectrolytes and counterions, especially for L-type diagrams. Phase diagrams of different highly charged polyelectrolytes, in presence of different multivalent cations, were established. Two general mechanisms of precipitation were found, which depend on the nature of the charged groups and of the counterions. In the case of sodium polyacrylate, our interest was focused on calcium ion, for its broad range of applications, and on the cobalt ion which offers the advantage that its interaction with polyelectrolytes can be studied by absorption spectrometry.

More specifically, in Section 2 (theoretical consideration) the point on electrostatic condensation and chemical association are made. In this section we also recall the electrostatic model [9], introduced to describe solubility

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of the sodium polystyrene sulfonate in presence of z-valent counterions, and we generalize this model when chemical association between counterions and charged groups of the polyelectrolyte can occur. In Section 3, experimental conditions are given. Section 4 is devoted to the presentation of different types of phase diagram obtained for a large variety of polyelectrolytes and of counterions. At the end of this section it appears that two types of mechanism are responsible of the precipitation: one is purely electrostatic and the other one is intimately related to a chemical association. In Section 5, entitled complexation between polyelectrolytes and multivalent counterions, we relate experiments, which allow us to determine the quantities and the types of complexes formed when chemical association occurs before phase separation. The understanding of the specific interactions between polyelectrolytes and counterions allows us to give a criterion to distinguish when electrostatic attraction or chemical association induces the precipitation. In Section 6, the phase diagram of sodium poly(acrylate) in presence of calcium chloride is described using a mean field approach presented in Section 2.

2 Theoretical considerations

For polyelectrolyte with a sufficiently high charge density along the backbone, some of counterions remain in the vicinity of the polymeric chain. This phenomenon, known as counterion condensation, was introduced for long time [14–18]. For monovalent counterions and charged monomers (-1), counterion condensation occurs when the mean distance between two charged monomers, b, along the chain backbone is smaller than the Bjerrum length $l_{\rm B} = e^2/4\pi\varepsilon\varepsilon_0 kT$ (= 7.2 Å in water). This length defines the distance at which electrostatic interaction between two elementary charges is equal to the thermal energy kT. Let us consider an anionic polyelectrolyte having counterions of valency z. If the distance b is larger than $l_{\rm B}z$, the effective charge per monomer, z_{eff} , remains constant (-1). If b is lower than $l_{\rm B}z$, ion condensation occurs and the effective charge is reduced to $(-1)b/zl_{\rm B}$. When a salt with a z-valent cation (concentration $C_{\rm S}$) is progressively added to a solution of anionic polyelectrolyte having monovalent counterions (monomer concentration C), condensation of z-valent counterions takes place and monovalent counterions are released. Three different domains of condensation can qualitatively be defined:

$$C_{\rm S} < C(1 - b/l_{\rm B})/z,$$

 $f' = 1 - b/l_{\rm B} - zC_{\rm S}/C \text{ and } f = C_{\rm S}/C;$
 $C(1 - b/l_{\rm B})/z \le C_{\rm S} \le C(1 - b/zl_{\rm B})/z,$
 $f' = 0 \text{ and } f = C_{\rm S}/C;$

$$C_{\rm S} > C(1 - b/zl_{\rm B})/z,$$

 $f' = 0 \text{ and } f = (1 - b/zl_{\rm B})/z;$ (1)

where f' and f are the fractions of monomer carrying monovalent and z-valent condensed counterion, respectively. This description is only qualitative and a more quantitative way to evaluate the electrostatic condensation is obtained with the Poisson-Boltzmann models [19–23].

Up to now, chemical association between counterions and charged groups of polyelectrolyte was assumed to be absent. Charge regulation model [24,25] allows chemically associated counterions and electrostatically condensed counterions to be distinguished. The computation of the fraction of counterions chemically associated with charged groups of the polyelectrolyte is performed using a mass action law that depends on the concentration $[A^-]$ of charged monomer and on the local counterion concentration $[M^{z+}]_{\rm L}$ in the immediate vicinity of the charged cylinder representing the polyelectrolyte:

$$[M^{z+}A^{-}] = K_1[A^{-}][M^{z+}]_{\rm L}$$

and $[M^{z+}]_{\rm L} = [M^{z+}]_{\rm bulk} \exp(-ze\Psi_{\rm local}/kT).$ (2)

 K_1 is the first association constant (monocomplexation) between monomers and counterions and Ψ_{local} is the local electrostatic potential of the polyelectrolyte. The quantity $[M^{z+}]_{\text{bulk}}$ is the bulk concentration. The local concentration is determined by solving the Poisson Boltzmann equations. This method was largely used for planar surfaces [24,25]. Now having introduced the different associations between polyelectrolytes and counterions, we are interested in the limit of stability of polyelectrolyte solutions.

To describe solubility of the sodium polystyrene sulfonate in presence of z-valent counterions [8] the electrostatic model [9] was introduced. This model takes into account a short-range electrostatic attraction between negatively charged monomers (-1) and those carrying condensed multivalent counterions which are positively charged (z-1). The following spinodal equation has been obtained:

$$\frac{1}{NC} + \frac{\sigma^3}{1 - \varphi} + \frac{z_{\text{eff}}^2}{2I} - 2(1 - f - f')f |V_{1Z}| = 0.$$
(3)

N is the degree of polymerization of the polymer, C is the number of monomers per unit volume, σ^3 represents the volume of the monomer and $\varphi = C\sigma^3$ is the volume fraction occupied by the polymer. The first term comes from the entropy of polymer and the second one represents the steric excluded volume. The third term corresponds to the electrostatic repulsion between monomers carrying an effective charge $z_{\text{eff}} = zf + f' - 1$, where f and f' are the fractions of monomer with a z-valent and monovalent condensed counterions, respectively. I represents the ionic strength of free ions. The last term arises from an attraction between the negatively charged monomers (-1)and those possessing an effective positive charge of valency (z-1), due to the electrostatic condensation. The local attraction V_{1Z} depends on the valency of the counterion and has the following form [9]:

$$V_{1Z} = -\frac{\pi (z-1)^2 l_{\rm B}^2}{\sqrt{8\pi l_{\rm B} I}} B \tag{4}$$

where B is a numerical factor of the order of 1. When the ionic strength is high enough, the electrostatic attractions are completely screened. For a given monomer concentration, the spinodal equation gives two solutions corresponding to the precipitation and the resolubilization limits as the salt concentration increases. The salt concentration at the resolubilization limit is independent of the polymer concentration for a high degree of polymerization, and increases with the valency z of counterion [9].

