# FORMATION OF POLYELECTROLYTE COMPLEXES

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Polyelectrolyte complexes are intermacromolecular complexes, i.e. macromolecular compounds formed by interpolymeric reaction between oppositely charged polyelectrolytes. The effect of the molecular parameters and reaction conditions on the formation and structure of polyelectrolyte complexes is reviewed.

## 1. INTRODUCTION

Polyelectrolyte complexes[1 - 3] are, besides hydrogen bonding complexes[4 - 16], stereocomplexes[17 - 27] and charge transfer complexes[26 - 32], a specific group of macromolecular substances forming by reaction between two or more polymers. This group is referred to as intermacromolecular complexes.

This paper summarizes knowledge of the formation of polyelectrolyte complexes (PECs) formed by homogeneous reactions; such complexes are among the most thoroughly studied groups of intermacromolecular complexes (IMCs).

## 2. FORMATION OF POLYELECTROLYTE COMPLEXES

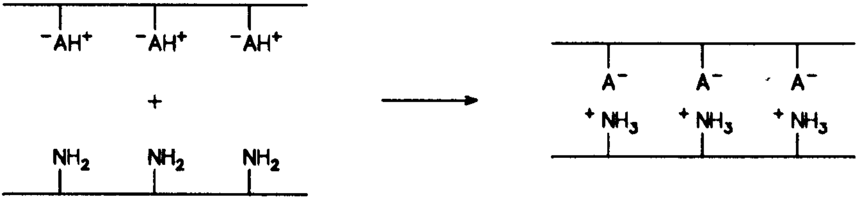
Polyelectrolytes (PELs) are polymeric substances whose macromolecules consist of monomeric units containing dissociable groups. A PEL solution thus formally includes macroions whose dissociable groups are mutually bonded by covalent bonds to give a single polymeric chain, and an equivalent number of oppositely charged small ions (counterions)[33,34].

Polyelectrolyte complexes result from mutual interactions between PELs which are capable of providing, by dissociation, oppositely charged polyions, i.e. polyanions and polycations. Electrostatic Coulomb interactions are the predominating intermolecular interactions in the PECs formed.

$$\text{polyanion} + \text{polycation} \longrightarrow \text{PEC} \qquad (A)$$

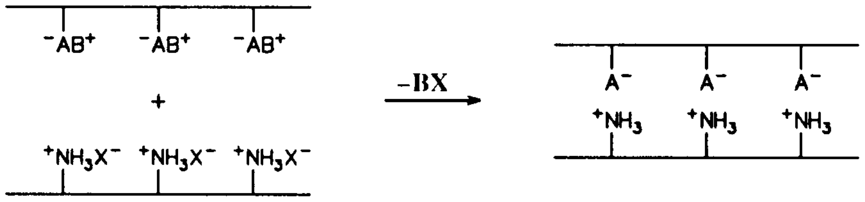
There are three routes to prepare polyelectrolyte complexes[35]:

*a*) Neutralization reaction between the free polyacid and the free polybase (Scheme 1).



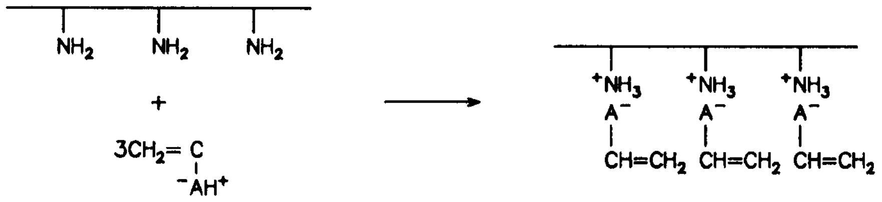
SCHEME 1

*b*) Reaction between an alkali salt of the polyacid and a halo salt of the polybase (Scheme 2).



SCHEME 2

*c*) Matrix polymerization of a monomer having an ionic nature, after its bonding to an oppositely charged polyion. In the first stage this monomer is bonded to a segment of the oppositely charged polyion (Scheme 3), in the second stage the bonded monomer polymerizes, mostly by the radical mechanism (Scheme 4).



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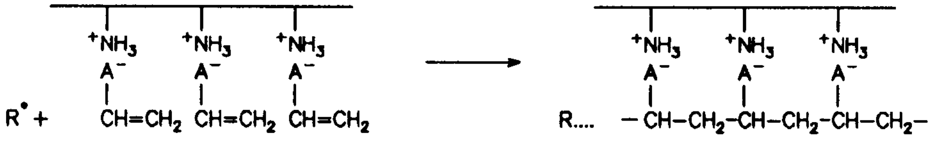


SCHEME 4

Although all of the reactions can occur as homogeneous or heterogeneous reactions, the majority of papers are devoted to the formation of PECs emerging from homogeneous reactions between polyacids and polybases (Scheme 1) or between their salts (Scheme 2).

## 3. THE EFFECT OF MOLECULAR PARAMETERS OF POLYELECTROLYTES ON THE FORMATION OF POLYELECTROLYTE COMPLEXES

### 3. 1. THE EFFECT OF STRENGHT AND CHARGE-DENSITY OF POLYELECTROLYTE

From the acid-base viewpoint, **PELs** can be categorized as polyacids, polybases and polyampholytes[33,34]. Polyacids and polybases can be classed as strong or weak with respect to their dissociation constants, in analogy to low-molecular-weight acids and bases. Strong polyacids and polybases are dissociated to high degrees within broad pH and ionic strength regions. For weak **PELs**, their dissociation degree β highly depends on the solution pH, ionic strength, etc.

The **PEC** formed then can be classed, with respect to the starting **PELs**, in three subgroups:

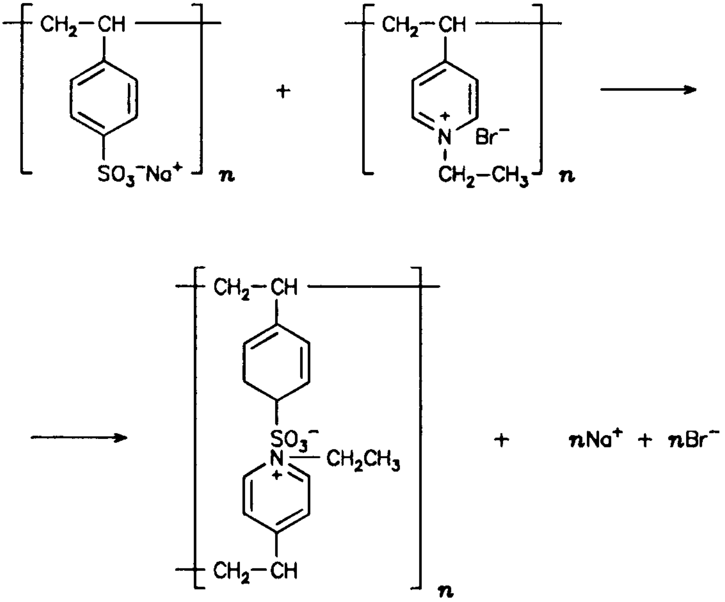
*Subgroup 1*: **PEC** formed by reaction between two strong polyelectrolytes (**SPELs**).

*Subgroup 2*: **PEC** formed by reaction between a strong polyelectrolyte (**SPEL**) and a weak polyelectrolyte (**WPEL**).

*Subgroup 3*: **PEC** formed by reaction between two **WPELs**.

#### 3. 1. 1. *Reaction of Two Strong Polyelectrolytes*

Early work[36 - 40] dealt with the formation of **PECs** by reaction between **SPELs**. Mixing solutions of two oppositely charged **SPELs** (such as poly(sodium styrene sulfonate), PSS-Na, and poly(N-ethyl-4-vinylpyridinium bromide), PEVP-Br, refs[41 - 43], Scheme 5)



SCHEME 5

in the stoichiometric ratio immediately gives rise to the formation of at least one ionic bond[1]. The adjacent reactive sites interact with the oppositely charged units in the nearest environment to give the stoichiometric **PEC** (with respect to the monomeric units) having the "scrambled egg" structure (structure of statistically balanced charges)[37] if the macromolecular chains are packed and adopting the conformation of Kühn's coils in solution (Fig. 1). The next possible structure is the so-called ladder structure, where the two polyions are connected by the zipping mechanism, one after

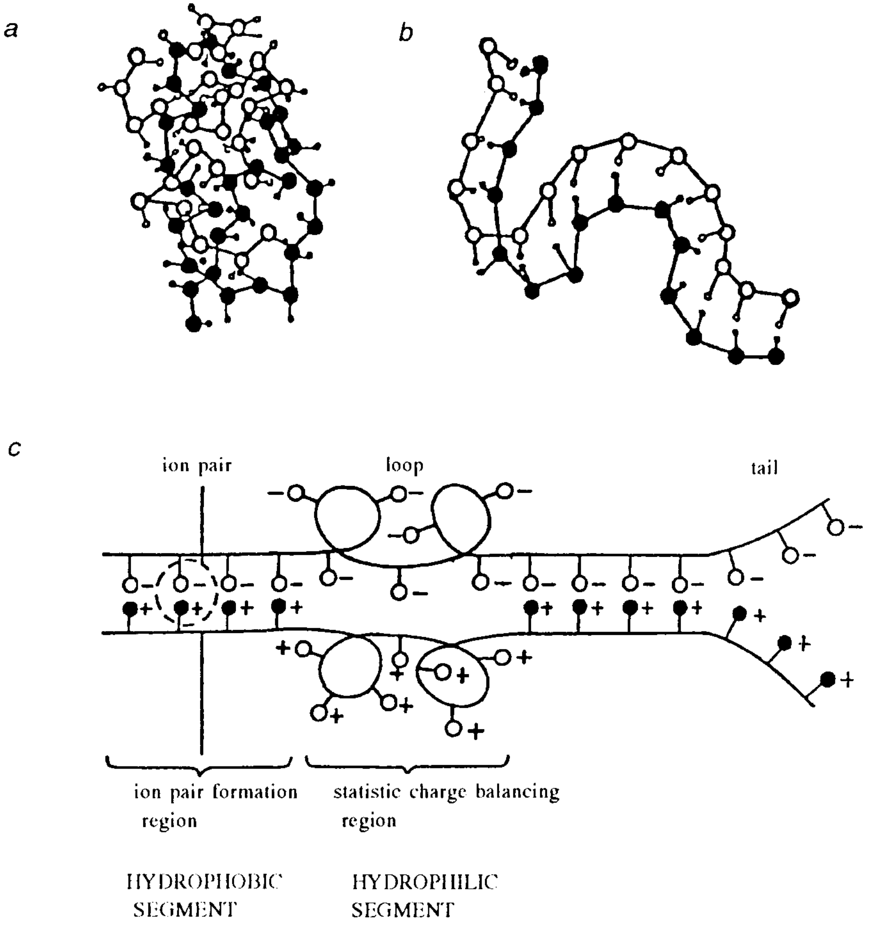


FIG. 1
A model of the molecular structure of a polyelectrolyte complex: *a* model with statistical charge balance (scrambled egg model), *b* ladder model, *c* model of a segment of the macromolecule of a real polyelectrolyte complex

the other[37]. The formation of such a structure presupposes gradual decoiling of chains of the two **PEL**s. The real **PEC**s formed by homogeneous reactions usually possess structures lying between the two extremes[44].

