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ORIGINAL CONTRIBUTION

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Effect of added salt on the stability of hydrogen-bonded interpolymer complexes

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Abstract Association of macromolecules in aqueous media through hydrogen bonding results in the formation of discrete interpolymer complexes (IPCs). In this work, the effect of added salt on the stability of IPCs consisting of polyacrylic acid and either a flexible polymer (polyethylene oxide or polyvinylpyrrolidone) or a semirigid polymer (hydroxy propylcellulose) is examined by a combination of spectrophotometry, viscometry and potentiometry. Addition of a neutral salt (e.g., NaCl) typically results in IPC aggregation. The response of the IPCs to salts that promote "salting-in" (i.e., LiSCN, NaSCN and GuSCN, where Gu denotes guanidine) is strongly cation-dependent, since Li^+ cations induce an increase in solution pH, whereas Gu^+ cations compete with polyacrylic acid for complexation sites. The degree of complexation (θ), calculated from potentiometric data, is greatest for IPCs in the absence of salt and is found to decrease in the order NaCl > NaSCN > GuSCN. Addition of salts that induce "salting-in" at polymer solution concentrations favoring complexation is found to enhance IPC solubility (and reduce θ) until the IPC particles are either completely solubilized or dissociated.

Key words Interpolymer complexes – macromolecular association – salting-in – hydrogen-bonded complexation – hydroxypropylcellulose

Introduction

Synthetic macromolecules capable of forming interpolymer association structures in aqueous media constitute an important, and intriguing, class of materials that have proven particularly valuable in i) the identification of fundamental mechanisms governing intermacromolecular complexation and ii) the design and development of environmentally responsive systems. Interpolymer complexes (IPCs), for instance, are currently employed in several commercial applications, including water purification, chemical recognition and drug ultrafiltration [1]. Due to the strong intermacromolecular interactions inherent in interpolymer complexation, IPCs also serve as convenient model systems to emulate, and eventually elucidate, important biological processes (e.g., stabilization of the double or triple helical structure of polynucleotides [2, 3] and enzymatic complexation [4]). For most IPC applications of technological relevance, the ionic strength of the aqueous solution plays a crucial role in both the complexation reaction and the ultimate development of IPC properties.

Kabanov [5] has investigated the effect of salt concentration on interactions between oppositely charged polyelectrolytes (e.g., polyphosphate or polycarboxylic polyanions and a polycation such as polyvinylpyridine quarternized with ethyl bromide) and reports that the

critical salt concentration inducing interpolyelectrolyte complex (IPEC) dissociation is dependent on the cation of salts with the same anion (Cl^-) and the polyanion. Magny et al. [6] have also examined the viscosity and fluorescence properties of hydrophobically modified poly(sodium acrylate) polymers in the presence of NaCl and observe an aggregation transition at a critical salt concentration. A similar salt-induced structural transition has been reported by Dautzenberg et al. [7] for ionically-modified polyacrylamide IPEC solutions. It is important to realize that these effects correspond to IPECs stabilized principally through ionic, not hydrogen-bonding, interactions. For IPCs in which complexation occurs by hydrogen bonding, the effect of adding salt is not as yet well-described.

An interesting, and generally overlooked, method by which the miscibility and associative behavior of non-electrolytic IPCs can be altered is through the addition of salts that promote "salting-in". Most common salts (e.g., NaCl and KCl) effect polymer "salting-out", in which polymer solubility decreases with increasing salt concentration [8, 9]. At sufficiently high salt concentrations, precipitation of the polymer from solution occurs. In contrast, several salts consisting of large, easily polarizable anions (e.g., ClO_4^- and SCN^-) are capable of perturbing and reorganizing the local structure of water [9–11]. Reorganization of water molecules in the presence of these salts enhances the hydrophilicity of nonpolar functionalities and may improve the net solubility of partially hydrophobic polymers. While these salts hold tremendous promise for tailoring the extent of hydrophilicity, and hence properties, of polymers capable of self-association in aqueous media, surprisingly few studies [9, 12–17] have been reported which address this issue.

Addition of SCN^- salts to the water-soluble lyotropic polymer hydroxypropylcellulose, for example, has been found to induce both mesophase swelling [14] and viscosity reduction [16]. Recent efforts [15] have shown that lignin, of considerable importance in the pulp and paper industry, can likewise be "salted-in" using a variety of SCN^- salts. Malmsten and Lindman [17] have also demonstrated that the aqueous gel envelope of pluronic poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymers can be controllably shifted to higher copolymer concentrations and temperatures upon addition of NaSCN salt. Thus, it is reasonable to expect that these salts can have a tremendous impact on the solubility of IPCs consisting of both hydrophobic blocks (i.e., sequences of hydrogen-bonded functional groups which associate in aqueous media) and hydrophilic blocks, non-associated groups which lead to "defects" in the IPC structure.