The spinodal equation (3) was derived from the divergence of the monomer-monomer scattering function at zero wave vector using a RPA or PRISM approach. As spinodal equations obtained in the context of RPA can be derived using Flory mean field approach [12], this more simple approach is used here to describe the stability of sodium polyacrylate in presence of divalent chloride salt, $M^{++}Cl_2^-$, where chemical association between charged monomers, A^- , and divalent counterions, M^{++} , are taken into account. The free energy per site can be written as:

$$F/kT = (\varphi/N)\log\varphi + (1-\varphi)\log(1-\varphi) + \varphi_{\rm M}\log\varphi_{\rm M} + \varphi_{\rm Cl}\log\varphi_{\rm Cl} + \varphi_{\rm Na}\log\varphi_{\rm Na} + \chi_{\rm d}f_{\rm d}\varphi(1-\varphi) + \chi_{\rm ele}(f_{\rm m}+f)(1-f'-f-f_{\rm m}-f_{\rm d})\varphi^2.$$
(5)

 $\varphi_{\rm Na}, \varphi_{\rm Cl}, \varphi_{\rm M}$ and φ are the volume fractions of free ions and charged monomers, respectively. The parameter $f_{\rm m}$ represents the monomer fraction chemically associated with one divalent counterion (monocomplexation A^-M^{++}), f_d is the monomer fraction with a dicomplex $(AM_{1/2})$, f is the monomer fraction carrying an electrostatically condensed counterion M^{++} and f' is the monomer fraction carrying an electrostatically condensed sodium ion Na⁺. The first five terms correspond to polymer, solvent and free ion entropies, respectively. The parameter χ_d is related to the interactions between the dicomplexes $(AM_{1/2})$ and water molecules. To obtain expression (5) water is assumed to be a good solvent $(\chi = 0)$ for charged entities: monomers and monocomplexes. The last term corresponds to the electrostatic attraction between bare monomers (A^{-}) and those carrying a divalent condensed counterion or a monocomplex $(A^{-}M^{++})$; the parameter χ_{ele} is equal to $V_{12}/\sigma^3 < 0$ (see Eq. (4)).

The number of entities in this mixture is high but, the electroneutrality condition

$$2\varphi_{\rm M} + \varphi_{\rm Na} = \varphi_{\rm Cl} + \varphi(1 - f' - 2f - 2f_{\rm m} - f_{\rm d}), \quad (6)$$

and the knowledge of the fractions f_i reduce the number of independent variables needed to describe the system to 3. The spinodal equation is found by considering [12]:

$$\det \left| \left| \frac{\partial^2 F}{\partial \varphi_i \partial \varphi_j} \right| \right| = 0.$$
(7)

The determinant $(3 \times 3 \text{ terms})$ can be written as:

$$\frac{1}{N\varphi} + \frac{1}{1-\varphi} + \frac{(1-f'-2f-2f_{\rm m}-f_{\rm d})^2}{4\varphi_{\rm M}+\varphi_{\rm Na}+\varphi_{\rm Cl}} + 2\chi_{\rm ele} \times (f_{\rm m}+f)(1-f'-f-f_{\rm m}-f_{\rm d}) - 2\chi_{\rm d}f_{\rm d} = 0.$$
(8)

By taking $\varphi = C\sigma^3$, we recover the spinodal expression of the electrostatic model (Eq. (3)) with a supplementary term due to the dicomplexation:

$$\frac{1}{NC} + \frac{\sigma^3}{1 - \varphi} + \frac{z_{\text{eff}}^2}{2I} - 2(1 - f' - f - f_{\text{m}} - f_{\text{d}}) \times (f_{\text{m}} + f) |V_{12}| - 2\sigma^3 \chi_{\text{d}} f_{\text{d}} = 0.$$
(9)

The term $z_{\text{eff}}^2/2I$, with $z_{\text{eff}} = (f'+2f+2f_{\text{m}}+f_{\text{d}}-1)$, arises from the entropy of the free ions [12] and represents the screened repulsive electrostatic interactions between negatively charged monomers, having an effective charge z_{eff} , and it is basically responsible of polyelectrolyte stability. It is important to point out that this model of mean field Flory type is only well adapted to describe concentrated polymer solutions [26].

3 Materials and methods

With the exception of one sample, the sodium dextran sulfate, all the polymers used had the same backbone but different ionic groups X: $(-CH_2-CHX_{-})_N$. Poly(acrylic acid) samples (PAA: $X = COO^{-}, H^{+}$) were purchased from Sigma Aldrich with nominal molecular weights: 2×10^3 (PAA1), 4.5×10^5 (PAA2) and 4×10^6 (PAA3) g/mole. Sodium polyacrylate fully or partially charged were obtained by adding sodium hydroxide to poly(acrylic acid) stock solutions. Electrochemical techniques show that the PAA1 and PAA2 have a carboxylation degree about 77% and 100%, respectively. Sodium poly(vinyl sulfonate) (NaPVS: $X = SO_3^-$, Na⁺) was purchased from Sigma Aldrich. All these polymers were polydisperse (≈ 2 , see Tab. 1) and two of them were fractionated by ultrafiltration through a 5 KDalton membrane. PAA1F and NaPVSF samples, with a polydispersity close to 1.3, were obtained from the fractionation of the samples PAA1 (acidic form) and NaPVS, respectively. Potassium poly(vinyl sulfate) (KPVS: $X = SO_4^-, K^+$) was purchased from Sigma Aldrich with a molecular weight close to 3×10^5 g/mole. Sodium Dextran sulfate (NaDS) was supplied by Pharmacia, with a nominal molecular weight of 5×10^5 g/mole. This polyelectrolyte, with a polysaccharidic backbone, contained 17% of sulfur corresponding to 2.3 sulfate groups per glucosyle group.

The polyelectrolytes used were characterized by aqueous gel permeation chromatography and light scattering (see Tab. 1). The polyelectrolyte and salt solutions were prepared using de-ionized water which had been passed through a MilliQ Millipore system of pore size 0.22 μ m (resistivity of 18 M Ω cm). For the different mixtures with the polyelectrolytes, the electrolytes used were: CaCl₂, MgCl₂, BaCl₂, CdCl₂, MnCl₂, CoCl₂, NiCl₂, CuCl₂, LaCl₃, and trivalent spermidine (+H₃N(CH₂)₄NH₂⁺(CH₂)₃NH₃⁺, 3Cl⁻) which is totally charged at pH 7 (pK \approx 10). The pH of the solutions was adjusted in such way that the concentration of the hydrolyzed multivalent ions was negligible [27].