If the **SPEL**s are mixed in a nonstoichiometric ratio, the stoichiometric polyelectrolyte complex (**SPEC**) precipitates whereas the excessive component remains in solution. This implies that the reactivity of the polyionic chain, whose electrostatic charge is partly neutralized by the counter-polyion, is higher than in the free chains, probably due to changes in conformation, in the electrostatic potential, and in the ionic atmosphere about the chain. The **SPEC** and unreacted chains of the excess **PEL** thus coexist in the reaction mixture[1,45].

Closely related to the **PEL** strength is its charge density which is determined by the density of distribution of the dissociable functional groups along the polymeric chain and by the dissociation constant of the functional groups[34]. The effect of the charge density on the stoichiometry of the **PEC** in this subgroup is apparently minimal.

### 3. 1. 2. *Reaction of a Strong Polyelectrolyte with a Weak Polyelectrolyte*

We refer to a **PEC** where there is one negatively charged polyanion group per positively charged polycation group, i.e. a **PEC** where the unreacted functional groups (of the polycation or polyanion) are not dissociated, as an electroneutral polyelectrolyte complex. An electroneutral **PEC** thus is a **SPEC** from the point of view of the oppositely charged functional groups.

In the reaction of a **WPEL** with an oppositely charged **SPEL** the dissociation degree of the **WPEL** affects the complex formation and final composition. This second **PEC** subgroup is currently receiving considerable interest, as is apparent from the large number of papers devoted to this phenomenon. The composition (Φ) of an electroneutral polyelectrolyte complex formed by a weak polyanion (**PA**) and a strong polycation (**PC**) can be calculated from the equation

$$\Phi = [\mathrm{PC}]/[\mathrm{PA}] = \beta_{\mathrm{PA}}\,, \qquad (1)$$

where the brackets denote the concentrations of the monomeric units in the complex*; $\beta_{\mathrm{PA}}$ is the dissociation degree of **PA** in the presence of **PC**, while the dissociation

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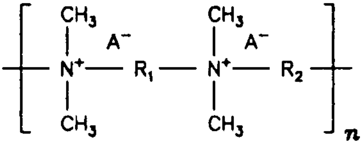
* This paper adheres to the conventional way of expressing the composition by means of concentrations. Generally in chemistry, however, brackets denote equilibrium molar concentrations of the species in question, hence, they should apply to the unreacted fractions rather than to the reacted fractions. It would be this more appropriate to express the composition in terms of the numbers of equivalents of **PC** per equivalent of **PA** as $\Phi = \nu_{\mathrm{PC}}/\nu_{\mathrm{PA}}$. The transition from the concentrations to the absolute amounts of substance has no effect because the volumes cancel in Eq. (*1*).

degree of the strong **PC** is assumed to be unity[1]. The **PC** can further induce dissociation of a weak acid, such as a poly(carboxylic acid), to 20 – 25%. All dissociated sites of the **WPEL** are assumed[1] to be able to react with the oppositely charged functional groups of the strong **PC** ($\beta_{PC} = 1$). Equation (*1*) applies to **PEC**s that have been obtained by neutralization reaction between a weak polyacid, such as poly(acrylic acid), and a strong polybase. For the reaction of poly(methacrylic acid) (**PMAA**) or poly(L-glutamic acid) (**PGA**) with a strong polybase (3,X-ionene, Scheme 6), however, the experimental values differ from the theoretical data, which can be due to conformation changes of the two poly(carboxylic acids) during the interaction[1].



$$\left[ -\overset{CH_3}{\underset{CH_3}{N^+}}(A^-) - R_1 - \overset{CH_3}{\underset{CH_3}{N^+}}(A^-) - R_2 - \right]_n$$

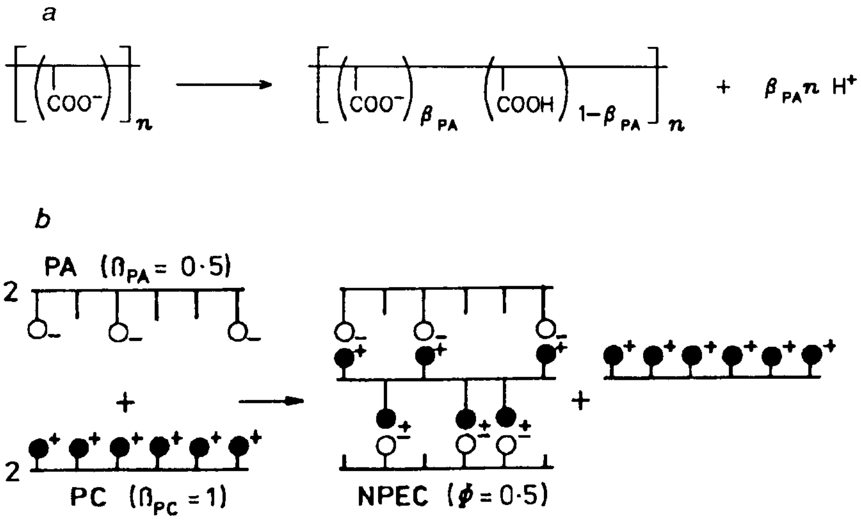
*m*, *m* ionene, $R_1 = R_2 = -(-CH_2-)_m-$
*m*, *k* ionene, $R_1 = -(-CH_2-)_m-$, $R_2 = -(-CH_2-)_k-$
*m*, X ionene, $R_1 = -(-CH_2-)_m-$, $R_2 = -CH_2-C_6H_4-CH_2-$
X, X ionene, $R_1 = R_2 = -CH_2-C_6H_4-CH_2-$
$A^- = Cl^-$ or $Br^-$

SCHEME 6

When mixing a poly(carboxylic acid) with a strong base of the pendent type (dissociable functional groups occur in the side chains) or of the integral type (dissociable functional groups are parts of the main chain) in the equimolar ratio, a nonstoichiometric polyelectrolyte complex (**NPEC**) with a composition Φ emerges and separates into a colloid phase while the excess polybase remains in solution (Scheme 7). If the ratio of the polymeric components corresponds to composition Φ, the two **PEL**s pass quantitatively into the **NPEC** (refs[46 – 48]).

In reactions of strong **PC**s of the integral type with weak poly(carboxylic acids) the strong charge density of the **PC** has been found[1] to induce dissociation of the polyacid, the **PEC** approaching the stoichiometric composition ($\Phi = 1$). Reaction of polyphosphates, which are salts of a strong polyacid with a very high charge density, with an acrylic acid–acrylic amide copolymer, was observed to give rise to the **SPEC** only if the acrylic amide mers were present in the copolymer chain in a relatively high fraction[49].

The effect of the charge density on the **PEC** formation between a strong **PA** and a weak **PC** was investigated based on the solubility of the formed **PEC** precipitate in organic solvents and ternary mixed solvents composed of water, an organic solvent miscible with water, and a low-molecular-weight electrolyte[50]. Poly(vinyl sulfate) with different charge densities served as the **PA**, poly(L-lysine), as the **PC**. **PEC**s exhibiting the highest stability (lowest solubility) emerged when using the **PA** with the highest sulfatization degree, hence, possessing the highest charge density[50].



Scheme 7

### 3. 1. 3. *Reaction of Two Weak Polyelectrolytes*

Reactions of weak polyacids with weak polybases give rise[1] to **PEC**s whose composition and structure depend appreciably on the dissociation degrees of the **PEL**s. Knowing the dissociation degrees $\beta_{PA}$ and $\beta_{PC}$ in the actual reaction conditions, the composition of the electroneutral **PEC** formed by the neutralization reaction can be calculated theoretically as

$$\Phi = [PC]/[PA] = \beta_{PA}/\beta_{PC}. \qquad (2)$$

This relation has been verified experimentally[51] for the reaction of poly(vinylpyridine) with poly(L-glutamic acid), for the reaction of partly carboxymethylated and aminoacetylated poly(vinyl alcohol)[52 - 57] and also for the reaction of quaternated cellulose-based polycations with carboxymethylcellulose[58] (CMC). In systems poly(ethylene imine) (PEI)–PMAA and PEI–poly(methacrylic acid-*co*-methacrylic amide), however, complexes with four different compositions emerged in dependence on the component ratio in the reaction mixture[59].

The effect of the charge density on the **PEC** formation in this subgroup were the subject of papers[35,60], which studied reactions of carboxyethylcellulose and carboxymethylcellulose as pendent type **PA**s with poly(dimethyldiallylammonium chloride), and of carboxymethylcellulose (CMC) with cationically modified poly(acrylic acid-*co*-acrylic amide). The results gave evidence that in these systems the difference in the charge densities of the components does not affect the stoichiometry of the **PEC**s formed. In contrast to this, however, are the results of ref.[61], where the effect of the charge density was examined for various combinations of cationically and anionically modified poly(acrylic amide) copolymers by conductivity and turbidimetric measurements. These measurements revealed an appreciable increase in the [PC]/[PA] ratio with decreasing charge density of the two **PEL**s; this ratio was somewhat higher if **PA** solution was added to **PC** solution than vice versa. This difference increased with decreasing **PEL** charge density[61].