The objective of this work is to examine the effect of adding both classes of salts on the bulk properties of polymer pairs that associate (by hydrogen bonding) in aqueous media to form IPCs.

Experimental

Materials

Polyacrylic acid (PAA), polyethylene oxide (PEO), hydroxypropylcellulose (HPC) and polyvinylpyrrolidone (PVP) were obtained from Aldrich and used without further purification or characterization. The molecular weights of these polymers (in kg/mol) were about 450, 100, 100 and 40, respectively. Several common salts (NaCl, NaSCN and LiSCN), as well as an organic-cation salt (GuSCN), were also purchased from Aldrich and used as-received. Note that Gu is used throughout this work to designate guanidine (iminourea), the chemical structure of which is given by $NHC(NH_2)_2$.

Methods

Dilute PEO/PAA and HPC/PAA polymer solutions (≤ 0.05 M, where concentration is expressed on a segmental basis) were prepared with distilled water, and salt concentrations were varied from 0.0 to about 2.2 M, depending on the salt examined. All analyses were performed at 25 °C. Spectrophotometric transmittance measurements were collected from 0.014 M solutions at a wavelength of 650 nm. The viscosities of 0.05 M PEO/PAA and 0.0125 M HPC/PAA solutions were measured with a Ubbelohde viscometer in an isothermal water bath. Potentiometric measurements were obtained from PEO/PAA and HPC/PAA solutions (0.05 M PAA) using a Corning pH meter 320 with Ag/AgCl glass electrodes.

Results and discussion

The formation of IPCs between PAA and three proton-accepting polymers, PEO, PVP and HPC, has been studied in aqueous solutions containing three salts that promote "salting-in" (SI), namely, GuSCN, NaSCN and LiSCN, and, for comparison, one salt that induces "salting-out", NaCl. Note that all of the SI salts studied here share a common anion (SCN^-), which is responsible for the observed [9–11] SI behavior. Since the efficacy of these salts should obey the lyotropic (Hofmeister) series [18], cation species is expected to have an additional influence on IPC stability. For instance, compounds comprised of Gu are known [19] to form hydrogen bonds with proton-accepting functionalities, in which case GuSCN

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should be able to compete with the proton-donating PAA during complexation with polymers such as PEO, PVP and HPC. Another consideration to be borne in mind in this study is that the LiSCN salt increases solution pH through hydrolysis (see Table 1), which consequently promotes PAA dissociation.

Effect of SI salts on solution turbidity

Transmittance measurements are presented as a function of salt concentration in Fig. 1 for each of the salts examined here. The data shown in these figures correspond to dilute solutions consisting of PAA and either PEO, PVP or HPC (as denoted in the captions). Formation of IPCs between PAA and each of these polymers yields a reduction in transmittance from 100% (i.e., 90.6% for PEO, 78.5% for PVP and 65.6% for HPC) at zero salt concentration. The transmittance without added salt is seen to be the lowest for the HPC/PAA pair, indicating that the HPC/PAA IPC particles are larger than those comprised of PEO or PVP. This observation is consistent with i) an increase in IPC hydrodynamic radius due to HPC chain rigidity and ii) enhanced IPC aggregation due to the presence of HPC hydrophobic groups. At relatively low concentrations (0.2 M) of added NaCl, solution transmittance is seen in Fig. 1a to decrease dramatically (to $< 2\%$) for all three polymers, implying IPC aggregation. This is attributed to salt-induced changes in solvent properties, and may also reflect shielding of dissociated $-COO^-$ groups (always present at a pH-dependent concentration in PAA molecules) by a low-molecular-weight electrolyte.

In marked contrast to Fig. 1a in which IPC formation is seen to occur over a broad NaCl concentration range (up to about 1.9 M), Fig. 1b reveals that addition of LiSCN to these polymer solutions promotes IPC aggregation at comparatively low salt concentrations (< 0.5 M). Recall that, as the concentration of LiSCN is increased, the solution pH likewise increases, resulting in PAA dissociation. Transmittance data in Fig. 1b suggest that at some polymer-specific critical concentration (and solution pH), the degree of ionized PAA is sufficiently great to induce IPC dissociation through decreased complexation. The LiSCN concentration at which HPC/PAA solutions first exhibit near 100% transmittance (signaling IPC dissociation, as discussed further in the section addressing solution viscosity) is relatively low (≈ 0.05 M), whereas IPC aggregates in the PEO/PAA and PVP/PAA solutions are stable