The cloud points, which correspond to the beginning of the demixion, were determined by visual inspection

Table 1. Characteristics of the polymers.

	Steric exclusion	Light scattering			
Sample	Exp. Cond.	$M_{\rm w}/M_{\rm n}$	$M_{\rm W}$ (g/mole)	Solvent	$M_{\rm W}~({\rm g/mole})$
PAA1	$0.1 \mathrm{M}, \mathrm{PEG}$	≈ 2	—	$\rm HCl~0.1~M$	2.8×10^3
PAA1F	$0.1 \mathrm{M}, \mathrm{PEG}$	1.4	_	$\rm HCl~0.1~M$	5.1×10^3
PAA2	0.5 M, SALS	2	$5.8 imes 10^5$	Dioxane	6×10^5
NaPVS	_	_	_	NaCl 1 M	2.5×10^3
NaPVSF	$0.1 \mathrm{M}, \mathrm{PEG}$	≈ 1.3	_	NaCl 1 M	5.1×10^3
KPVS	$0.1 \mathrm{M}, \mathrm{SALS}$	1.6	4.3×10^5	NaCl 1 M	4.1×10^5
NaDS	$0.1 \mathrm{M}, \mathrm{SALS}$	1.6	1.0×10^6	NaCl $0.2~{\rm M}$	1.3×10^6

In Steric Exclusion Chromatography measurements the eluent was aqueous solution of $LiNO_3$ except for the NaDS where $LiNO_3$ was replaced by $NaNO_3$. In the experimental conditions (Exp. Cond.) is given the salinity of the eluent and the manner to determine the characteristics of the samples: PEG the columns were calibrated with polyethylene glycol standards and SALS a small angle light scattering detector was on line. Light scattering measurements where performed with a goniometer and the solvent used was water in presence of an electrolyte or dioxane.

of the solutions (at room temperature). In the NaPA2/CaCl₂ mixtures, the cloud point was also determined from the abrupt increase of the absorption, at 400 nm, as a function of the concentration of calcium chloride added. Phase separations were always reversible and the demixion limits were estimated to be determined with a precision of the order of 10%.

The compositions of the precipitate and of the supernatant of few biphasique NaPA2/CaCl₂ mixtures were determined after centrifugation. The monomer concentrations in the two phases were obtained by Total Organic Carbon measurements (Dohrmann DC 80 or DC180). Concentrations of calcium, lanthanum and sodium ions were measured by atomic absorption spectroscopy.

The activity of the calcium ions in presence of sodium poly(acrylate) was measured with an ion-sensitive electrode (Orion 93-20). In first approximation, this gave a measure of the concentration of the free calcium ions in solution. Conductivity measurements were performed with a conductometer Taccussel CD 810, that had a large sensitivity ranging from 10^{-9} to 1 S/cm, and was used to determine the association constants.

To determine the absorbance of metal ions, a spectrophotometer UV/VIS Perkin Elmer Lambda 900 was used. The measurements, over a spectral domain ranging from 200 to 800 nm, were performed using 1 cm quartz cell and a reference cell containing pure water. This technique was well suited to quantify the association of carboxylate groups with cobalt ions but was inappropriate for calcium ions.

Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) experiments were run on D21 spectrometer at LURE (Orsay) with a fluorescence set-up. EXAFS provides information on the local environment of a metal [28]. It consisted in scanning the incident X-ray radiation energies in order to observe the oscillating absorption beyond a photoionization edge of the metal. The present experimental set up was well adapted to perform EXAFS measurements near the K edge of the cobalt (7710 eV).

4 Phase diagrams

4.1 Phase diagrams of polyelectrolytes in presence of multivalent counterions without chemical association: general behavior

To explain the phase diagrams of sodium poly(styrene sulfonate) NaPSS in the presence of z-valent counterions [8] the electrostatic model, presented in the precedent section (see Eq. (3)), was used [9]. With the electrostatic model, the nature of polymer-backbone, of the charged groups and of the counterions is not taken into account. In order to find when this approach is valid different polyelectrolytes/counterions mixtures were investigated and their phase diagrams are reported in this section. At first, NaPSS was replaced by sodium poly(vinyl sulfonate) (NaPVS), which possesses the same charged group and practically the same charge density as NaPSS $(b/l_{\rm B} = 0.36)$. The NaPVS remains soluble in presence of divalent counterions (Ca, Mg, Co, Cu, Ni, Mn, Cd) except with barium. As in the case of NaPSS [4,6], only barium induces a precipitation. This point will be discussed later in Section 4.2.2. Despite the fact that NaPVS and NaPSS backbones are different, their behaviors in presence of $LaCl_3$ (pH = 3) remain very similar (Fig. 1). The demixion therefore seems to be mainly controlled by electrostatic attractions and not by the nature of the backbone.

In order to see if the nature of charged groups is a pertinent parameter, the sulfonate groups (SO_3^-) of the NaPVS were replaced by sulfate groups (OSO_3^-) by using the KPVS. The KPVS was studied with the same multivalent counterions and the same behavior as the two previous polyelectrolytes were found. The nature of charged group (sulfate and sulfonate) does not seem to have any incidence on the phase diagram. We also examined the solubility of sodium dextran sulfate (NaDS), which has practically the same charge density [29], but a more hydrophilic and less flexible backbone than the previous polyelectrolytes. The NaDS was also stable



Fig. 1. Experimental phase diagrams of different anionic polyelectrolyte/trivalent cation systems: NaPSS/LaCl₃ (full triangles); NaPVSF/LaCl₃ (full lozenges); KPVS/LaCl₃ (full circles); NaDS/LaCl₃ (full squares); NaPA2/spermidine (open squares); KPVS/spermidine (open triangles). The finite twophases region " 2φ " is surrounded by a one-phase region " 1φ " at high and low salt concentration. The full lines are only guides for the eyes.

with all divalent counterions except with barium ion in agreement with previous observations [3]. With $LaCl_3$, at pH 3, the solubility of NaDS is similar to all other polyelectrolytes. However, the upper limit of the two-phases region occurs at slightly higher salt concentration (Fig. 1). Therefore, for sulfate or sulfonate groups, the nature of backbone of the polymer has little effect on the phase diagram. To see the generality of this behavior, the lanthan um in the $KPVS/LaCl_3$ mixture was replaced by the spermidine which is a linear organic cationic molecule fully charged (+3) at pH 7. Although this molecule is very different from lanthanum, the result is largely unchanged (Fig. 1). The lower concentration limit is nearly the same for the two cations though the resolubilization occurs at a higher spermidine concentration. Therefore, the electrostatic interactions can be considered, in first approximation, as the principal driving force for phase separation of highly charged strong anionic polyelectrolytes in presence of multivalent counterions, where no chemical associations occurs.

