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# Hofmeister effect on thermo-responsive poly(propylene oxide): Role of polymer molecular weight and concentration

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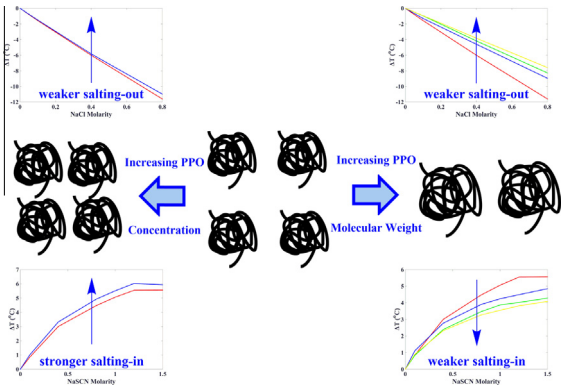
## GRAPHICAL ABSTRACT

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## ABSTRACT

Although a vast amount of research has been dedicated to investigate the Hofmeister effect on the stability of polymer solutions, a clear understanding of the role of polymer properties in this phenomenon is still missing. Here, the Hofmeister effect of NaCl (destabilizing) and NaSCN (stabilizing) salts on aqueous solutions of poly(propylene oxide) (PPO) is studied. Four different molecular weights of PPO were investigated, to determine how the variation in the polymer coil size affects the Hofmeister effect. The investigation was further conducted for different PPO concentrations, in order to understand the effect of inter-chain interactions on the response to addition of salt. The temperature-driven phase separation of the solutions was monitored by differential scanning calorimetry, which provides the precise value of the phase separation temperature, as well as the enthalpy change accompanied with the transition. It was observed that increasing the molecular weight weakens the effect of the both salts, which is interpreted in terms of a scaling law between the molecular weight and the accessible surface area of the polymers. Increasing the PPO concentration further diminished the NaCl effect, but amplified the NaSCN effect. This difference is attributed to an electrostatic stabilization mechanism in the case of NaSCN.

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## 1. Introduction

Thermo-responsive polymers are macromolecules that display a sudden change in solubility and conformation in a well-defined temperature regime and their possible applications are multiple, ranging from viscosity control [1,2] to controlled wettability [3,4]

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and are further of great importance in many biomedical applications [5,6]. Besides temperature-responsiveness, it has been demonstrated that the aqueous solution stability of such macromolecules can be tuned by addition of different salts, an effect generally recognized as the Hofmeister effect [7–11]. It was first postulated that destabilization (salting-out) by strongly hydrated ions and stabilization (salting-in) by poorly hydrated ions was due to their "water structure making" and "water structure breaking" effects, respectively [12–14]. Some anomalies from the order of ion hydration strengths compared to the Hofmeister series however indicated that information on how ions alter the water structure cannot solely elucidate such an intricate phenomenon, which is involved with the hydration of both ions and polymer chains, as well as direct interactions between the ions and the polymer backbone [15–19]. Hence in an approach toward understanding the Hofmeister effect on polymer solutions, one must consider that the mutual interactions of ion, water and polymer determine the solution stability [20–24].

In one description that takes the ion-polymer interplay into account, known as the solute partitioning model, Pegram and Record have suggested that the salting-out effect is a result of the exclusion of ions from the polymer hydration shell, while the salting-in effect is due to the favorable accumulation of ions at the polymer interface [25,26]. Accordingly, the partition coefficient, which is the ratio of the concentration of ions near the polymer surface to the concentration of ions in the bulk solution, determines both the strength and the direction of the Hofmeister effect of salts. The partition coefficient of a certain ion strongly depends on the chemistry of the surface, as different values have been reported for the partition coefficient of certain ions over hydrophobic surfaces and polar groups. Although this thermodynamic exclusion/accumulation picture can successfully explain why salts have different effects on polymer stability, it does not render a clear microscopic description for the stabilization and destabilization mechanisms.