Table 1 Measured pH of 1.2 M salt solutions at 25 °C

Salt	pH
NaCl	6.4
NaSCN	6.3
GuSCN	5.0
LiSCN	9.6

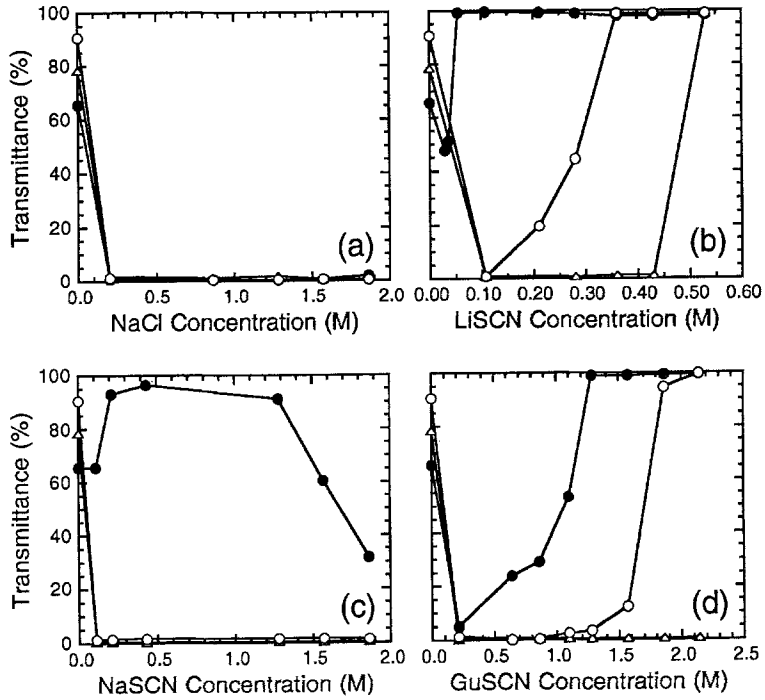


Fig. 1 Transmittance data of IPC solutions presented as a function of (a) NaCl, (b) LiSCN, (c) NaSCN and (d) GuSCN concentration for three polymers: PEO (○), PVP (△) and HPC (●). The concentration of IPC is constant at 0.071 M

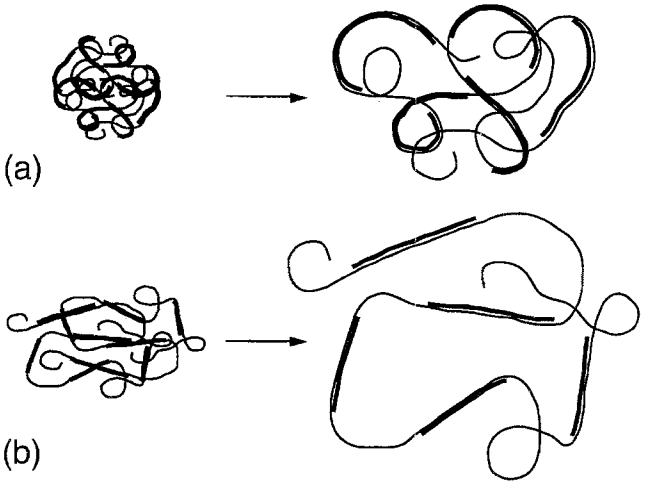
at concentrations up to about 0.36 and 0.53 M LiSCN, respectively.

From Fig. 1b, it can be concluded that the stability of the IPCs studied here increases in the following order: PVP/PAA > PEO/PAA > HPC/PAA. This observed trend is in agreement with a prior study [20] of PVP and PEO complexed with polymethacrylic acid (PMA), in which PVP replaces PEO in PEO/PMA IPCs. While IPCs composed of HPC have not been previously investigated, we attribute the low stability of HPC/PAA IPCs seen in Fig. 1b to the rigidity of the HPC backbone, which hinders the formation of relatively compact IPC particles (see the illustration provided in Fig. 2). Since SI is usually observed in solutions at relatively high salt concentrations (*ca.* 0.5 M), pH-induced PAA ionization and, consequently, IPC dissociation prevents SI of HPC/PAA, as well as PVP/PAA and PEO/PAA, IPCs from being detected in the presence of LiSCN.

If NaSCN is substituted for LiSCN (as in Fig. 1c), SI of HPC/PAA IPCs is observed over salt concentrations ranging from 0.5 to 1.3 M (where the transmittance exceeds 90%). Since, according to Table 1, the pH does not change appreciably upon addition of NaSCN, this increase in transmittance for HPC/PAA solutions is not attributed to complex (via PAA) dissociation (as it was in the case of the LiSCN solutions). Upon further addition of NaSCN, the HPC/PAA IPCs aggregate and eventually phase-separate from solution. The PVP/PAA and PEO/PAA IPCs, on the other hand, do not form soluble IPCs and aggregate over the entire salt concentration range examined. It is important to recognize that these IPC aggregates in the presence of NaSCN are less visually opaque and are presumably more swollen than their NaCl analogs at similar salt concentrations. Upon comparing the results in Fig. 1c, IPCs composed of HPC are more sensitive to local solution environment than PEO- or PVP-type IPCs (due to their rigidity and large, defect-filled structure, as discussed above) and that HPC/PAA complexation occurs even in the presence of SI SCN^- anions. One explanation for this difference in complexation behavior is that IPC particles consisting of flexible polymers (e.g., PVP and PEO) form relatively compact association structures, and addition of SCN^- anions induces SI by swelling PVP/PAA and PEO/PAA IPC aggregates.