A similar phase behavior was observed in the case of a weak anionic polyelectrolyte, partially charged (75%) NaPA2, in presence of spermidine (Fig. 1). Indeed, conductivity measurements on mixtures of acetate/methylamine and of vinylsulfonate/methylamine show that there is no chemical association between the primary ammonium (NH₃⁺) and the carboxylate (or sulfonate) groups [30]. A general phase diagram seems to occur when only electrostatic forces are prevailing between charged groups and counterions. At this level, it is interesting to note that such phase diagrams were also observed for DNA/polyamine mixtures [11,13].

4.2 Phase diagrams of polyelectrolytes in presence of multivalent counterions with chemical association

4.2.1 Sodium polyacrylate/multivalent counterions systems

The phase diagram of the NaPA2/LaCl₃ (pH = 7) system was established and presented, similar to the previous



Fig. 2. Experimental NaPA2/CaCl₂ phase diagram: cloud points (full squares); composition of supernatant (full triangles) and of precipitates (open circles). Only few initial compositions of solutions before the demixion (open lozenges) with the corresponding tielines (dash lines) are reported. The full line is only a guide for eyes to indicate the boundary of the two-phases region " 2φ ". No resolubilization was observed in excess of calcium chloride.

ones, a lower phase separation line that remained at the same position: $[La^{+++}]/[COO^{-}] = 0.24 \pm 0.1$. The only but major change was the absence of resolubilization at high salt concentration. This difference comes from the chemical association between the lanthanum and the carboxylate groups (see Tab. 2) which prevents the resolubilization. Apart the resolubilization phenomenon in excess of salt (case of trivalent counterions), the main difference between NaPA and all strong polyelectrolytes, bearing sulfonate or sulfate groups, appears with inorganic divalent counterions. With all the divalent counterions studied a phase separation without resolubilization was observed (until the solubility limit of salt added). In order to understand the effect of chemical association on polyacrylate solubility, the phase diagram of fully charged NaPA2 in presence of CaCl₂ was carefully determined. For salt concentrations above the concentration where the cloud point appears, the solutions separate into a precipitate, with a high polymer concentration, and a supernatant with a very low polymer concentration (Fig. 2). When the carboxylate concentration is higher than 0.003 M, the salt concentration limit of the two-phases regime is an increasing function of monomer concentration. Moreover this limit is nearly independent on the temperature (L-type). Above 0.005 M, the limit is quasi-linear: $[Ca^{++}]/[COO^{-}] = 0.36 \pm 0.02.$

We can notice that the demixion lines obtained in the different systems, NaPVS/LaCl₃, NaPA2/LaCl₃ and NaPA2/CaCl₂, have a common law: [Counterions] \approx [Charged Groups] $\times (0.7/z)$ where z is the counterion valency. When [COO⁻] < 0.002 M, the salt concentration at demixion increases when the carboxylate concentration decreases and is more dependent on temperature. Similar phase diagrams were observed in alginate and acrylamide/acrylate copolymers [7]. Figure 2 shows that the salt and monomer concentrations in the supernatant are close to those determined from the appearance of cloud points. Within experimental error we found that the composition of the precipitate was nearly independent of the initial polyacrylate concentration.

Ions	$\log K_1$	$\log K_2$	Ionic radius (Å)	$-\log k$
Mg^{++}	0.55	—	0.66	11.4
Ca^{++}	0.57	$\approx 0.30(*)$	0.99	12.7
Ba^{++}	0.45	—	1.34	13.4
Mn^{++}	0.70	—	0.80	10.6
Co^{++}	0.70	0.50	0.72	9.7
Ni ⁺⁺	0.84	0.60	0.69	9.9
Cu^{++}	1.85	1.20	0.72	7.7
Cd^{++}	1.35	0.85	0.97	10.1
La^{+++}	1.82	1.20	1.02	8.5
		$K_3 = 10^{0.7}$		$(LaOH^{++})$

Table 2. Association constants with COO⁻ groups.

 K_1 and K_2 are the formation constants of monocomplexes and dicomplexes, respectively. For divalent ions M^{++} the constants are defined as follow: $[M^{++}COO^{-}] = K_1[M^{++}][COO^{-}]$ and $[M(COO)_2] = K_2[M^{++}COO^{-}][COO^{-}]$. These constants are estimated from a compilation of the stability constants of carboxylic acids with inorganic cations given in the literature [27,38] at ionic strength of 0.1 M (or larger). (*) Constant determined from conductivity measurements [30]. k is the constant formation of hydrolyzed ions MOH^+ at zero ionic strength [27]: $[MOH^+][H^+] = k[M^{++}]$.



Fig. 3. Experimental phase diagrams obtained for different anionic polyelectrolyte/divalent cation systems: NaPA1/CaCl₂ (open squares); NaPA1F/CaCl₂ (open circles); NaPA2/CaCl₂ (open lozenges); NaPA3/CaCl₂ (open triangles); NaPA2 partially charged (75%)/CoCl₂ (full circles); NaPVSF/BaCl₂ (full squares). The lines joining cloud points are only guides for eyes.

In the precipitate, the concentration of polymer and calcium are close to 4 M and 2 M, and a weak concentration of sodium ([Na⁺] \approx [Ca⁺⁺]/30) was detected. More precisely we have [COO⁻]_p/[Ca⁺⁺]_p = 2.1 ± 0.2, which is close to the stoichiometric composition (equivalent to nine water molecules per carboxylate group).

In order to observe the influence of molecular weight on phase separation boundaries, we determined the phase diagrams of NaPA1, NaPA2, NaPA3 and NaPAF samples in presence of CaCl₂ (Fig. 3). At low concentration, precipitation appears first for the largest molecular weight. At high polymer concentration, in the L-type regime, the demixion lines become nearly independent of molecular weight. In this domain, a study on NaPA2 with different divalent counterions (Ba⁺⁺, Ca⁺⁺, Cd⁺⁺, Cu⁺⁺, Mg⁺⁺, Mn⁺⁺, Ni⁺⁺) showed that their efficiencies to precipitate the sodium poly(acrylate) are practically the same.