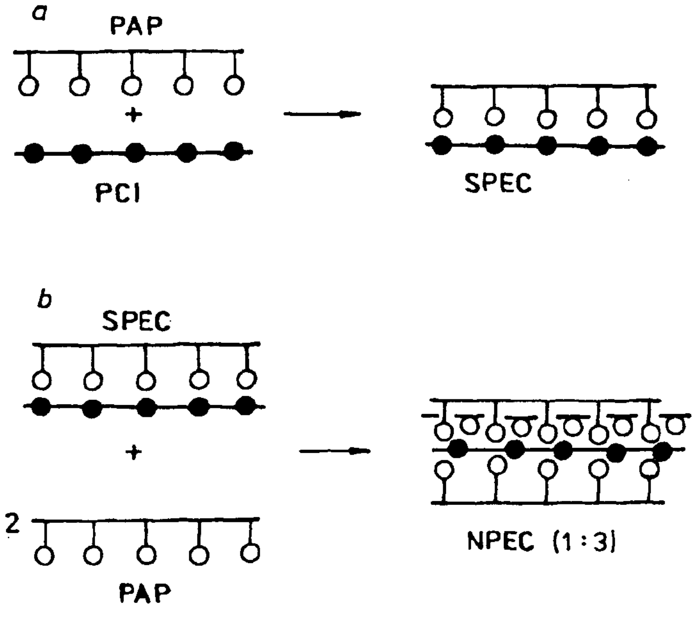
The effective charge density affects the form[62,63] of the **PEC**. Stoichiometric **PEC**s formed by **PEL**s with low charge densities separate from aqueous solutions as concentrated liquid phases; they are referred to as coacervate complexes. **SPEC**s which are formed by **PEL**s possessing high charge densities, separate from solution as gels or precipitates. The water content of gels can vary within wide limits in dependence on external conditions. Gels are considerably more stable and resistant to low-molecular-weight electrolytes than coacervate complexes are[62]. If the reaction conditions are varied, e.g. if the solution ionic strength is increased, **NPEC**s formed from **PEL**s with high charge densities separate as precipitates. While **NPEC**s formed from **PEL**s with low charge densities decompose readily, **NPEC**s formed from **PEL**s with high charge densities are more stable and dissociate completely to the components only at high solution ionic strength values[63]. The above results lead to the following partial conclusions: (i) Reactions of oppositely charged polyions formed by dissociation of high-charge-density **SPEL**s give rise to **SPEC**s. (ii) If one or both of the **PEL**s are weak, the effective charge density depends on the dissociation degree, hence, the latter will affect the composition of the **PEC**. (iii) The form of occurrence of the **PEC** formed (coacervate, gel, rigid solid) depends on the effective charge density of the two polyions: low-charge-density polyions give rise to polyelectrolyte coacervates, whereas very high-charge-density polyions form rigid solids.

## 3. 2. EFFECT OF THE IONIC FUNCTIONAL GROUP POSITION AND POLYELECTROLYTE STRUCTURE

Various steric effect that might influence the formation of **PEC**s have been examined, e.g. the position of the dissociable groups, the shielding effect of bulky substituents, rigidity of the polymeric chains, hydrophobicity of the chains, polymer configuration, etc. With respect to the position of the functional group capable of carrying charge, **PEL**s can be classed as pendent type and integral type[64], the charged groups being considerably less shielded in the latter than in the former[1].

### 3. 2. 1. *Reactions of Two Strong Polyelectrolytes*

In the case of two strong polyelectrolytes, addition of a solution containing polyanions of the pendent type (**PAP**) to a solution of polycations of the pendent type (**PCP**) gives rise to the separation of **SPEC** precipitate. The amount of the precipitate is proportional to the amount of **PAP** added up to the equivalence point, further it remains virtually constant (Fig. 2*a*). The reverse process, addition of **PCP** to **PAP**, is similar (Fig. 2*b*). If a polycation of the integral type (**PCI**), most frequently a **PEL** called ionene[1,64], is precipitated with a **PAP**, **SPEC** precipitates in a quantity proportional to the **PAP** addition up to the equivalence point (Fig. 2*c*); additional **PAP** after the equivalence point induces dissolution of the **SPEC** and formation of an **NPEC** with a constant composition, which is water soluble. At a certain **PAP**-to-**PCI** ratio, all the **SPEC** dissolves. Different [PCI]/[PAP] ratios can occur in the **NPEC***, e.g. 1 : 3 (ref.[64]), generally 1 : *b* where *b* is an integer higher than unity. In the reverse arrangement, the soluble **NPEC** with the given [PCI]/[PAP] ratio is first formed, the excess **PAP** remaining in solution. Only after the given ratio is attained in the whole system, additional **PCI** leads to the formation of the **SPEC**, which separates from the solution as a precipitate while the amount of the **NPEC** in the solution decreases. After attaining the equivalence point



SCHEME 8

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* Here and in analogous cases, [PEL] is the concentration of the monomeric PEL unit in the PEC, cf. Eq. (*1*).

the amount of the insoluble SPEC remains constant while the excess PCI remains in the solution (Fig. 2*d*). This reaction course is shown in Scheme 8. A similar solution has been observed for mixtures of the sodium salt of poly(acrylic acid) (PAA-Na) with 5,6-ionene bromide, where the solution complex with the [PCI] : [PAP] = 1 : 3 ratio was formed[65].

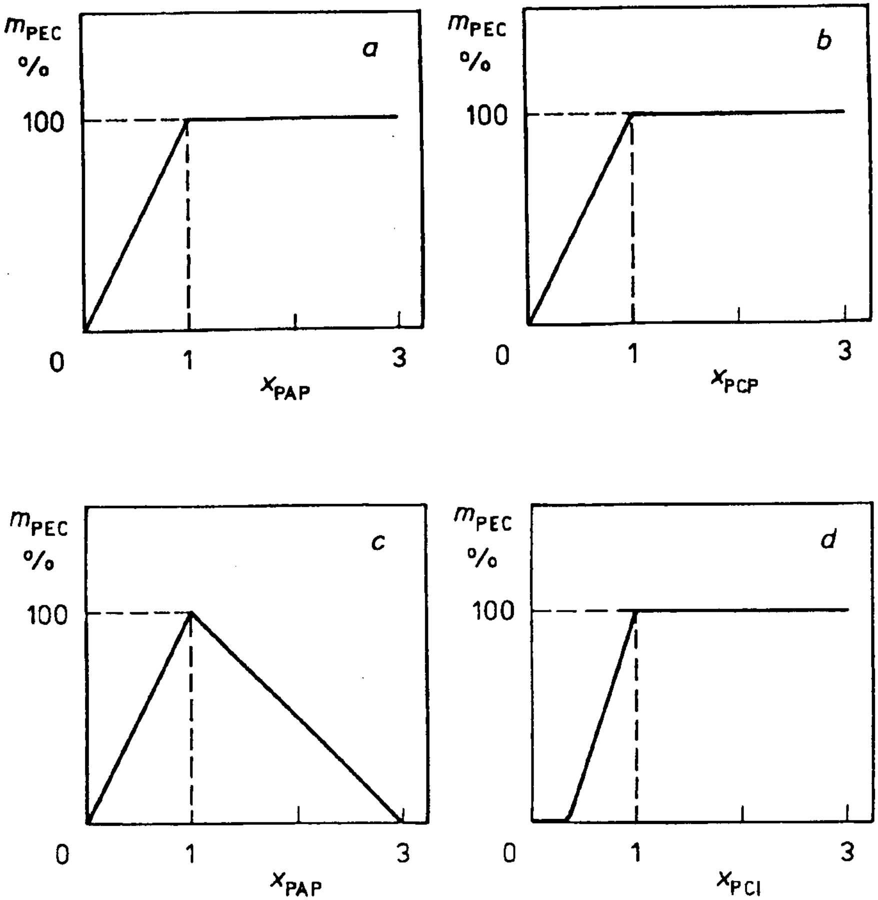

FIG. 2

Precipitation curves: *a* precipitation of a strong polycation of the pendent type (**PCP**) with a polyanion of the pendent type (**PAP**), *b* precipitation of a strong **PAP** with a strong **PCP**, *c* precipitation of a strong polycation of the integral type (**PCI**) with a strong **PAP**, *d* precipitation of a strong **PAP** with a strong **PCI** (taken from ref.[64], modified). Symbols: $m_{PEC}$ relative mass of the insoluble **PEC** per mass of the precipitate formed on mixing the two **PEL**s in a stoichiometric ratio, $X_{PAP}$ number of **PAP** equivalents per **PC** equivalent in the reaction mixture, $X_{PCP}$ number of **PCP** equivalents per **PAP** equivalent in the reaction mixture, $X_{PCI}$ number of **PCI** equivalents per **PAP** equivalent in the reaction mixture

### 3. 2. 2. *Reaction between a Strong Polyelectrolyte and a Weak Polyelectrolyte and Reaction between Two Weak Polyelectrolytes*

The effect of the structure of the **PELs** on the formation of the **PEC** for a **SPEL** and a **WPEL** has been examined in ref.[66]. The authors[66] attempted at a quantitative description of the effect of the steric arrangement on the degree of conversion in the **SPECs** formed. The degree of conversion (Θ) is the ratio of the number of ion pairs actually formed in the complex to the maximum number of ion pairs that can form; it can attain values from 0, if no ion pair occurs and the complex has formed through electrostatic interaction of the polyions, to 1, if the maximum possible number of ion pairs has formed. For systems of poly[2-(N,N-dimethylamino)ethyl methacrylate] (PDMAEMA) as a weak polybase and a salt of a strong acid (PSS-Na) and a copolymer of this acid with two kinds of nonionogenic comonomers of different bulkiness, the Θ value in the **SPECs** was found to linearly decrease with increasing fraction of the nonionogenic groups ($x$) in the copolymer according to the substituent bulkiness. This effect has been quantified by means of constant $s$, called the "shielding coefficient", in the relation

$$\Theta = \Theta_0 - sx\,, \tag{3}$$

where $\Theta_0$ is the degree of conversion in the **SPEC** formed from PDMAEMA and PSS-Na at a certain pH and ionic strength of the solution. The constant $s$ is higher for higher substituent bulkiness. Linear poly(ethylene imine) has been observed[67] to displace poly(N-tert-butylazirine) from complexes with **PAA** or **PMAA**, which is consistent with the assumption that the stability of ionic bonds in the formed **PEC** is reduced by the presence of a bulky nonpolar substituent at the functional group of an integral type **PEL**.

The length of the N-alkyl substituent of the quaternizing nitrogen atom in the poly(4-vinylpyridine) cation also affects the stability of the **PEC** (ref.[68]). This effect was evaluated in terms of the amount of low-molecular-weight electrolyte added, at which the **PEC** dissociated to the starting polyions. The stability was examined for the **NPEC** formed by interaction between quaternized poly(vinylpyridine) and salts of PMMA or polyphosphates, and for the **SPEC** where polyphosphate was used as the **PA**. The **PEC** stability was found[68] to decrease for the substituent series methyl > ethyl > propyl > aryl.

The hydrophobicity of strong **PCIs** (ionenes) was examined by fluorescence measurement in ref.[69] and was found to increase with the length of the carbon chain between the positively charged groups, hence in the series 4,4 < 2,X < 6,X ≈ X,X ≈ 6,6 < 8,8 < 10,10-ionene. Hydrophobic interactions did not affect the stoichiometry of the **PECs** formed, which is determined by the Coulomb interactions, but contributed to the increase in the stability of the **PECs** formed[70,71].