Transmittance measurements of IPCs in solutions containing different concentrations of GuSCN salt are provided in Fig. 1d. At low salt concentration (*ca.* 0.2 M), IPC aggregates similar to those detected in the NaCl and NaSCN solutions exist. An increase in salt concentration is accompanied by transmittance increases first in the HPC/PAA solution, then in the PEO/PAA solution, and lastly in the PVP/PAA solution. The dissociation of IPCs in Fig. 1d most probably reflects competition between PAA and Gu^+ cations for proton-accepting functionalities along the PEO, PVP and HPC backbones. In the case of these relatively weak IPCs, a critical salt concentration ($\approx$1.2 M for HPC/PAA IPCs and $\approx$2.2 M for PEO/PAA IPCs) appears sufficient to permit successful competition with the PAA carboxylic groups and consequently reduce the magnitude of cooperative interactions between polymer chains. It is interesting to note that, in contrast to solutions containing NaSCN salt (Fig. 1c), the solubility of HPC/PAA IPCs does not increase in the presence of GuSCN (Fig. 1d), suggesting that the SI effect is sensitive to Gu^+-induced disruption of hydrogen-bonded sequences in the IPC particles.

Fig. 2 Schematic illustration of IPCs which form between a flexible polymer and (a) a flexible or (b) a semirigid polymer. Upon addition of salts that promote "salting-in", the normally compact IPCs are expected to swell. In this work, the proton-donating PAA molecules are longer than any of the proton-accepting polymers (PEO, PVP and HPC)



Effect of SI salts on solution viscosity

The viscosities (η) of these aqueous polymer solutions have also been measured to i) detect the formation of IPC particles through interpolymer association and ii) determine the response of these particles to SI salts. In Figs. 3 and 4, reduced viscosities are presented as functions of the molar ratios of PEO to PAA ($R_{PEO} = C_{PEO}/C_{PAA}$) in Fig. 3 and of HPC to PAA ($R_{HPC} = C_{HPC}/C_{PAA}$) in Fig. 4. Reduced viscosity (η_{red}) is defined as the ratio of specific viscosity (η_{sp}) to solution concentration (expressed here in M), where η_{sp} is given by $(\eta_{solution}/\eta_{water}) - 1$. As seen in Fig. 3, aqueous PEO/PAA solutions in the absence of salt undergo η_{red} reduction from about 0.30 to 0.09 M^{-1} as R_{PEO} is increased from 0.0 to 1.0. Previous studies [21]

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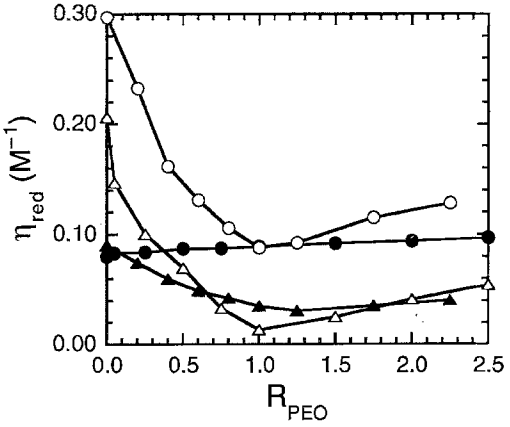

Fig. 3 Reduced viscosity (η_{red}) of PEO/PAA IPC solutions displayed as a function of the molar concentration ratio of PEO to PAA (R_{PEO}) in the following solutions: no salt (○), 1.2 M NaSCN (△), 1.2 M GuSCN (▲) and 1.7 M GuSCN (●). The concentration of PAA in each solution is 0.0125 M

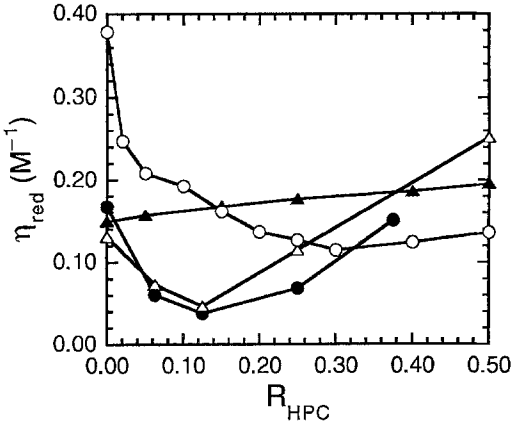

Fig. 4 η_{red} of HPC/PAA IPC solutions vs. R_{HPC} in different solutions: no salt (○), 1.2 M NaSCN (△), 1.2 M GuSCN (▲) and 0.6 M GuSCN (●). The concentration of PAA is constant at 0.05 M

have shown that interpolymer complexation in aqueous media results in a viscosity decrease, such as the one seen in Fig. 3. Viscosity reduction in associating polymer solutions is generally attributed to compaction of IPC structures, in which case the hydrodynamic volume of an IPC particle is less than the sum of the hydrodynamic volumes of the individual associating macromolecules.