4.2.2 Phase diagram of NaPVSF/BaCl₂ system

Now, let us consider the particular case of the barium ion which is able to precipitate all polyelectrolytes (carrying carboxylate sulfate or sulfonate groups). As shown in Figure 3, the phase diagram of the NaPVSF/BaCl₂ is similar to that of NaPA2/CaCl₂. Furthermore no resolubilization was observed in both systems. The precipitation of poly(vinyl sulfonate) is probably due to a chemical association between barium ions and sulfonate groups. It is well known that the barium-vinyl sulfonate monomer $((C_2H_3 SO_3_2Ba$) is poorly soluble (solubility product close to 5×10^{-4} M²) which means that the chemical binding of barium with vinyl sulfonate monomers is strong. All divalent cations other than barium $(M^{++} \neq Ba^{++})$ do not precipitate poly(vinyl sulfonate), that is probably due to the high solubility of their sulfonate monomers $((C_2H_3 SO_3)_2M$). In conclusion the demixion of polyelectrolytes in presence of inorganic divalent counterions is due to the chemical bonding between the counterions and the charged groups of the polyelectrolyte.

5 Complexation between polyelectrolytes and multivalent counterions

Our aim was to determine the quantity and the type of complexes formed before phase separation, especially for the system PANa/Ca. Unfortunately, the chemical association of calcium with carboxylate groups is not well detected by spectroscopic methods [30,31]. Therefore we replaced the calcium ion by the cobalt ion for this study. Cobalt was chosen because calcium and cobalt have practically the same ability to precipitate the polyacrylate (Fig. 3) and their complexation constants with COO⁻ groups are close (see Tab. 2). Moreover, formation of complexes between cobalt ion and COO⁻ groups can be well characterized by UV/VIS spectroscopy.



Fig. 4. Molar absorption spectra of cobalt ions and of cobalt complexes (full lines). From the bottom to the top: cobalt ions $(A_0(\lambda))$; monocomplexes $(A_m(\lambda))$; dicomplexes $(A_d(\lambda))$. For comparison the experimental absorption spectrum of cobalt (0.0125 M) in presence of sodium polyacrylate NaPA1 ([COO⁻] = 0.04 M) is reported (squares).

5.1 Monocomplexation and dicomplexation (UV/VIS spectroscopy)

In order to determine the effect of complexation of the cobalt ion with acrylate group on the absorption spectrum, we first determined the variation of the absorbance of sodium acetate/cobalt chloride mixtures in the wavelength range 400–650 nm. The cobalt concentration was kept constant (0.002 M) while the acetate concentration was varied between 0.01 and 3 M. The absorbance spectrum of cobalt, without sodium acetate shows a maximum at a wavelength of 512 nm whereas the sodium acetate (without cobalt) has no detectable absorbance. When the acetate concentration increases the amplitude of the absorbance increases and the position of the maximum shifts up to 520 nm.

For a given wavelength λ the molar absorbance, $A(\lambda)$, can be written as follows:

$$A(\lambda) = x_{\rm m} A_{\rm m}(\lambda) + x_{\rm d} A_{\rm d}(\lambda) + (1 - x_{\rm m} - x_{\rm d}) A_0(\lambda)$$
(10)

where $x_{\rm m} = [\rm COO^- \rm Co^{++}]/[\rm Co^{++}]_{\rm initial}$ and $x_{\rm d} = [\rm Co(\rm COO)_2]/[\rm Co^{++}]_{\rm initial}$ represent the fraction of monocomplex and dicomplex, respectively. The quantities $A_{\rm m}(\lambda), A_{\rm d}(\lambda)$ and $A_{\rm 0}(\lambda)$ are the molar absorbances of monocomplex, dicomplex and non-associated cobalt, respectively. As the fractions $x_{\rm m}$ and $x_{\rm d}$ can be calculated using the complexation constants $(K_1 \text{ and } K_2)$ given in Table 2, from the spectra obtained on seven mixtures it was possible to determine the molar absorbance of the cobalt in the monocomplex and dicomplex state. It is important to notice that for high acetate concentrations a precise value of the second association constant is not needed. Indeed, when $\log K_2 = 0.5$ is replaced by 0.3, the dicomplex fraction only varies by 10%. We fitted the measured absorbances $A(\lambda)$ to expression (10) where $A_{\rm m}(\lambda)$ and $A_{\rm d}(\lambda)$ were two adjustable parameters. The molar absorbances $A_{\rm m}(\lambda)$ and $A_{\rm d}(\lambda)$ found are given in Figure 4.

Now, from a given experimental spectrum, obtained with a polyacrylate sample, the knowledge of $A_0(\lambda)$, $A_{\rm m}(\lambda)$ and $A_{\rm d}(\lambda)$ allows us to determine the cobalt fractions in the monocomplex and dicomplex states. For instance, for 0.0125 M of cobalt in presence of 0.04 M of polyacrylate, the molar absorbance of the cobalt $A(\lambda)$ is very close to $A_{\rm d}(\lambda)$ (Fig. 4) and we find that the cobalt fractions of the complexes are $x_{\rm d} = 0.85 \pm 0.05$ and $x_{\rm m} = 0.15 \pm 0.05$. Hence, a weak polyacrylate concentration is equivalent to a high acetate concentration. This result shows that cobalt ions mostly form dicomplexes with polyacrylate.

The wavelength shift, in the case of polyacrylate, can be induced by a modification of the cobalt symmetry, due to the high electrostatic potential induced by the polyelectrolyte, or by the variation of cobalt coordination. We checked these two possibilities by UV/VIS spectroscopy on NaPVS/CoCl₂ mixture and by EXAFS experiments on NaPA1/CoCl₂ mixture. In high concentration of NaPVS and without NaPVS the cobalt absorbance amplitude is the same, meaning that the electrostatic potential has no influence on the electronic structure of the cobalt. This result also proves the absence of complexation between cobalt and sulfonate groups, which is consistent with the absence of precipitation in the NaPVS/CoCl₂ mixture. EXAFS measurements were realized on a pure cobalt chloride solution (0.015 M) without added polymer and in presence of 75% charged NaPA2 (0.08 M). Without polymer, the distance between cobalt and oxygen was found to be 2.07 Å, in agreement with the value 2.09 Å reported in reference [32]. The presence of NaPA does not change the coordination number of cobalt, which remains hexacoordinated [33], but creates a very weak distortion: four oxygen atoms at 1.96 Å and two others at 2.10 Å. The second neighborhood of the cobalt should be water-oxygen or carboxylate-carbon. But these elements have similar electronic contrasts. Therefore, the second neighborhood cannot be extracted quantitatively. The Fourier transform of the signal, which expresses the electronic density as a function of the distance, presents a weak peak at 6 Å from the cobalt center, which is probably due to carbon. The weak amplitude and the large thickness of the peak do not allow quantitative analysis. Thus the wavelength shift in UV/VIS is not due to the variation of cobalt coordination. As it appears for highly concentrated sodium acetate solutions, the change of cobalt absorbance in presence of polyacrylate is only due to chemical association between cobalt ions and carboxylate groups.