The effect of configuration on the **PEC** structure was studied for the system of poly(L-lysine) with poly(methacrylic acid) with different tacticities (isotactic, syndiotactic, atactic)[72]. The change in the α-helical structure of the poly(L-lysine) in the complex was investigated in dependence on the PMAA configuration. Isotactic PMAA with a high structure regularity causes an α-helical structure in the **PEC**, whereas commercial PMAA, which is virtually atactic, with a low structure regularity, causes two effects: formation of the α-helix, and a destructive effect. The helical structure content increases in order: atactic ≤ commercial < syndiotactic << isotactic[72]. Conformation changes in the macromolecular chains of the **PEL** were also investigated during the formation of **PEC**s with **PEL**s having a specific conformation, such as α-helix, β-structure of the compound leaf, double helix, etc. According to the structure of the arranged **PEL** (conformation, charge density, position of the dissociable group, rigidity, side chain length), the conformation of the oppositely charged **PEL** in the **PEC** changes[73 - 89].

For **PEC**s formed by reactions of **PEL**s with rigid polymeric chains such as modified polysaccharides, their stoichiometry was examined. The glycolchitosan–sulfated cellulose and glycolchitosan–hyaluronic acid systems do not form **SPEC**s whereas the glycolchitosan–heparin system does[90 - 92]. More recent papers[93 - 97] dealing with reactions of chitosan with synthetic or modified natural **PEL**s such as PAA, 2,5-ionene, PDMAEMA, CMC, glycosanaminoglycan, etc., report that if the optimum reaction conditions (pH, ionic strength) are adhered to, **SPEC**s can also be obtained with such rigid polymeric chains.

Some specific effect are observed in heterogeneous reactions of crosslinked **PEL**s with linear **PEL**s[98 - 103]. However, there exist few original works dealing with the formation of **PEC**s under heterogeneous conditions, and so no general conclusion can be made.

The above facts show that interactions of two oppositely charged pendent type **SPEL**s invariably afford stoichiometric (1 : 1) insoluble **PEC**s. Interactions of integral type **PEL**s result in insoluble **SPEC**s as well, these, however, are soluble in excess **PEL** of the pendent type; the system then simultaneously contains insoluble **SPEC** and soluble **NPEC**, the latter having, for the given **PEL**s, a constant composition with [PCI]:[PAP] = 1 : *b*. Steric effects do not influence appreciably the stoichiometry of the complexes but they affect the Θ value as well as the **PEL** conformation in the **PEC**. The Θ values invariably decrease with increasing substituent bulkiness and the number of defects in the **PEC** structure increases. If there are many defects in the structure, at Θ << 1, the **SPEC** precipitate in the aqueous solution can dissolve. This is due to the hydrophilic nature of the **PEC** molecule, which in this case can be looked upon as a block polymer containing alternating hydrophobic and hydrophilic blocks[44,104,105]. The formation of defects can also be due to the fact that the majority of polyions adopt the conformation of statistical coils[34] before the reaction, the ionic reaction being virtually instantaneous[1,46,106].

### 3. 3. EFFECT OF THE POLYMERIZATION DEGREE OF THE POLYELECTROLYTE

The last molar parameter to be dealt with in this paper in relation to the effect on the **PEC** formation is the polymerization degree of the polyelectrolyte, $P_{\mathrm{PEL}}$*.

### 3. 3. 1. *Reaction between Two Strong Polyelectrolytes*

No effect of the polymerization degree on the **PEC** formation has been observed for pairs of **SPELs**[1,36]. If solutions of **SPEL** salts are mixed in the equivalent ratio, the **SPEC** is formed irrespective of whether both of the **PELs** involved have high polymerization degrees or whether one has a high degree of polymerization whereas the other has a low degree of polymerization. If the **SPELs** are mixed in a nonstoichiometric ratio, the overstoichiometric amount of the one **SPEL** remains in solution while the **SPEC** separates from the solution, regardless of the combination of the polymerization degrees.

### 3. 3. 2. *Reactions between Strong and Weak Polyelectrolytes*

If a solution of a **WPEL** is added to a solution of an oppositely charged **SPEL** with a comparable polymerization degree, insoluble **SPEC** forms in an amount corresponding to that of the **WPEL** added, the excess **SPEL** remaining in solution. This is so until the equivalence point is reached; thereafter, addition of the **WPEL** brings about dissolution of the precipitate and formation of an **NPEC** having a constant composition ($\Phi_c$). After all of the **SPEC** has been transformed into that **NPEC**, additional quantities of the **WPEL** do not induce change in the **NPEC** composition[65,107 - 109]. The formation of the water-soluble **NPEC** from the **SPEC** formed by addition of a **WPEL** to a **SPEL** having a nearly identical $P_{\mathrm{PEL}}$ is shown in Scheme 9.

In the reverse procedure, viz. addition of a solution of a **SPEL** to a solution of a **WPEL**, a soluble **NPEC** with a constant composition is formed, the excess **WPEL** remaining in solution. When the amount of the added **SPEL** is higher than as corresponds to the quantitative formation of the **NPEC** from the **WPEL**, the insoluble **SPEC** is formed and coexists with the **NPEC** once formed. The amount of **SPEC** in the mixture increases until the equivalence between the **SPEL** and **WPEL** is reached.

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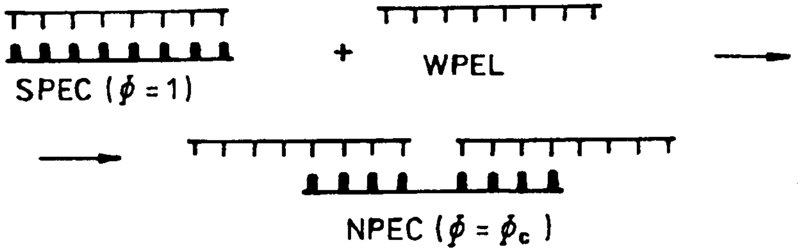
* In the papers cited, fractionated **PELs** were invariably used with a narrow polymerization degree distribution, where the assumption that $P_w \approx P_n \approx P_{\mathrm{PEL}}$ is warranted.

Additional **SPEL** does not bring about any change and its overstoichiometric quantity remains unreacted in the solution[65,108,109].



Scheme 9

If a **WPEL** with a high polymerization degree – the host polyelectrolyte (**HPE**) – is reacted with a **SPEL** with a low polymerization degree – the guest polyelectrolyte (**GPE**) – in a nonstoichiometric ratio, an **NPEC** with excess **HPE** forms if the latter is present in excess. The unreacted segments of the **HPE** chain cause solubility of the **NPEC** in aqueous solution and determine the resulting charge of the whole complex. In this case the composition is defined as the ratio of the number of **GPE** mers to the number of **HPE** mers in the **NPEC** formed, and can be expressed as[110]

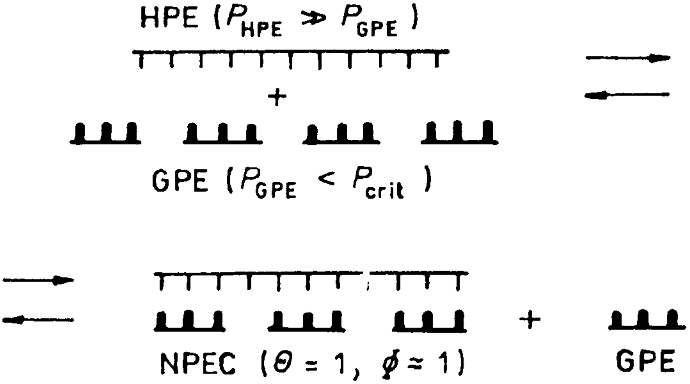
$$\Phi = [\mathrm{GPE}]/[\mathrm{HPE}] \qquad (4)$$

(the above remarks concerning the quantities in brackets hold true).

The $\Phi$ values are between 0 and 1, and determine the **NPEC** properties. Until this value exceeds a characteristic value $\Phi_{\mathrm{char}}$, which depends on the properties of the **PELs** forming the **NPEC** and mostly lies between 0.2 and 0.5, the reaction products are soluble in water and in aqueous solutions of salts[107].

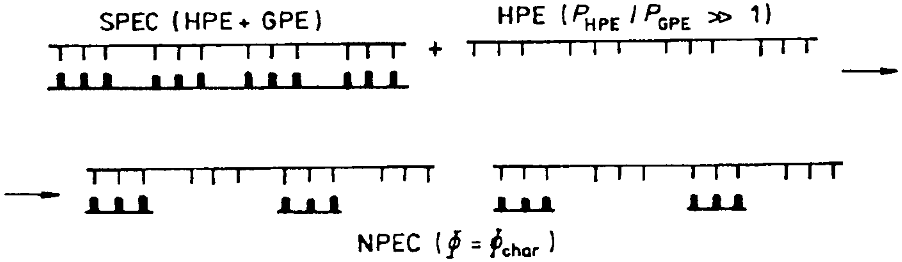
If solutions of **GPE** and **HPE** are mixed in the equimolar ratio, the **SPEC** ($\Phi = 1$) is formed with $\Theta \leq 1$. The $\Theta$ value depends on the effective charge density of the weak **HPE**. If $\Theta < 1$, this value increases on decreasing the polymerization degree of the **GPE** ($P_{\mathrm{GPE}}$) at the same effective charge density of the weak **HPE**. When a certain $P_{\mathrm{GPE}}$ value, the so-called critical polymerization degree $P_{\mathrm{crit}}$, is attained, the maximum number of ion pairs forms in the **SPEC** ($\Theta = 1$). At $P_{\mathrm{GPE}} \leq P_{\mathrm{crit}}$, $\Theta$ is always unity but the composition of the complex, which is dependent on the effective charge of the **HPE** and its polymerization degree ($P_{\mathrm{HPE}}$) as well as on the **GPE** used, is different from 1; an insoluble **NPEC** whose composition is near to unity is formed[106]. An equilibrium, represented by Scheme 10, establishes in the solution between the **NPEC** and free **GPE** molecules. The $P_{\mathrm{crit}}$ value depends on the actual **PEL** pair and actual reaction conditions; values of tens of monomeric units are commonly encountered[106,111].

If the **GPE** is added to the solution of **HPE**, an **NPEC** is formed whose composition corresponds to the **GPE**-to-**HPE** ratio and varies with the addition of the **GPE** so that the Φ value increases proportionally to the **GPE** amount added. This implies that the **GPE** chains are distributed uniformly among all the **HPE** chains in the reaction mixture. (This is different from systems containing a **WPEL** and a **SPEL** with roughly identical $P_{\mathrm{PEL}}$'s, where an **NPEC** with a constant composition forms and excess **WPEL** remains in solution.) This change in the **NPEC** composition proceeds until a characteristic Φ value ($\Phi_{\mathrm{char}}$) is attained; additional **GPE** leads to the formation of the insoluble **SPEC**, so that a precipitate of the **SPEC** and the dissolved **NPEC** ($\Phi = \Phi_{\mathrm{char}}$) coexist. The amount of the **SPEC** increases and that of the **NPEC** decreases proportionally to the addition of the **GPE** until equivalence between the **GPE** and **HPE** is reached. Only the **SPEC** exists in the system in this point. Additional, overstoichiometric **GPE** does not affect the **SPEC** and remains unreacted in the solution[62,108,110,112–116].