Gradual addition of one polymer (in this case PEO) to another (PAA) results in IPC formation and a corresponding decrease in η_{red} until a minimum in η_{red} is achieved. The molar ratio of the two associating polymers at this point (R_i^*, where i = PEO or HPC) reveals the stoichiometry of the IPC [21]. From Fig. 3, R_{PEO}^* in the absence of SI salts is, as expected, about 1.0, indicating that, at complete complexation, each PEO segment is hydrogen-bonded to a carboxylic group in PAA. Upon addition of 1.2 M NaSCN, the entire $\eta_{red}(R_{PEO})$ curve, while shifted downward (due to PAA compaction in the presence of salt), still exhibits a minimum at $R_{PEO}^* \approx 1.0$. Thus, the salt effects a reduction in viscosity but, at concentrations between 0.1 and 2.0 M (according to the transmittance data in Fig. 1d), does not appreciably alter interpolymer composition. Similar behavior is not, however, observed in Fig. 3 when the same concentration of GuSCN, rather than NaSCN, is added to the solution. In pure PAA, the η_{red} of the solution is considerably lower than that of the solutions without salt or with NaSCN. As R_{PEO} is increased, the reduction in η_{red} is less pronounced than in the other two cases. In addition, R_{PEO}^* is increased to about 1.2–1.3, indicating that the IPCs are enriched in PEO, since some of the PEO complexation sites are complexed with Gu^+, not PAA.

This observation is again indicative of the competition between Gu^+ cations and PAA carboxylic functionalities to donate protons to PEO. In the presence of 1.2 M GuSCN, the PEO/PAA IPC particles are partially dissociated and exhibit a relatively large fraction of non-associated defects. Consequently, addition of NaSCN yields smaller (more compact) IPCs than those generated upon addition of an equal amount of GuSCN, which explains the measured difference in η_{red}. If, as in Fig. 3, the concentration of GuSCN is increased from 1.2 to 1.7 M, no reduction in η_{red} is observed. In fact, η_{red} increases very slightly as R_{PEO} is increased from 0.0 to 2.5. Such behavior indicates that PEO/PAA IPCs are not stable at this salt concentration over the range of R_{PEO} explored due to enhanced interactions between PEO molecules and Gu^+ cations. Comparison of the results displayed in Figs. 1d and 3 reveals that the transmittance and viscosity data are consistent. At 1.2 M GuSCN, the transmittance data in Fig. 1d demonstrate that the solution is turbid, comprised of IPC particles which, due to their compact nature, effect a decrease in solution viscosity (Fig. 3). As the concentration of GuSCN is increased beyond 1.5 M, transmittance increases to near 100% (Fig. 1d), indicating complete IPC particle dissociation. As alluded to above, the invariant $\eta_{red}(R_{PEO})$ curve corresponding to 1.7 M GuSCN in Fig. 3 is characteristic of IPC instability.

Comparable η_{red} data are provided as functions of R_{HPC} ($= C_{HPC}/C_{PAA}$) in Fig. 4 for HPC/PAA solutions. In this figure, the formation of HPC/PAA IPCs is confirmed, since η_{red} clearly decreases from about 0.38 to 0.11 M^{-1} with R_{HPC} in the absence of added SI salt. The minimum in the $\eta_{red}(R_{HPC})$ curve is seen to occur at $R_{HPC}^* \approx 0.30$, which suggests that three repeat units of HPC complex with 10 repeat units of PAA. Each repeat unit of HPC, however, possesses four functional groups capable of complexing with PAA. Thus, in terms of complexation sites, the viscosity data shown in Fig. 4 imply that not all of the available

sites along the HPC backbone interact with the carboxylic functionalities of PAA. This is not surprising in light of steric hindrance limitations, as well as the rigidity of HPC macromolecules and their tendency toward self-association. In contrast to the results provided in Fig. 3 for the PEO/PAA system, addition of 1.2 M NaSCN to HPC/PAA solutions not only results a more pronounced initial η_{red} reduction, but also shifts the position of the minimum (R^*_{HPC}) from 0.30 to about 0.11.