5.2 Complexation and phase diagram

The fraction of dicomplexes near the phase separation was determined in two different ways. First the ratio $[Co^{++}]/[COO^{-}]$ was fixed and secondly the $[Co^{++}]$ was increased up to the phase separation at constant $[COO^{-}]$.

To begin the ratio $[\text{COO}^-]/[\text{Co}^{++}]$ was fixed to 4 and the polyacrylate NaPA1 (charged at 95%) was used. As the NaPA1 concentration increases the fractions of cobalt ions in dicomplex and monocomplex forms remain constant: $[\text{Co}^{++}]_{\text{dicomplex}}/[\text{Co}^{++}]_{\text{added}} \approx 80\%$ and $[\text{Co}^{++}]_{\text{monocomplex}}/[\text{Co}^{++}]_{\text{added}} \approx 20\%$. This result



Fig. 5. Variation of fractions of acrylate groups in monocomplex state (circles) and dicomplex state (triangles) at the approach of the phase separation. Cloud point occurs at $[Co^{++}]/[COO^{-}] = 0.36$. The carboxylate concentration of NaPA2 sample (charged at 75%) was fixed to 0.0075 M. The squares represent the total fraction of acrylate groups chemically associated with cobalt. It appears that all cobalt counterions are associated with carboxylate groups.

is in contradiction with a classical mass action law where the cobalt concentration is calculated using the total volume of the solution. Even if the complexation constants are large, we never expect that the fractions are constant. The only way to explain this result is to suppose that the relevant concentration is the local counterion concentration in the immediate vicinity of the polyelectrolyte, which should remain constant whatever is the polymer concentration. Thus, the dicomplexation depends on local charge density of polyelectrolyte and probably occurs between two neighboring monomers.

To study the complexation when the demixion limit (L-type) is approached, the concentration of NaPA2 (charged at 75%) was fixed to 0.01 M (0.0075 M of COO^-). The cobalt absorption spectrum was observed as a function of the CoCl₂ concentration up to phase separation. We found that, all the cobalt ions were chemically bound to carboxylate groups. In Figure 5 the fractions of acrylate groups in monocomplex and dicomplex states are reported. The fraction of cobalt in the dicomplex state is close to 85% and increases by around 10% near the demixion. This weak increase near phase separation should be associated to the polymer shrinking, which increases the number of contact between distant monomers [34] and the counterion condensation [35].

In order to have information on the nature of dicomplexes, viscosity evolution studies as a function of divalent counterion concentration, up to phase separation, were performed. Addition of divalent salt can increase the viscosity if ionic cross-linking occurs (gel formation). With the NaPA2/CoCl₂ system (charged at 75%) at a polymer concentration of 2 wt% in the semi-dilute regime ([COO⁻] = 0.21 M), we found that the viscosity strongly decreases as the cobalt concentration increases (Fig. 6). Cobalt ions provoke the collapse of the chains. Dicomplexation essentially occurs between two neighboring monomers of the chain. Few bridges may be formed but not enough to make a gel.

The conclusions drawn for the system $NaPA2/CoCl_2$ can reasonably be extended to $NaPA2/CaCl_2$ system



Fig. 6. Variation of the viscosity of NaPA2 solutions in presence of CoCl₂ and CaCl₂ salts at the approach of the phase separation. The normalized viscosity of the mixture (polymer plus salt) is equal to $(\eta_{polymer+salt} - \eta_{water})/(\eta_{polymer} - \eta_{water})$ where $\eta_{polymer}$ is the viscosity of NaPA2 solution without salt. The full squares and full triangles correspond to the NaPA2 partially charged (75%), at a monomer concentration of 0.225 M, in presence of CoCl₂ and CaCl₂, respectively. The open triangles and open circles correspond to the NaPA2 fully charged (100%) in presence of CaCl₂ at a monomer concentrations of 0.28 and 0.028 M, respectively.



Fig. 7. Fractions of calcium associated (chemically or electrostatically) with NaPA2, near the demixion, measured with a specific calcium electrode for three concentrations of carboxylate: 0.0028 M (open squares); 0.0053 M (open triangles); 0.028 M (dots). All the calcium ions are associated with the polyelectrolyte before phase separation.

(charged at 100%). The association constants of calcium and cobalt with carboxylate groups are of the same order of magnitude (see Tab. 2), so we can expect that all calcium counterions are chemically associated with polyacrylate before phase separation. Moreover, specific electrode measurements show that, before the demixion, all the calcium ions are in the immediate vicinity of the polyelectrolyte as cobalt counterions (Fig. 7). Indeed, Figure 6, shows that calcium and cobalt ions reduce the viscosity in the same way.

With highly charged polyelectrolytes, gel formation can be induced with trivalent cations but not with divalent cations. With trivalent cations, first the dicomplexation occurs between neighboring monomers and finally the tricomplexation happens with a monomer which belongs to another chain or a monomer of the same chain which is far from the two first complexed monomers. In semi-dilute solution, bridges can be created if the third complexation



Fig. 8. Variations of the fractions of cobalt in complex forms, determined by UV/VIS spectroscopy, as a function of the concentration of added NaCl: dicomplexes (triangles); monocomplexes (squares). The thin solid line represents the total fraction of cobalt chemically associated. The carboxylate concentration of NaPA2 (charged at 75%) was 0.028 M and the cobalt concentration was 0.0065 M.

constant is high enough which is the case for Fe^{+++} (gel) but not for La⁺⁺⁺ (no gel).