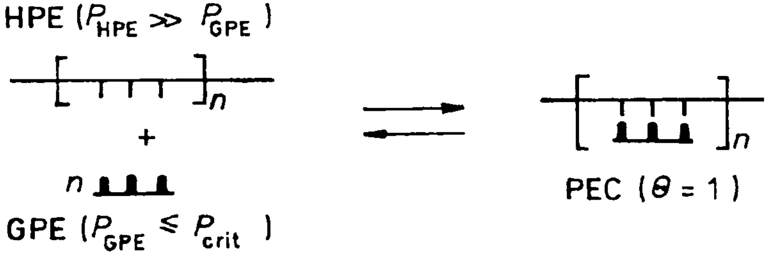
SCHEME 10

The behaviour of the **GPE–HPE** system thus depends on whether the former is added to the latter or vice versa but the properties of the resulting **PEC** formed on adding the **GPE** to the **HPE** or vice versa are the same irrespective of the preparation procedure, provided that **PEC** of the same composition and the same Θ value has formed[80,81]. If the **HPE** solution is added to the **GPE** solution, **SPEC** precipitates in an amount proportional to that of the **HPE** added till the equivalence point is reached. Overstoichiometric **HPE** causes dissolution of the **SPEC** and formation of a soluble **NPEC** (Scheme 11) with a characteristic composition[108,110,112–116]. In a simplification, its structure is that of a block copolymer with alternating hydrophilic and hydrophobic blocks[44,104]. The former involve a charged **HPE** chain which is hydrated and sustains the **NPEC** in solution, whereas the latter involve double chains of **HPE** and **GPE** macromolecules linked by ionic bonds, because due to the electrostatic interactions the functional group lose, partly or completely, their hydration shells whereby this segment loses its hydrophilic nature.



SCHEME 11

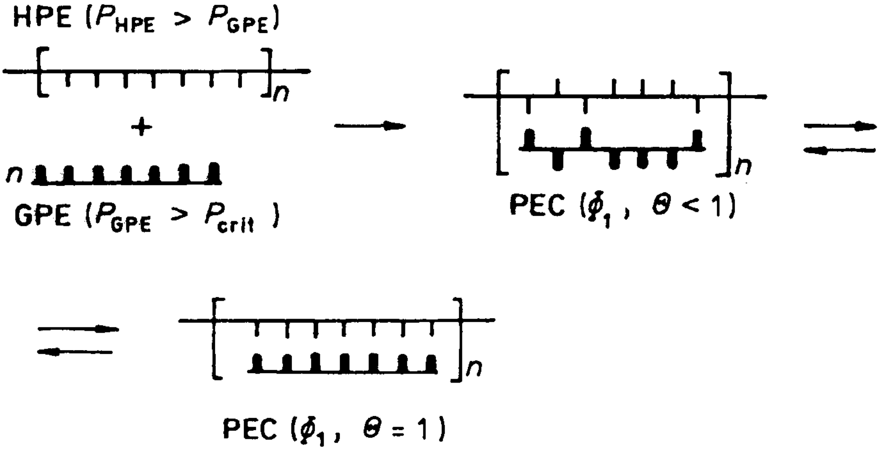
The above analysis indicates that the polymerization degree of the polyelectrolyte affects appreciably the formation of the complex. Various combinations of the macromolecular chain and component proportions in solution can lead to **SPEC**s, which can be water insoluble or soluble, and to **NPEC**s having various properties. Hence, the **PEC**s formed differ in their composition as well as in their degree of conversion. This implies that equilibria of two kinds establish in the solution. The one equilibrium pertains to reversible association of segments of **HPE** macromolecules with oligomeric **GPE** molecules, as shown in Scheme 12. This equilibrium occurs provided that $P_{HPE} >> P_{GPE}$ and that $P_{GPE} < P_{crit}$. Since we always have $\Theta = 1$ in such circumstances, the



SCHEME 12

equilibrium only affects the ratio of the oligomeric **GPE** molecules bonded to the **HPE** chains to those in solution, hence, the composition of the complex formed. The other kind of equilibrium pertains to the behaviour of the **HPE** and **GPE** macromolecules if the polymerization degree of the latter is higher than the critical value. This equilibrium is shown in Scheme 13. In this case one must discriminate between bonded pairs (forming ion pairs) and nonbonded pairs of oppositely charged functional groups in the **HPE** and **GPE** chain segments. In such conditions of the reaction ($P_{GPE} > P_{crit}$ and $P_{HPE} > P_{GPE}$), no free **GPE** macromolecules occur in the solution as long as

[GPE]/[HPE] ≤ 1 in the reaction mixture, but the Θ value of the PECs formed, with a composition Φ, can change.



SCHEME 13

The determination of the degree of conversion was also the concern of ref.[117], which studied the protein–sulfosynthane (a strong oligoelectrolyte) system. The Θ value (referred to as the sulfo-group bonding parameter, $p$) of the PEC formed was found and calculated to be unity.

### 3. 3. 3. *Reaction between Two Weak Polyelectrolytes*

Reaction of two oppositely charged WPELs with approximately identical polymerization degrees, mixed in a nonstoichiometric ratio, gives rise to NPECs whose composition is identical with the reactant ratio[118]. In contrast to that, reaction in the poly(potassium methacrylate)–PEVP-Br system only provides the water-insoluble SPEC, regardless of the component ratio[47].

## 4. EFFECT OF REACTION CONDITIONS ON THE FORMATION OF POLYELECTROLYTE COMPLEXES

The nature and formation of PECs can also be affected by the reaction conditions such as solution pH, ionic strength, solvent and temperature.

### 4. 1. EFFECT OF pH OF MEDIUM

The pH of the medium is among the most important reaction conditions with respect to the **PEC** formed because the activity of $H^+$ ions determines the instantaneous degrees of neutralization of the two **PELs** and thus also their dissociation degrees (particularly for **WPELs**) and the effective charge densities. In other words, the $H^+$ activity affects appreciably the strength of the polyions formed, and since the stoichiometry as well as the structure of the **PECs** is dependent on the charge densities of the polyions, the pH value will affect significantly the formation of the **PECs**, particularly if at least one of the **PELs** is weak.

#### 4. 1. 1. *Reaction of Two Strong Polyelectrolytes*

Strong polyelectrolytes can be assumed to be completely dissociated in solution over a wide pH region. This implies that over a wide pH region, the insoluble **SPEC** is formed, both during the reaction of two oppositely charged pendent type **PELs** and during the reaction of a pendent type **PEL** with an integral type **PEL**[1,34]. The case where the reaction mixture contains an integral type **PEL** and an overstoichiometric amount of a pendent type **PEL** is an exception[64]. The formation of an **NPEC**, however, is due to the position of the charged functional groups in the integral type **PEL** rather than to the pH value.

#### 4. 1. 2. *Reaction between a Strong Polyelectrolyte and a Weak Polyelectrolyte*

If one of the reacting **PELs** is a **WPEL** (2nd **PEC** subgroup), the pH plays an important part in the **PEC** formation because it affects the dissociation degree of the **WPEL** and thereby the effective charge density of the polyion formed by its dissociation, which in turn affects the composition ($\Phi$) and degree of conversion ($\Theta$) of the **PEC**, the dissociation degree of the **WPEL** being independent of the initial degree of neutralization.

The composition of the **PEC** formed by reaction of a completely dissociated **SPEL** and a **WPEL** dissociated to degree $\beta$ can be calculated from Eq. (*1*). This equation demonstrates that the **PEC** will be the closer to the stoichiometric composition the more closely the dissociation degree of the **WPEL** approaches unity. The $\beta$ value of the **WPEL** can primarily be affected via the solution pH. Thus, a suitable pH is a precondition for the formation of the **SPEC**: this is the basic region for weak polyacids, and the acid region for weak polybases.

The pH also affects the $\Theta$ value of the **PEC**. According to the $\Theta$ value and the reaction conditions, the **SPECs** and **NPECs** can be soluble or insoluble in aqueous media. The maximum degree of conversion of the **SPEC** at which the complex is still soluble (i.e. the $\Theta_{char}$ value) depends on the nature of the **PELs** and typically lies[46,78,104,119 - 121] within the range 0.2 to 0.5.

If equivalent amounts of a **WPEL** and a **SPEL** are mixed at a pH which is unfavourable to the dissociation of the former, an insoluble **NPEC** is formed. This **NPEC** has a constant composition and contains excess **WPEL**, whereas the **SPEL**, if present in excess, remains in solution. The degrees of conversion of insoluble **NPECs** are lower than 1 (refs[46 - 48, 66, 121]). The most common **NPECs** emerging from reactions of poly(carboxylic acids) with various counter-**PELs** in acid region exhibit $\Phi$ within the region of 0.1 – 0.5 (ref.[1]). By changing the pH, the insoluble **NPEC** can be converted to the insoluble **SPEC**, viz. by increasing the pH of systems involving a weak polyacid and by decreasing the pH in systems involving a weak polybase. Over a certain pH range, the insoluble, constant-composition **NPEC** (whose $\Theta$ value is pH dependent) and the unreacted **SPEL** coexist. Starting from a certain pH, which depends on the nature of the **WPEL**, the **NPEC** composition also changes and ultimately transforms into the **SPEC**. At the pH at which the **SPEC** forms, the degree of conversion in the latter is lower than $\Theta_{char}$ and the **SPEC** is soluble in aqueous medium. Additional change in pH brings about increase in the $\Theta$ value, and after the $\Theta_{char}$ value is reached, the insoluble **SPEC** separates. The changes in the **PEC** composition and in the $\Theta$ values occur across a narrow pH region[119], as Fig. 3 demonstrates. In fact, pH change leading to an increase in the neutralization degree in the **WPEL** also brings about increase in its dissociation degree, which in turn gives rise to new reaction sites forming ionic bonds with the oppositely charged groups of the **SPEL**; this is associated with an increase in the $\Theta$ value and a change in the **PEC** composition.