While the mechanism responsible for this shift in IPC stoichiometry is not yet well-understood, it is conceivable that added salt induces a decrease in solution pH and consequently increases the degree of PAA dissociation. In this case, as discussed again in a later section, more PAA molecules would be needed for complexation. Another explanation is that the presence of dissociated SCN^- anions in solution reduces the extent of intra-molecular HPC self-association through an increase in HPC hydrophilicity (see Fig. 1c). By doing so, PAA molecules would be permitted facilitated access to complexation sites along the HPC backbone. This interpretation is also consistent with observations reported elsewhere [22] demonstrating that the solid-like character (as measured in terms of the dynamic elastic modulus, G') of isotropic HPC aqueous solutions (without PAA) increases as the concentration of various SI salts (including NaSCN) increases due to the formation of transient structures. In either case, HPC/PAA complexation in the presence of 1.2 M NaSCN is clearly non-stoichiometric.

If, however, GuSCN is substituted for NaSCN at the same molar concentration, an increase in η_{red} with R_{HPC} is seen (Fig. 4), indicating that HPC/PAA IPCs are not stable in the presence of 1.2 M GuSCN (in agreement with the transmittance data provided in Fig. 1d). The slight increase evident in η_{red} over the range $0.0 \leq R_{HPC} \leq 0.5$ can be attributed to the addition of a semirigid molecule (HPC) to the salted solution. If, as in Fig. 4, the concentration of GuSCN is halved to 0.6 M, the dependence of η_{red} on R_{HPC} appears almost identical to the data displayed for 1.2 M NaSCN (including the value of R^*_{HPC}). According to the transmittance data shown in Fig. 1d, HPC/PAA IPCs are not completely aggregated at this GuSCN concentration and, in this regard, behave similarly to SI IPCs in the presence of NaSCN (Fig. 1c).

Effect of SI salts on solution pH

Results obtained from potentiometry are presented in Fig. 5 and show that the addition of the salts investigated in this work to PEO/PAA solutions with 0.6 M NaCl, NaSCN and GuSCN has a significant effect on solution pH and on IPC structure. (Data collected at 1.2 M NaSCN and GuSCN for PEO/PAA solutions and at 0.6 M for HPC/PAA solutions are almost identical to the results in Fig. 5 and are not included here for that reason.) As this figure demonstrates, an increase in R_{PEO} results in a corresponding increase in pH with and without salt. This increase is greatest, however, for solutions in the absence of any of the salts examined in this work. Solutions to which NaSCN and GuSCN are added behave similarly in terms of a slight increase in pH with R_{PEO}. For a given value of R_{PEO}, the relative order of pH is given by $H_2O > NaSCN \approx GuSCN > NaCl$. A salt-induced change in the solution pH, and hence the number of $-COO^-$ groups in the PAA molecules, helps to explain the viscosity data for NaSCN and GuSCN salt solutions (Fig. 4), as discussed further below.

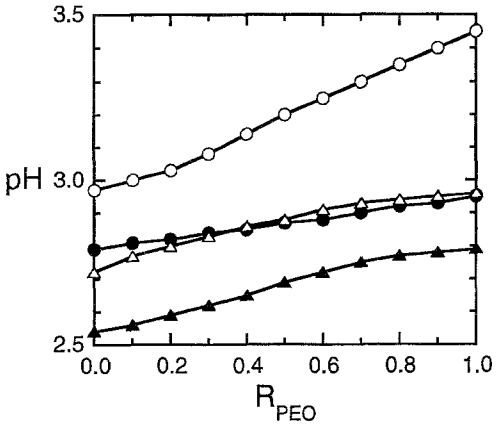

Fig. 5 Dependence of solution pH on R_{PEO} for solutions with no salt (○), 0.6 M NaSCN (△), 0.6 M GuSCN (●) and 0.6 M NaCl (▲). The concentration of PAA is 0.05 M

Complexation involves two types of equilibria, i.e., intermacromolecular hydrogen bonding and intramolecular dissociation of PAA. These respective equilibrium reactions are shown below:

$$-COOH \leftrightarrow O < \div -COOH \cdots O < \quad (1)$$

$$-COOH \div -COO^- \leftrightarrow H^+ \quad (2)$$

Due to interpolymer complexation (Eq. (1)), the concentration of free –COOH groups on the PAA molecules decreases. This decrease subsequently results in a corresponding decrease in the concentration of protons (Eq. (2)), in which case the solution pH increases (as observed in Fig. 5). Since complexation is sensitive to the degree of PAA dissociation, potentiometric measurements can be used to quantify the degree of complexation (θ), defined as the ratio of the concentration of associated carboxylic groups to the total concentration of carboxylic groups [23]. This parameter is calculated from

$$\theta = 1 - C/C_0 = 1 - ([H^+]/[H^+]_0)^2 , \quad (3)$$

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where C_0 and C denote the molar concentrations of free (unbound) –COOH groups before and after addition of a proton-accepting polymer (i.e., a polybase), respectively. Likewise, $[H^+]$ refers to the hydrogen ion concentration in the presence of, and $[H^+]_0$ in the absence of, the polybase. Note that Eq. (3) is valid only if it can be assumed that $[H^+] \ll C$ [23].