5.3 Affinity of divalent counterions to polyacrylate: mixtures NaPA2/divalent counterions/NaCl

Let us first consider the effect of sodium chloride on the NaPA2 (charged at 75%)/CaCl₂ phase diagram. When the concentration of NaCl increases, the cloud point appears at higher CaCl₂ concentrations. For instance, for a solution having a monomer concentration of 0.01 M, the addition of 0.01 M of NaCl changes the position of the cloud point by only 5%, which is the order of magnitude of experimental uncertainty. But when NaCl concentration is close to 0.2 M, which is much higher than divalent concentration, the displacement of the cloud point is not negligible (190%). The same behavior was observed with cobalt ion, where it was possible to measure the variation of complexation fraction (UV/VIS spectroscopy) as a function of added NaCl concentration. Figure 8 shows that the cobalt dicomplex fraction decreases when the NaCl concentration increases. Thus we conclude that the solubility of sodium polyacrylate is intimately related to the dicomplexation. The cobalt dicomplex fraction depends on the competition between Na^+ and Co^{++} . So we can expect that for divalent counterions having a larger affinity to carboxylate groups, the ability of sodium counterion to displace them should be reduced. Let us compare the effect of sodium chloride on a 0.01 M polyacrylate solution in presence of different divalent counterions. Without monovalent added salt, the divalent counterion concentration at the demixion is nearly the same $(0.0035 \pm 0.0003 \text{ M})$ whatever is the nature of divalent cation (Fig. 9). Except for copper, the concentration of divalent counterion needed to precipitate the polyacrylate in presence of 0.2 M NaCl increases and the amplitude of the variation strongly depends on the nature of divalent counterion. Then it is possible to classify divalent counterions, according to their power to



Fig. 9. Concentration $C_{\rm s}^*$ of the divalent salt $M^{++} {\rm Cl}_2^-$ at the demixion limit for solutions of NaPA2 (partially charged (75%), $[{\rm COO}^-] = 0.01$ M) in presence of different divalent counterions without added NaCl (open bar chart) and with 0.2 M of NaCl (hatched bar chart). Without added NaCl, the divalent salt concentrations $C_{\rm s}^*$ are nearly the same (0.0035 M) whatever is the nature of divalent cation.

precipitate the NaPA:

$$Mg^{++} < Ca^{++} < Ba^{++} < Mn^{++} < Co^{++} < Ni^{++}$$

 $< Cd^{++} \ll Cu^{++}.$

This classification is similar to the one established from potentiometric measurements [36,37]. We can also classify counterions as a function of their association constants (see Tab. 2):

$$Ba^{++} < Mg^{++} < Ca^{++} < Mn^{++} = Co^{++} < Ni^{++}$$

 $< Cd^{++} \ll Cu^{++}$

Except for the barium, the two classifications are identical. Thus, the demixion limit is directly correlated with the fraction of counterions associated with COO^- groups, which depends on the association constant between divalent counterions and COO^- groups. The barium counterion has the larger ionic radius (see Tab. 2) which could favor the dicomplexation between two neighboring charged monomers. In contrast with the other mixtures, the solubility of NaPA2/CuCl₂ decreases when sodium chloride is added. Because of its high association constant, the fraction of copper associated with COO^- groups is insensitive to sodium counterions, but NaCl salt screens the repulsion between the negatively charged monomers which favors the precipitation of the polyelectrolyte.

5.4 Criterion for the complexation of divalent counterions with anionic polyelectrolytes

The stability of polyelectrolyte solutions in presence of multivalent counterions depends on the affinity between their functional groups and counterions. Two extreme cases can be encountered: in the first one the electrostatic attraction is the principal driving force for phase separation whereas in the second one the precipitation



Fig. 10. Fractions of divalent counterions M^{++} in complex forms as a function of the first association constant K_1 . Assuming that the first and second constants are related, $\log K_1/\log K_1K_2 = 0.6$ (see text and Tab. 2), fractions of monocomplexes (short dash) and of dicomplexes (long dash) are computed using the tube model with $[M^{++}]/[A^-] = 0.36$. When no dicomplexation occurs $(K_2 = 0)$, the fraction of monocomplexes are computed in two manners: with the charge regulation model (full line) and the tube model (dash dot line).

is induced by complexation of the polyelectrolyte with the multivalent ions. Now, let us try to find a criterion which allows us to distinguish between these two limiting cases from the simple knowledge of association constants between the divalent counterions and the functional groups of the polymer.

Assuming that there is no dicomplexation the fraction of divalent counterions in monocomplex state can be calculated using charge regulation model. The polyelectrolyte is assumed to be a cylinder of diameter 5 Å with a mean distance between charges b = 2.5 Å. In Figure 10 the fraction of counterions in monocomplex form as a function of the value of monocomplexation constant is reported. Figure 10 shows that the complexation fraction sharply increases above $K_1 = 10^{-2}$.

Unfortunately, the introduction of two complexation constants is not possible in the charge regulation model presented above. In order to take into account the dicomplexation, which is the driving force for phase separation, we use another procedure. The added divalent counterions are assumed to be confined in a cylindrical tube of radius R around the polyelectrolyte having a thread shape. Of course this hypothesis is only meaningful when no free divalent counterions are present in the solution (which is experimentally the case). The local monomer and counterion concentrations depend on both the distance between charged monomers and the tube radius: one monomer is confined in a volume of $\pi b R^2$. The local charged monomer, $[A^-]_L$, and divalent counterion, $[M^{++}]_L$, concentrations (in moles per unit volume) are

$$[A^{-}]_{\rm L} = 1/(6 \times 10^{23} \pi b R^2) \text{ and } [M^{++}]_{\rm L}$$
$$= [M^{++}]([A^{-}]_{\rm L}/[A^{-}])$$
(11)

where $[M^{++}]$ and $[A^{-}]$ are the macroscopic concentrations. The concentration of monocomplexes and dicom-

plexes are computed using mass action laws

$$[MA^{+}]_{L} = K_{1}([A^{-}]_{L} - [MA^{+}]_{L} - 2[M(A)_{2}]_{L}) \times ([M^{++}]_{L} - [MA^{+}]_{L} - [M(A)_{2}]_{L}),$$

$$[M(A)_{2}]_{L} = K_{2}[MA^{+}]_{L}([A^{-}]_{L} - [MA^{+}]_{L} - 2[M(A)_{2}]_{L}).$$

(12)

Using the complexation constants, K_1 and K_2 , of the cobalt with carboxylate groups, given in Table 2, we adjust the parameter R to fit the complex fractions of cobalt in dicomplex state (85%) and monocomplex state (15%) deduced from UV/VIS spectroscopy measurements. We find that the best value is $R \approx 7$ Å when b is chosen to 2.5 Å.

Now, whatever the values of the complex constants, the fractions of divalent counterions in complex states can be computed using expressions (11, 12) with $R \approx 7$ Å. For instance, in Figure 10 the fraction of divalent counterions in monocomplex state is reported when the second constant K_2 is fixed to zero. We can see that the fraction determined with the tube method has the same behavior as the one obtained using charge regulation model.

Empirically, we noticed that for a given functional group, the ratio $\log K_1 / \log K_1 K_2$ is approximately a constant [27,38], this constant is of the order of 0.6 for acrylate groups. Thus fractions of counterions in monocomplex and dicomplex states as function of K_1 can be computed (Fig. 10). When the first association constant is small $(K_1 < 10^{-2})$, divalent counterions are not chemically associated and are basically electrostatically condensed (which is certainly the case for most inorganic counterions with sulfonate groups). In those conditions, no phase separation is expected for divalent counterions. When $K_1 > 1$, it is more than 65% of counterions which form dicomplexes. This condition is fulfilled for all divalent inorganic counterions with carboxylate groups (see Tab. 2).