The effect of the degree of conversion in the **PEC** on its properties has been examined viscometrically and by sedimentation measurements for the reaction of equivalent amounts of poly(sodium phosphate) (PPh-Na) and PDMAEMA (ref.[119]) (Fig. 4)*. At $\Theta < 0.25$, the sedimentation coefficient decreases and the reduced viscosity increases due to the attachment of PPh-Na to the **PEC** particles, which is associated with an increase in their hydrodynamic volume. The minimum sedimentation coefficient value and the maximum reduced viscosity are then obtained during the formation of the soluble **SPEC** whose $\Theta$ value is 0.25. At higher $\Theta$ values the viscosity of the system decreases and the sedimentation coefficient increases due to conformation changes in the **SPEC** particles, leading to their higher compactness. This effect is caused by

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* The $\Theta$ values for the behaviour of the system to which Fig. 4 pertains are calculated for the **SPEC**. Hence, the $\Theta$ value is calculated here as the ratio of the formed ionic bonds in the complex (**NPEC** or **SPEC**) to the maximum number of functional groups capable of carrying a charge in the **WPEL**. In the **NPEC**, the **WPEL** is present in excess, and therefore the $\Theta$ value in Fig. 4 does not correspond to the true $\Theta$ for this **NPEC** as defined. For $\Theta = 0.2$, the true degree of conversion in an **NPEC** with, e.g., $\Phi = 0.2$, equals one.

hydrophobization of the **SPEC** macromolecules. At $\Theta = 0.5$, the **SPEC** loses its solubility and separates from the solution as a precipitate or coacervate[119].

If the insoluble, constant-composition **NPEC** emerging from the reaction between a low-dissociated **WPEL** and a **SPEL** is isolated and transferred into water at the same pH as was that of the reaction mixture, it remains insoluble, but a pH change (addition of an acid or base) transforms it into a soluble **NPEC** having the same composition. The basis of this transformation is conversion of undissociated functional groups of the **WPEL** into the dissociated state and thereby, formation of hydration shells about these charged groups. It is also prerequisite for the formation of the soluble **NPEC** that its $\Phi$ value be lower than the corresponding $\Phi_{char}$ value[108,110,116]. The behaviour of soluble **NPEC**s formed by reaction of a **WPEL** with a **SPEL** in an unsuitable pH region where dissociation of the **WPEL** is suppressed, followed by conversion of the insoluble **NPEC** into the soluble **NPEC** by changing the pH, is the same as the behaviour of soluble **NPEC**s obtained by mixing nonequivalent quantities of the corresponding alkali salt of the weak polyacid and a salt of the strong polybase in a suitable pH region, provided that the two resulting **NPEC**s have the same composition and degrees of conversion[108,109].

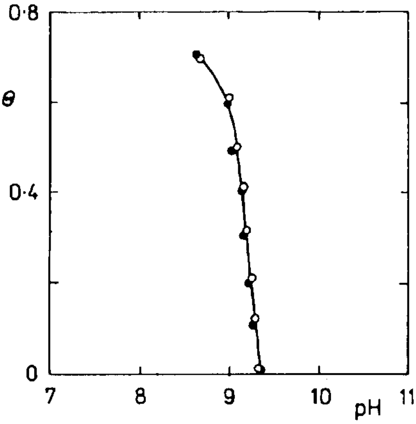


FIG. 3

Dependence of the degree of conversion in polyelectrolyte complexes on the final pH of the reaction mixture. Aqueous solutions of polyelectrolytes (15 meq $l^{-1}$) mixed in equimolar proportions: ○ complex from PPh-Na and PDMAEMA, ● complex from PAA-Na and PDMAEMA

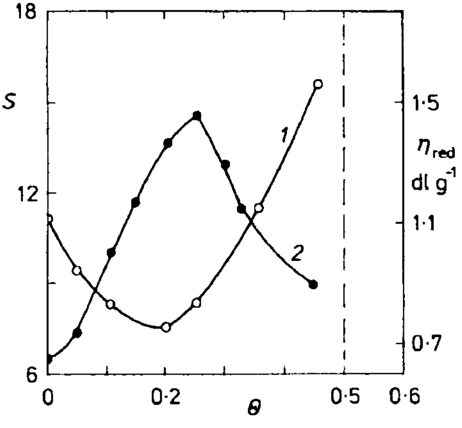


FIG. 4

Dependences of the sedimentation coefficient of the **SPEC** (*1*) and of the reduced viscosity (*2*) of the reaction mixture on the degree of conversion after mixing aqueous solutions of PPh-Na and PDMAEMA (15 meq $l^{-1}$) at 20 °C. Broken line shows boundary between the homogeneous system (soluble **SPEC**) and the heterogeneous system (insoluble **SPEC**)

### 4. 1. 3. *Reaction between Two Weak Polyelectrolytes*

In the reaction of two **WPELs** (3rd **PEC** subgroup), the **SPEC** is only formed across the narrow pH range where the two **WPELs** are dissociated to the maximum degree. The **SPEC** has the character of a polyelectrolyte coacervate[1,51]. At lower or higher pH's the complex does not form at all, if the degree of dissociation of the weak polyacid or polybase is very low, or there forms an insoluble **NPEC** containing excess of that **WPEL** which is less dissociated in the conditions applied.

For **SPECs** obtained by reactions of pairs of **WPELs**, the pH dependence of the degree of conversion has been examined in the acid as well as in the basic region[78,108]. In the basic region the shape of the curve is similar to that shown in Fig. 3, it is, however, shifted to lower pH values. In the acid region, however, the curves are less steep than in the basic region, as are the dependences observed for **SPECs** between weak polyacids and strong polybases. As compared to the weak acid–strong base combination, the curves in the acid region for the weak polyacid–weak polybase are shifted to higher pH values[78,108].

Insoluble **NPECs** formed by reactions of pairs of **WPELs** mixed in equivalent ratios at a higher or lower pH can be transformed, by a suitable pH change, into the soluble **SPECs** (at lower $\Theta$ values) or insoluble **SPECs** (at $\Theta > \Theta_{char}$). The situation is similar for the **PEC** subgroup formed by combination of a **WPEL** with a **SPEL**. The pH must be changed so as to reach that value at which the two **WPELs** simultaneously exhibit the maximum dissociation degree, that is, towards the neutral region[108].

If the insoluble **NPEC** has been isolated from the reaction mixture and transferred into an aqueous solution at the same pH, it can be converted into the soluble **NPEC** of the same composition by a suitable pH change, i.e, by adding a low-molecular-weight base or acid. In contrast to the 2nd **PEC** subgroup (**SPEL–WPEL** combination), soluble **NPECs** in this subgroup can have a positive or negative charge according to the solution pH. If the insoluble **NPEC** has been formed in the acid or basic region, the resulting charge of the soluble **NPEC** is negative or positive, respectively. Another prerequisite for the formation of the soluble **NPEC** also is a $\Phi$ value not higher than $\Phi_{char}$. For a given combination of two **WPELs** there can exist two different $\Phi_{char}$ values in dependence on the functional groups of that **PEL** which is contained in excess in the **NPEC**.

## 4. 2. EFFECT OF SOLUTION IONIC STRENGTH

The ionic strength of the solution is determined by the concentration of the **PELs** and/or the concentration of the low-molecular-weight electrolyte. The effect of the ionic strength has only been examined for inert uni-univalent electrolytes.

A simple electrolyte dissociates into small ions, whereupon the average concentration of counterions and co-ions in solution increases. The counterions are attracted by the electrostatic field of the polyion and their concentration in its vicinity thus increases, whereas co-ions are displaced from its vicinity. Due to the increased concentration of counterions in the ionic atmosphere of the polyion the shielding between the polyion groups of the same charge increases, as does the number of ion pairs formed between the charged groups of the polyion and the counterions (Manning counterion condensation[34,122 - 128]), due to which the effective charge density of the polyion decreases[37,129 - 136]. As a result of the two effects, the polyion coil contracts, and this effect is further intensified by the high concentration of co-ions in the surrounding solution. During the fast ionic reaction the polyionic coils fail to copy their shapes and form a **PEC** by the zipping mechanism acting in the case of dilute solutions of the simple salts, where **PEC**s with a ladder molecular structure emerge[37] (Fig. 2*b*). Ion pairs between oppositely charged functional groups thus only form within certain polyion segments; the remaining segments only mutually compensate their electrostatic fields. **PEC**s with the prevailing scrambled egg structure are formed[37]. This implies that the degree of conversion is lower than 1 and decreases with increasing ionic strength.

### 4. 2. 1. *Effect of the Polyelectrolyte Own Concentration in Solution*

#### 4. 2. 1. 1. Reaction between Two Strong Polyelectrolytes

In the first subgroup of **PEC**s, which are formed by reaction between two **SPEL**s, the **SPEC**s can be expected to form across a wide **PEL** concentration region because the **SPEL**s should be completely dissociated. This presumption has been confirmed experimentally in ref.[1], where a PMAA salt ($\alpha = 1$) in conditions of its complete dissociation was reacted with a strong polycation, viz. 2,X-ionene, to obtain the **SPEC** ($\Phi = 1$) irrespective of the final **PEC** concentration.

#### 4. 2. 1. 2. Reaction between a Strong Polyelectrolyte and a Weak Polyelectrolyte

In the second subgroup of **PEC**s, formed by reaction of a **SPEL** with a **WPEL**, the concentration of the **PEL** affects the composition of the **PEC**. As the concentration increases, the dissociation degree of the **WPEL** decreases and so does the charge density, whereupon the composition of the **PEC** changes[1]. Actually, the number of reaction sites capable of reacting with the **SPEL** decreases and an **NPEC** is formed (the $\Phi$ value lowers). Despite these conclusions, the authors[121] found that if salts of **WPEL**s are reacted with salts of oppositely charged **SPEL**s, **PEC**s emerge whose $\Theta$ values are independent of the starting **PEL** concentration ($c_0 = 0.5 - 10$ meq $l^{-1}$). No effect of the component concentrations on the "yield" of the insoluble **PEC** was also observed in the reaction between a solution of fully protonated gelatine and a solution of the sodium salt of sulfo-synthane (a strong oligoelectrolyte)[137].

#### 4. 2. 1. 3. Reaction between Two Weak Polyelectrolytes

In the third subgroup of **PEC**s, formed by reaction between two **WPEL**s, the **PEL** concentration should have a substantial effect on the composition of the **PEC**. This composition should depend on how the dissociation degree varies for the two **WPEL**s on increasing their concentration in the solution. If the dissociation degrees of the two **WPEL**s changed in the same manner, the composition of the **PEC** formed should not change (Eq. (*2*)).

### 4. 2. 2. *Effect of Concentration of Low Molecular Weight Salt*

#### 4. 2. 2. 1. Reaction between Two Strong Polyelectrolytes

The reaction of two **SPEL**s gives rise to the insoluble **SPEC** across a wide region of salt concentrations[1,36]. If the solutions contain a low-molecular-weight electrolyte in an extremely high concentration, the **PEL**s separate from the solution due to the Manning counterion condensation[34,122 – 128].