The variation in θ with respect to R_{PEO} and R_{HPC} is presented in Figs. 6 and 7, respectively, for solutions in which the PEO/PAA and HPC/PAA IPCs exhibit a measurable response to the addition of salt. In the absence of polybase, addition of any of the salts studied here is seen in Fig. 5 to lower the pH of the pure PAA solution (in which $R_{PEO} = 0$). By doing so, the salts, especially NaCl, serve to increase the ionization potential of PAA. According to Eqs. (1) and (2), ionization of –COOH groups in PAA reduces the concentration of hydrogen bonds available for interpolymer complexation and, as a consequence, decreases θ, as reflected in Fig. 6 for PEO/PAA solutions and Fig. 7 for HPC/PAA solutions. In these figures, θ is shown as a function of R_i/R_i^* (i = PEO or HPC), where $R^*_{PEO} \approx 1.0$ and $R^*_{HPC} \approx 0.3$ (see Figs. 3 and 4), so that a fair comparison can be made. It is evident from Figs. 6 and 7 that the degree of IPC complexation is greatest in PEO/PAA solutions without salt ($\theta \approx 0.9$) and lowest in HPC/PAA solutions containing either NaSCN or GuSCN salt. The relative magnitude of θ calculated for each of the solutions examined here can be ranked as follows:

PEO/PAA IPC: $H_2O > NaCl \approx NaSCN > GuSCN$

HPC/PAA IPC: $H_2O \approx NaCl > NaSCN \approx GuSCN$

In this case, lower values of θ indicate that the extent of hydrogen bonding between the associating polymers is reduced and that the resulting IPCs consist of more defects (i.e., non-associated functional groups). According to Fig. 7, for instance, θ for HPC/PAA IPCs in NaSCN solution is significantly lower (by as much as ≈ 0.35) than that calculated for the NaCl solution, in agreement with the transmittance results, confirming formation of soluble IPCs in NaSCN solution (compare Figs. 1a and 1c). The formation of soluble HPC/PAA IPCs indicates exclusion of the hydrophobic interactions that constitute an additional factor in complex stabilization [24]. In marked contrast, there is virtually no difference in θ for PEO/PAA IPCs in NaSCN and NaCl. For both types of IPCs, though, addition of GuSCN results in the lowest values of θ, again substantiating that the Gu^+ cations compete with the carboxylic groups of PAA for the proton-accepting sites on the associating polybases. It is of interest to note that a similar competitive effect has been previously observed [25] for hydrogen-bonded IPCs in mixed water-dioxane solutions in which dioxane is a strong hydrogen-bonding molecule capable of interacting with the polybase. Dioxane-induced dissociation of PEO/PAA and PEO/PMA IPCs has been found to occur at a critical dioxane concentration.

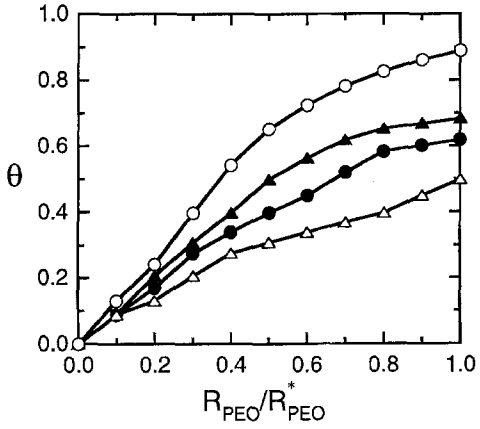

Fig. 6 Degree of complexation (θ), calculated from potentiometric measurements, as a function of R_{PEO}/R^*_{PEO}, where $R^*_{PEO} \approx 1.0$, for four solutions: no salt (○), 1.2 M NaSCN (●), 1.2 M GuSCN (△) and 0.6 M NaCl (▲). The concentration of PAA is 0.05 M

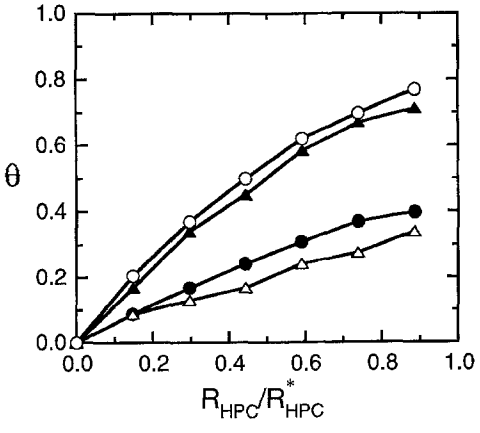

Fig. 7 θ presented as a function of R_{HPC}/R^*_{HPC}, where $R^*_{HPC} \approx 0.3$, for four solutions: no salt (○), 0.6 M NaSCN (●), 0.6 M GuSCN (△) and 0.6 M NaCl (▲). The concentration of PAA is 0.05 M