6 Phase diagrams of NaPA/CaCl₂ systems: mean field model

First, let us try to describe the NaPA2/CaCl₂ phase diagram by using expressions (4, 10). It is necessary to know the parameters: N, σ^3 , f', f, $f_{\rm m}$, $f_{\rm d}$, B, $\chi_{\rm d}$. As the NaPA2/CaCl₂ and NaPA2/CoCl₂ systems are very similar, when the concentration of divalent salt ($C_{\rm S}$) is lower than 0.4 times the monomer concentration (C), we assume that all added calcium ions are chemically bound to the polymer with a fraction of calcium in the dicomplex state of 90% (Figs. 10 and 12). In this domain of concentration, the three monomer fractions f, $f_{\rm m}$ and $f_{\rm d}$ are estimated as follow: f = 0, $f_{\rm m} = 0.1C_{\rm S}/C$, and $f_{\rm d} = 2(0.9C_{\rm S}/C)$. The fraction of monomer f' carrying a condensed sodium is computed following expression (1): $f' = f'_0 - 2C_{\rm S}/C$ when $C_{\rm S} < f'_0 C/2$ and f' = 0 when $C_{\rm S} > f'_0 C/2$, where the initial sodium fraction, $f'_0 = 1 - b/l_{\rm B}$ is fixed to 0.65 (sodium ions are stoichiometrically replaced by calcium ions). The values of B and σ are chosen to be equal to 0.2 and to 5 Å



Fig. 11. Variation of interaction terms of the spinodal equation near the phase separation as a function of the added calcium (the polymer concentration is fixed to 0.01 M): repulsive electrostatic term (thin full line); attractive term due to the dicomplexation in absolute value (thick full line); attractive electrostatic term in absolute value (dash line).

(as in Ref. [9]). Using expressions (4, 9), the adjustable parameter χ_d is determined from the experimental demixion limit measured in the system $NaPA2/CaCl_2$ in the concentration range 0.005 M < C < 0.06 M, where most of experimental determinations of demixion were done. At this monomer concentration range the entropic term is small and the value of χ_d deduced is weakly dependent on the exact value of the effective degree of polymerization taken. We find that the results are correctly described with $\chi_d \cong 20$ (N = 8000). This large value corresponds to a high attraction between monomers that carry calcium in dicomplex state. In other words the dicomplexes are hydrophobic, which indicates that the chemical association is followed by a partial dehydration of Ca^{++} ion and COO^{-} group [39–42]. It is important to notice that the value of χ_d is strongly dependent on the value of σ . To give an idea about the relative importance of the different interactions controlling the precipitation, we have reported in Figure 11 the different interaction terms of the spinodal equation calculated for C = 0.01 M. By increasing the salt concentration the hydrophobic term $(2\sigma^3\chi_d f_d)$, due to the dicomplexation, increases and becomes nearly a constant above $C_{\rm S}/C \approx 3$ whereas the repulsive electrostatic term, which stabilizes the polyelectrolyte, decreases sharply. In first approximation, precipitation occurs when the hydrophobic term is equal to the repulsive term in absolute value, which corresponds to he crossing point of the two upper curves in Figure 11. The crossing point is weakly dependent on the variation of χ_d . Therefore, for two different divalent counterions which are completely associated with carboxylate groups, similar demixion curves will be observed if their χ_d values are of the same order of magnitude. When complexation is absent, the electrostatic attractions are not strong enough to induce phase separation.

In Figure 12 the spinodal curves calculated for the three degrees of polymerization of the samples PAA1, PAA2, PAA3 are reported. The increasing of the demixion limit for weak polymer concentrations (Fig. 12) is due to the entropic term, which becomes dominant in this



Fig. 12. Theoretical phase diagrams of mixtures sodium polyacrylate/CaCl₂. Lines are the spinodal curves computed for different degrees of polymerization N: from the top to the bottom N is equal to 38, 8×10^3 , and 4×10^5 .

regime. When $C_{\rm S} \geq 0.4C$, condensation is stopped (see Eq. (1)) and the number of monomer that carry cobalt in complex state increases slightly. In this complicated region, we have assumed that $f_{\rm m}$ and $f_{\rm d}$ remain constant: $f_{\rm m} = 0.1 \times 0.41 = 0.041$ and $f_{\rm d} = 2 \times 0.9 \times 0.41 = 0.74$. The position of the minimum of the demixion line depends on the degree of polymerization and on $\chi_{\rm d}$ value. The theoretical phase diagrams describe the experimental results semi-quantitatively.

It is important to notice that the association constants decrease with salt concentration at low ionic strength in the Debye-Hückel approximation [43] but at high ionic strength they tend to a constant [27]. At the same time the complex fraction always increases with salt concentration. The absence of resolubilization is the signature of a dominant dicomplexation. In contrast, if the monocomplexation is dominant precipitation is expected to be followed by a resolubilization due to charge inversion [10].

7 Conclusion

In the case of strong polyelectrolytes (sulfonates, sulfates) no chemical associations occur and their solubility depends on electrostatic interactions. Other factors such as the nature of polymer backbone (hydrophobicity, rigidity), the nature of charged groups and the nature of counterions have little effect. The important parameter is the counterion valency. A finite diphasic zone exists only for counterions with a valency higher or equal to 3. For weak polyelectrolytes, like poly(acrylate), complexes are formed with inorganic counterions. The polyacrylate chemically reacts with all inorganic multivalent counterions and a L-type demixion takes place. Before phase separation, the high electrostatic polyelectrolyte potential leads nearly all counterions to form complexes with charged monomers. Chemical association partially dehydrates counterions and charged groups of the polymers therefore the complexes formed are hydrophobic. The demixion limit is related to the fraction of monomer in dicomplex state, which depends on the polyelectrolyte charge density. The complexation increases as the counterion concentration increases and therefore inhibits polymer resolubilization at high counterion concentration. For highly charged polyelectrolytes in presence of divalent counterions the majority of counterions form dicomplexes between two neighboring monomers on the same chain. No gel formation is observed before the demixion. The understanding of these local interactions allows us to describe the phase diagrams of sodium poly(acrylate)/CaCl₂ mixtures semiquantitatively taking into account the chemical bonding between COO⁻ and Ca⁺⁺ counterions.

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