If the concentration of the low-molecular-weight salt in a dilute solution of the **PEL**s is fairly but not extremely high, ion pairs form between the functional groups of the polyions and the low-molecular-weight counterions. The number of ion pairs depends on the ionic strength and on the salt used. If two **SPEL**s with charge densities reduced in this manner are reacted, the **SPEC** should form again, its degree of conversion, however, should be different ($\Theta < 1$) in dependence on the concentration and kind of the low-molecular-weight salt used. If the two oppositely charged **SPEL**s form together stronger ionic bonds than with their counterions, the reaction will be associated with a displacement of the low-molecular-weight counterions from the formed ionic bonds with the polyion, and the **SPEC** will emerge with a degree of conversion approaching or equal to unity. This **SPEC** cannot be dissolved or dissociated into components by addition of the simple salt. A mixed ternary solvent containing water, a water-miscible organic solvent and a low-molecular-weight electrolyte, such as water–acetone–NaBr, must be used to dissolve the **SPEC** (refs[1,36,37]).

#### 4. 2. 2. 2. Reaction between a Strong Polyelectrolyte and a Weak Polyelectrolyte

If simple electrolytes are present in the **PEL** solutions in low concentrations, a low number of ion pairs form between the weak polyion and the counterions, and so the insoluble **SPEC** with $\Theta \approx 1$ should emerge. As the concentration of the salt is raised, the number of ion pairs should increase and the $\Theta$ value of the **SPEC** should decrease. This implies that the number of hydrophilic regions (loops, tails) in the **SPEC** structure increases. After attaining a certain proportion between the hydrophobic and hydrophilic regions in the structure, the **SPEC** dissolves. The $\Theta$ value, naturally, decreases. The soluble **SPEC** then can be looked upon as a special block copolymer which consists of hydrophobic and hydrophilic blocks[44,104,105,108]. Further increase in the salt concentration in the system ultimately results in complete dissociation of the **SPEC** to the starting components[62,138,139]. The salt concentration in solution at which the soluble **SPEC** with a low Θ value emerges, depends on the interaction of the low-molecular-weight counterion with the **WPEL** and on the properties of the **PEL**s used.

Instead of the soluble **SPEC**, an insoluble **NPEC** enriched with the **WPEL** can form in the same conditions; the functional groups of the incorporated **WPEL** which have not formed ion pairs with the oppositely charged groups of the **SPEL** are neutralized with counterions (ion pairs formed). Which kind of **PEC** is formed, is determined by the kind of the low-molecular-weight salt.

The concentrations of low-molecular-weight electrolytes at which the heterogeneous systems transform into homogeneous systems (the **SPEC**s dissolve), for a given **SPEC** concentration in the system, can be characterized by phase separation curves in the phase diagrams[138]. Phase diagrams of some systems are shown in Fig. 5. The curves are unsymmetrical, exhibiting a maximum at low **PEC** concentrations. The phase diagrams agree in their shape with those of coacervate complexes forming on mixing **PEL**s with low charge densities[140 - 142]. For coacervate complexes, the homogeneous systems exist at lower concentrations of the simple salts. The concentration of the low-molecular-weight electrolyte at which the insoluble **SPEC** transforms to the soluble **SPEC** depends on the chemical structure of the **PEL**s involved (Fig. 5). Moreover, this value is also affected by the kind of the low-molecular-weight salt and by the molecular weight of the **PEL**s (ref.[138]). This phenomenon is associated with the different ability of the counterions to bond to charges of the corresponding polyions. It is clear that the higher the ability of the counterion to bond to the charged group of the polyion, the lower the concentration of the corresponding low-molecular-weight electrolyte requisi-

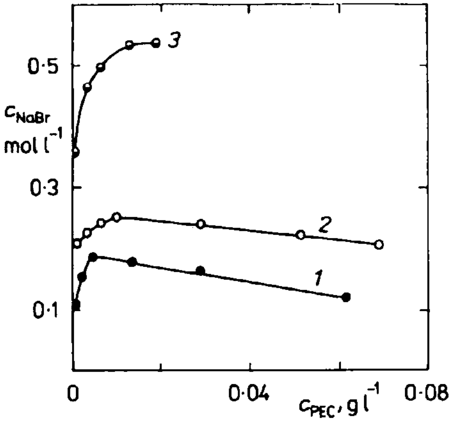


FIG. 5

Phase diagrams of polyelectrolyte complex–water–NaBr systems at 20 °C. PEC: *1* PMAA-Na–PEVP-Br, *2* PAA-Na–PEVP-Br, *3* PPh-Na–2,5-ionene te to disturb the ion pairs formed between the oppositely charged functional groups of the two **PELs**. The bonding of alkali metal cations to the polymethacrylate anion is higher for potassium ions than for sodium ions, and the bonding of halide ions to the poly(N-ethyl-4-vinylpyridinium) cation increases in order $F^- < Cl^- < Br^-$. These facts are consistent with the data of the Manning condensation of the counterions of the **PELs** alone[34,122 - 128]. For **PELs** with lower molecular weights (lower polymerization degrees), the **SPEC** dissolves at a lower concentration of the low-molecular-weight electrolyte[138].

The behaviour in aqueous solutions of simple salts is considerably different for soluble **NPECs**, formed by reaction of a **WPEL** with a relatively high polymerization degree (**HPE**) and a **SPEL** with a relatively low polymerization degree (**GPE**), where the **HPE** is present in the **NPEC** in excess and is responsible for its solubility[62,67,110,114,143,144]. The behaviour of the soluble **NPEC** ($\Phi$ = [GPE]/[HPE] $\leq \Phi_{char}$) in aqueous solutions of low-molecular-weight electrolytes is apparent from turbidimetric titration of the NPEC with a solution of a simple salt (Fig. 6). The titration curve exhibits three different regions, I, II, III. In regions I and III the system is single-phase, homogeneous, whereas in region II it is two-phase, heterogeneous. Such beha-

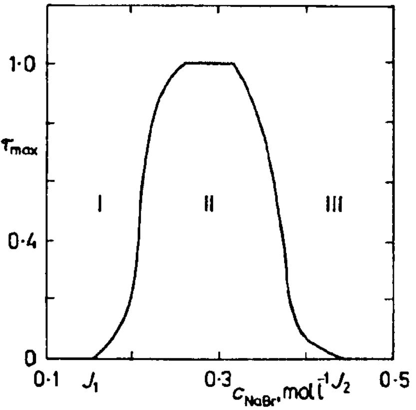


FIG. 6
Turbidimetric curve for the titration of the **NPEC** ($\Phi$ = 0.33) formed by reaction between PMAA-Na ($M_w = 2.6 \cdot 10^5$ g mol$^{-1}$) and PEVP-Br ($M_w = 6.0 \cdot 10^4$ g mol$^{-1}$), with NaBr solution at pH 7.5 and temperature 20 °C

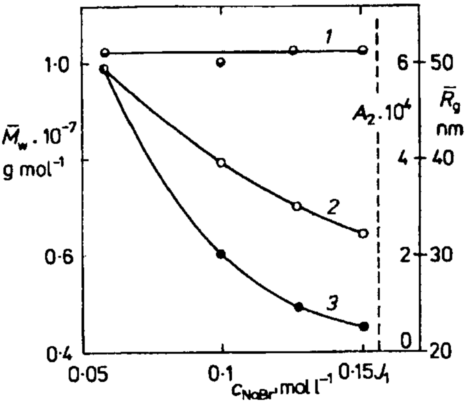


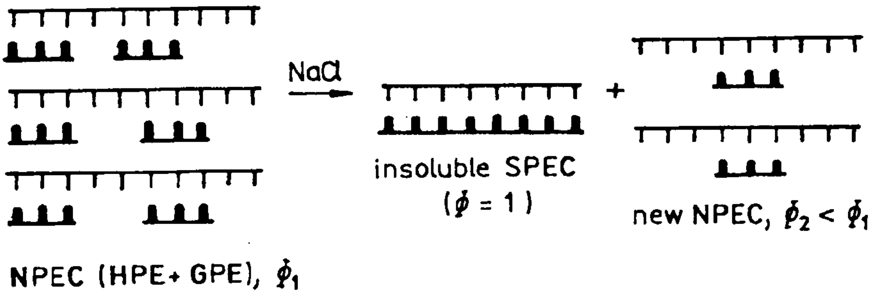
FIG. 7
Dependence of molar parameters of the **NPEC** ($\Phi$ = 0.33) formed by reaction between PMAA-Na ($M_w = 2.6 \cdot 10^5$ g mol$^{-1}$) and PEVP-Br ($M_w = 6.0 \cdot 10^4$ g mol$^{-1}$) on the concentration of NaBr at pH 7.5; *1* mass average of the **NPEC** molar mass ($M_w$), *2* gyration ratio ($R_g$), *3* second virial coefficient ($A_2$). Broken line shows boundary between regions I (soluble **NPEC**) and II (insoluble **NPEC**)

viour is characteristic of all **NPEC** solutions so far studied, formed by mixing **GPE**s with **HPE**s in nonstoichiometric ratios. In region I, where the ionic strength of the solution $J$ is lower than the critical value $J_1$, the **NPEC** behaves in the solution like a **PEL** with flexible polymeric chains. Fig. 7 demonstrates that increase in the concentration of NaBr in the solution is accompanied by a change in the molecular characteristics of the **NPEC**. As the ionic strength of the solution is increased, the size of the **NPEC** particles decreases, as do the gyration radius values and the second virial coefficient values ($A_2$), while the molar mass of the **NPEC** remains constant in this region. Thus in region I, the **NPEC** behaves like a **PEL** in a simple salt solution. At $J_1$, the $A_2$ value approaches zero and the **NPEC** loses its solubility, the insoluble **PEC** separates. The $J_1$ value depends, in otherwise identical conditions, on the chemical structure of the **HPE** and **GPE** constituting the **NPEC**, on the **NPEC** composition ($\Phi$ value) and on the kind of the salt used[112]. If the $\Phi$ value is lower, the formation of the insoluble **PEC** requires a higher ionic strength. If $\Phi$ approaches zero, the **NPEC** is soluble over the entire ionic strength region examined.

For an **NPEC** having a constant composition, the ionic strength necessary for the formation of the insoluble **PEC** depends on the low-molecular-weight electrolyte, on the ability of the counterions to bond to the charged functional groups of the **HPE**: their nature affects the $J_1$ value whereas that of the co-ions does not. The $J_1$ value increases with decreasing degree of association of the low-molecular-weight counterions of the **HPE**. For instance, for a polyanion carrying carboxy functional groups, the solubility of the **NPEC** in salt solutions increases in order[145] $LiCl < NaCl < KCl < (CH_3)_4NCl$; this is also the decreasing order of bonding constants of cations to a polyanion containing carboxy functional groups[145].