Conclusions

Results presented here, obtained with spectrophotometry, viscometry and potentiometry, demonstrate that added salts can have significant effects on the formation, structure and properties of hydrogen-bonded IPCs between PAA and either PEO, PVP or HPC. Addition of a salt that induces polymer "salting-out" (e.g., NaCl) to an IPC solution typically results in IPC aggregation and, eventually,

phase separation over a relatively broad range of salt concentrations. Other salts provide an opportunity to tailor, for instance, the degrees of both IPC complexation and interparticle aggregation. This possibility is very important, since the existence of soluble, yet highly complexed, IPC particles in aqueous media has not, until now, been reported. In this work, we have also shown that HPC forms a stable complex with PAA and that the solubility and properties of HPC/PAA IPC particles are more sensitive to the type of salt added than are PEO/PAA particles. Moreover, the response of these IPCs to added salt is dependent not only on the anion (usually associated with the "salting-in" effect), but also on the cation species. In solutions containing GuSCN, dissociated Gu^+ cations compete with the carboxylic groups of PAA for complexation sites on both PEO and HPC, thereby resulting in IPCs with highly defective structures. Thus, addition of a salt capable of disrupting the formation of hydrogen bonds between the associating polymers (by either interacting specifically with the functional groups of one of the polymers or promoting dissociation of the polyacid) can induce IPC dissociation at a critical salt concentration. The results presented in this work provide evidence of important salt-IPC interactions which can be exploited to regulate the stability and ultimate properties of hydrogen-bonded IPCs for various technological applications.

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References

1. Tsuchida E, Abe K (1982) Adv Polym Sci 45:100–104
2. Huang RCC, Bonner Y, Murray K (1964) J Mol Biol 8:54–64
3. Osada Y (1980) J Polym Sci Polym Lett Ed 18:281–286
4. Zezin AB, Izumrudov VA, Kabanov VA (1989) Makromol Chem, Macromol Symp 26:249–264
5. Kabanov VA (1994) In: Dubin P, Bock J, Davies RM, Schulz DN, Thies C (eds) Macromolecular Complexes in Chemistry and Biology, Springer-Verlag, Berlin, pp 152–160
6. Magny B, Iliopoulos I, Audebert R (1994) In: Dubin P, Bock J, Davies RM, Schulz DN, Thies C (eds) Macromolecular Complexes in Chemistry and Biology, Springer-Verlag, Berlin, pp 51–61
7. Dautzenberg H, Koetz J, Linow K-J, Philipp B, Rother G (1994) In: Dubin P, Bock J, Davies RM, Schulz DN, Thies C (eds) Macromolecular Complexes in Chemistry and Biology, Springer-Verlag, Berlin, pp 119–133
8. Conway BE (1981) Ionic Hydration in Chemistry and Biophysics, Elsevier, Amsterdam, pp 444–461
9. von Hippel PH, Schleich T (1969) In: Timasheff SN, Fasman GD (eds) Structure and Stability of Biological Macromolecules, Marcel Dekker, New York, pp 483–559
10. Luck WAP (1980) In: Rowland SP (ed) Water in Polymers, Amer Chem Soc, Washington, DC pp 43–71
11. Balzer D (1993) Langmuir 9:3375–3384
12. Yang K-S, Cuculo JA, Theil MH (1992) J Polym Sci Polym Phys Ed 30:315–324
13. Cuculo JA, Smith CB, Sangwatanaroj U, Stejskal EO, Sankar SS (1994) J Polym Sci Polym Chem Ed 32:229–239
14. Wang B-C (1995) Ph.D. Dissertation, North Carolina State University
15. Roberts JE, Khan SA, Spontak RJ (1995) AIChE J (in press)
16. Prevysh VA, Spontak RJ, Khan SA (1995) In: Mikos AG, Leong KW, Radomsky ML, Tamada JA, Yaszemski MJ (eds) Polymers in Medicine, Mater Res Soc, Pittsburgh, pp 137–142
17. Malmsten M, Lindman B (1992) Macromolecules 25:5440–5445
18. Bull HB (1951) Physical Biochemistry. John Wiley & Sons, New York, pp 85–89
19. Hermans J Jr (1966) J Amer Chem Soc 88:2418–2422
20. Kabanov VA, Papisov IM (1979) Vysokomol Soyed A21:243–281
21. Osada S (1979) J Polym Sci Polym Chem Ed 17:3485–3498
22. Prevysh VA, Wang B-C, Khan SA, Spontak RJ (1996) Macromolecules (submitted)
23. Osada Y, Sato M (1976) J Polym Sci Polym Lett Ed 14:129–134
24. Bokias G, Staikos G, Iliopoulos I, Audebert R (1994) Macromolecules 27:427–431
25. Prevysh VA, Cohen Y (1995) Polym International (submitted)