In a more microscopic approach, Cremer and coworkers have focused on explaining the Hofmeister effect of different sodium salts on poly(N-isopropylacrylamide) (PNIPAM) aqueous solution [27,28]. For this system, they have suggested that the Hofmeister effect can be explained by a combination of three principal mechanisms. First, polarization of the water molecules around the strongly hydrated anions disturbs the hydration of polar amide bonds of PNIPAM, and so results in a salting-out effect. In more general term, this effect may be described as a competition for hydration water between the ions and the polar group. Such a competition will lead to destabilization of the polar group, due to the relatively stronger hydration strength of ions [29]. Second, the presence of ions can interfere with hydrophobic hydration of the polymer, by changing the surface tension between the (hydrophobic) polymer surface and water. This mechanism was formerly believed to have a relatively weak linear salting-out effect, but recently it has been suggested to cause either stabilization (by decreasing the surface tension) or destabilization (by increasing the surface tension), depending on chemistry and dielectric constant of the polymer [30,31]. For instance, $SCN^-$ is reported to increase the surface tension of PNIPAM (less hydrophilic polymer, low dielectric constant), but decreases the surface tension of lysozyme (more hydrophilic polymer, high dielectric constant) in water [30]. Third, poorly hydrated anions can directly bind to the moieties on the polymer backbone with a partial positive charge, and then induce an electrostatic repulsion between the chains. Accordingly, the notable nonlinearity in salting-in effect of weakly hydrated ions like $SCN^-$ is correlated to the limited number of binding sites on a polymer chain, and then follows the trend of the Langmuir isotherm binding model [32,33].

Irrespective of using a thermodynamic or a molecular description of the Hofmeister effect, it is expected that the effect should depend on the chemical structure and the accessible surface area of the polymer, as well as the possible inter-chain interaction between the polymer chains. With respect to the chemical structure, it has previously been observed that different polymers are not similarly affected by the presence of salts. For instance, poly (propylene oxide) (PPO) shows smaller changes in phase separation temperature in response to different salts, compared to poly (ethylene oxide) (PEO) [29,34]. Another interesting observation is that addition of NaSCN leads to a relatively small salting-in effect on PNIPAM with a maximum below 1M salt, where after it at higher salt concentrations shows a linear salting-out effect. In contrast, NaSCN has a relatively stronger salting-in effect on PPO, which does not seem to reach a maximum even at very high salt concentrations [35,36]. Although not often discussed in the literature on the Hofmeister effect, these differences due to different chemical structures are expected and can be rationalized from both the descriptions discussed above. Since most previous studies of the Hofmeister effect merely concerned with the effect of different ions and their interaction with a particular polymer, the questions regarding the effect of accessible surface area of the chains and inter-chain interaction have remained untouched. These parameters are related to the polymer chemistry, as well as the polymer molecular weight, the polymer concentration and the solvent quality. Hence, the "next stage" of studies on the Hofmeister effect should be focused on finding the role of the polymer properties in this phenomenon, and a better understanding of this can be gained by including the well-known descriptions and concepts from polymer physics.

In the present work, the Hofmeister effect of two sodium salts on aqueous solutions of PPO with different molecular weights and varying concentrations was investigated. As shown formerly in case of PPO solutions [29,35], NaCl and NaSCN show strong linear salting-out and non-linear salting-in effects, respectively. By changing the molecular weight of PPO from 1000, 2000, 2700 to 4000 g $mol^{-1}$, we varied the hydrophilic/hydrophobic character of the polymer due to a relative decreasing influence of the end groups, as well as the accessible surface area due to a systematic change in the coil size. Solutions were further prepared at PPO concentrations of 0.5, 1 and 2 wt.%, which correspond to solutions of separated polymer coils in the diluted regime, but with different average coil–coil separation distance. To detect the phase separation of the solutions, differential scanning calorimetry (DSC) was employed. Hereon, we first investigate the phase separation of the different PPO samples in salt-free aqueous solution, then the effect of the two salts on the PPO solutions is studied.

## 2. Materials and methods

Poly(propylene oxide) with different molecular weights (1000, 2000, 2700 and 4000 g/mol) and pure analytical grades of NaCl (99.5%) and NaSCN (98.5%) salts were all supplied by Sigma–Aldrich. Solutions of PPO samples (concentrations of 0.5, 1 and 2 wt.%) in pure water and salt solutions were prepared by mixing for 24 h at 1 °C.

Measurements were conducted using a differential scanning calorimeter (Nano DSC, TA Instruments), with a constant heating rate of 0.4 °C/min, and under a pressure of 3 atm. All the salt and PPO solutions were degassed before the measurements to avoid bubble formation upon heating. The measured raw heat data were converted to molar heat capacity as explained formerly, and were used to obtain the phase separation temperature, enthalpy change and heat capacity change values (see more in Supplementary Section S1) [29]. Measurements were repeated 3 times for the salt-free

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