In the second region, with $J_1 < J < J_2$, the **GPE**-to-**HPE** ratio in the **NPEC** changes abruptly in the two phases formed. The **SPEC** ($\Phi = 1$) segregates in the concentrated phase or precipitate, independently of the composition of the starting **NPEC**. The behaviour of the dilute phase which is in equilibrium with the concentrated phase is considerably more complex[110,114,143,144]. This can only contain the **HPE** released from the initial **NPEC**, or a new **NPEC** with a lower **GPE** content, because a portion of the **GPE** has been spent on the formation of the **SPEC**. The composition of the new **NPEC** ($\Phi_2$) differs from that of the initial **NPEC** ($\Phi_1$); we have $\Phi_2 < \Phi_1$, the $\Phi_2$ value being lower for higher ionic strengths of the solution[114].

The restructuring of the **NPEC** when passing from region I to region II leads to the **SPEC**, which separates in the form of a concentrated phase from the salt solution. The formation of the **SPEC** during disproportionation (Scheme 14) and its separation into the concentrated phase or precipitate is explained[110] in terms of the lower solubility of the **SPEC** as compared to the initial **NPEC** in the existing conditions; the disproportionation mechanism, however is not quite clear. The authors[106] suggest two different mechanisms: the one involves separation of the **NPEC** from the solution into the concentrated phase (due to the lower solubility as a result of the Manning condensation caused by the high $J$ value) and its successive rebuilding in the concentrated phase, associated with the formation of the **SPEC** and separation of the excess **HPE** into the dilute phase. The other mechanism involves the formation of the **SPEC** in the solution as a result of the chemical reaction of **GPE** chain transfer from one **NPEC** particle to another, and subsequent precipitation of the **SPEC**. The two mechanism do not exclude one another and their concurrent operation is conceivable.



SCHEME 14

Increase in ionic strength in region II is associated with a decrease in the Θ value in the **SPEC** due to the Manning condensation. The behaviour of **SPECs** formed from **NPECs** on increasing the ionic strength is similar to that of **SPECs** formed by mixing the **PELs** in stoichiometric ratios, as described above. In turbidimetric measurements, the system haze decreases with increasing concentration of the simple salt in the solution, and at ionic strength $J_2$ the system becomes homogeneous again. The $J_2$ value depends on the nature of the **GPE** and **HPE** involved as well as on the kind of the low-molecular-weight salt. Unlike the $J_1$ value, the $J_2$ value is dependent on the initial concentration of the **NPEC** in the solution[62] (Fig. 8).

The transition from the heterogeneous system to the homogeneous system (from region II to region III) is due to the conversion of the insoluble **SPEC** to the soluble **SPEC**. This change is caused by the dissociation of a certain number of ionic bonds between the **WPEL** and the **SPEL** in the **SPEC** and change in the ratio of the hydrophilic to hydrophobic regions in favour of the former. The phase separation curves between regions II and III in Fig. 8 have a shape similar to that of curves in Fig. 5 for the **SPEC** obtained by reaction of a **SPEL** and a **WPEL**. Additional increase in the salt concentration[62,110,143] in region III also brings about dissociation of the **SPEC** to the starting **GPE** and **HPE**.

**NPECs** formed from **GPEs** and **HPEs** which are stabilized by introducing cross-link covalent bonds between the polycations and polyanions constitute a particular group[100,146]. At a covalent bond content as low as 10% in the **NPEC**, the phase separation does not take place up to a salt concentration which is sufficient for a complete disturbance of the intermolecular ionic bonds[114,144]. This implies that the introduction of cross-link bonds prevents redistribution of the **GPE** among the **HPE**, disproportionation does not occur in such a system, and the complex retains its solubility over a wide range of ionic strength of the solution[100,146].

### 4. 2. 2. 3. Reaction between Two Weak Polyelectrolytes

The effect of addition of a low-molecular-weight salt on the composition of the **PEC** formed by reaction of two **WPELs** in the optimum reaction conditions (pH, low **WPEL** concentration) should be as in the case of the 2nd **PEC** subgroup (**SPEL** + **WPEL**). By adding a low-molecular-weight salt, the insoluble **SPEC** can be converted into the soluble **SPEC** and further completely dissociated into the starting components. The shape of the phase separation curves is as in Fig. 5, the phase changes, however, take place at lower ionic strengths, hence, at lower concentrations of the same simple electrolytes[107,109 - 111,138,140 - 142].

Soluble **NPEC** in this 3rd subgroup can be formed by mixing nonequivalent amounts of a **WPEL** with a relatively high degree of polymerization with a **WPEL** with a relatively low degree of polymerization, in the optimum pH region. The former **WPEL** must be present in excess. Such an **NPEC** behaves in the presence of simple salts in the same manner as an **NPEC** obtained from a **WPEL** and a **SPEL**, only the $J_1$ and $J_2$ values are lower[62,108,110,114,143].

## 4. 3. SOLVENT EFFECT

Polyelectrolytes are low soluble in organic solvents, therefore few studies concerned with the solvent effect on the formation of polyelectrolyte complexes have been pub-

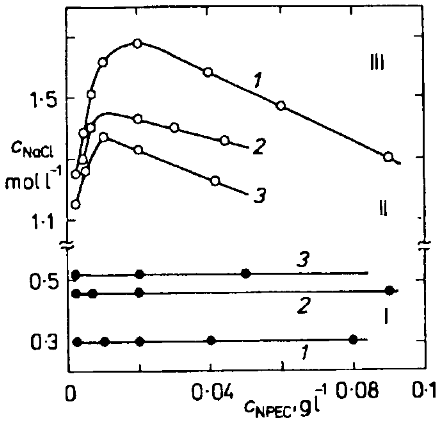


FIG. 8

Phase diagrams of the NPEC–water–NaCl system at pH 7.0. Composition of the NPEC (Φ) formed by reaction between PAA-Na ($M_w$ = 1.8 . $10^5$ g mol$^{-1}$) and poly(ethylene imine) ($M_w$ = 1.0 . $10^4$ g mol$^{-1}$): *1* 0.5, *2* 0.33, *3* 0.25. ● Transition of the soluble NPEC (region I) to the insoluble SPEC (region II); ○ dissolution of the SPEC (region III) lished[1,46,140 – 143]. The following effects are expected in organic solvents[1]: (i) stronger Coulomb forces, (ii) lower dissociation of the polyelectrolyte components due to the lower dielectric constant of solvent, and (iii) considerably lower hydrophobic interactions.

The effect of a water-miscible solvent on the composition of the **PEC** has been examined for the PMAA–PEVP-Br system[46]. The changes in the **PEC** composition ($\Phi$ = [PMAA]/[PEVP-Br]) accompanying changes in the water–ethanol solvent composition are shown in Fig. 9. Up to 30% ethanol, no change in the **PEC** composition appears. Over the region of 30 to 40 % (v/v) ethanol at pH 3.5 – 3.7, the $\Phi$ value decreases down to a value of 2.5 and then remains constant irrespective of the further increasing ethanol content of the solvent. The change in the **PEC** composition is due to disturbance of the compact conformation of PMAA, which is stabilized by the hydrophobic and hydrogen bonds between the carboxy groups[147,148].

The behaviour of the PMAA–PEVP-Br system in 40% (v/v) ethanol approaches closely that of this system in water. As ethanol is further added, the **PEC** composition changes: at the water–ethanol volume ratio 50 : 50, we have $\Phi$ = [PAA]/[PEVP-Br] = 2.5, which is the same as for the PMAA–PEVP-Br mixture in 50% ethanol[46]. In the system of PMAA with poly(4-vinylbenzyltrimethylammonium chloride) (PVBTMAC) in methanol, a **PEC** gel forms with $\Phi$ = [PVBTMAC]/[PMAA] = 0.5, whereas in water the gel possesses $\Phi$ = 0.17 (refs[149,150]).

### 4. 4. EFFECT OF TEMPERATURE

The effect of temperature on the stoichiometry of polyelectrolyte complexes has been studied in ref.[83] for a **WPEL–SPEL** system and for a **WPEL–WPEL** system. Under

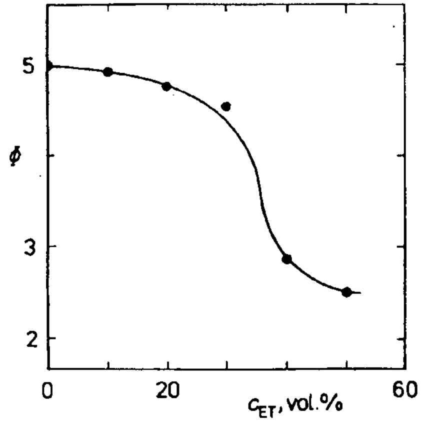


FIG. 9

Dependence of the **PEC** composition ($\Phi$ = [PMAA]/[PEVP-Br]) on the ethanol content in the water–ethanol mixed solvent (pH 3.5 – 3.7), for the mixing of aqueous-ethanolic solutions (5 meq $l^{-1}$) of PMAA ($M_w$ = 3.0 . $10^6$ g $mol^{-1}$) and PEVP-Br ($M_w$ = 1.0. $10^6$ g $mol^{-1}$)

optimum conditions (pH, ionic strength), stoichiometric **PELs** were observed over the temperature region of 0 – 45 °C.

For **NPECs**, the effect of temperature has been studied[67] in a system where one of the **PELs** contained the bulky nonpolar poly(N-tert-butylaziridine) substituents. At 40 to 60 °C, when interactions of the nonpolar groups begin to play a substantial part, **NPECs** containing such groups remain soluble in aqueous solutions even though the ionic strength of the solution is increased to a value which is nearly the $J_2$ value at normal temperature. As the warm aqueous **NPEC** solution with a salt concentration corresponding to the precipitate–solution equilibrium ($J_1$) at low temperature is cooled down, the **SPEC** precipitates from the solution. Such precipitate can no more be dissolved by heating the system – the **NPEC**–water–NaCl system is irreversible. For instance, at a certain combination of NaCl and temperature equal to 50 °C, the same system can be homogeneous or heterogeneous. The authors[67] explain this fact in terms of stabilization of the **NPEC** structure on heating the salt-free sample due to increase in hydrophobic interactions between the nonpolar groups. Heating the solution of the water-soluble **NPEC** brings about fixation of its structure by hydrophobic interactions, as in the case of introduction of covalent bonds into the **PEC**.

Similar results concerning the effect of temperature on the behaviour of **PECs** have been obtained in refs[149,150], where the viscosity of the PMAA–PVBTMAC system was examined in water and in methanol. In both systems, the viscosity decreased appreciably on heating, the viscosity change, however, was irreversible in water and reversible in methanol. The authors suggest that in water the complex is stabilized by irreversible conformation changes resulting from hydrophobic interactions, whereas in organic solvents the hydrophobic interactions are negligible.

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