

Effect of urea on ion pair formation. The hydrophilic effect of urea



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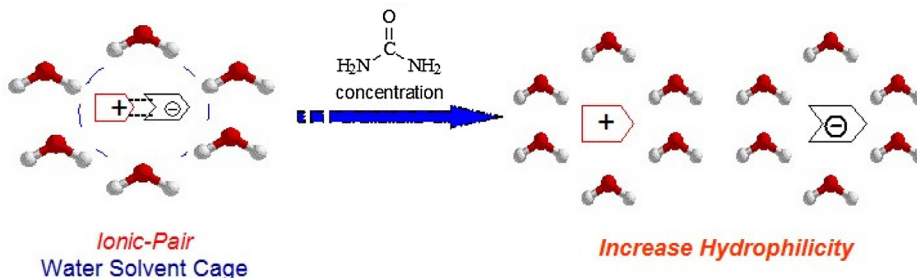
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HIGHLIGHTS

- Urea hinders ion pair formation. Effect assigned to the increase in the dielectric constant and unspecifically solvation of the free ion species.
- A Hydrophilic enhancement due to Urea is found to be effective towards separated ions and lost of binding specificities.

GRAPHICAL ABSTRACT



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ABSTRACT

Denaturant effect of urea has been interpreted by two mechanisms, the direct interaction of the additive with biomolecules or lyophilic colloidal aggregates or the indirect mechanism via rupture of the water 3D structure. In contrast we focused that urea produces a higher polarity of aqueous mixtures that causes the denaturation. In the realm of this effect is how charges, dipoles and so in solutions and in suspensions are stabilized by urea addition. For example, ion association is in the center of the interactions that leads to ionic micelle formation. Here, using ⁷⁹Br NMR line broadening and solubility data of bis (tri-methyl)- α,ω -alkanediammonium, (1-n-1)Br₂ (n = 2-4) (bolaform salts) and of tetramethylammonium bromide and the effect of adding perchlorate, we demonstrated the effect of urea in weakening ion pair association and stabilizing solvent separated ions. The high association constant of perchlorate with ammonium salts was used to titrate the ammonium-bromide interactions. Bromide counterions in bolaform salts derivative having two, three, and four methylene spacers or in tetramethyl ammonium salts were replaced by perchlorate. Although addition of urea to water is well known to lead to an increase of the dielectric permittivity, urea leads to a decrease of anion selectivity and the new pairs bind unspecific both anions. Since ion pairing between ionic surfactants head groups and its counterions is directly correlated to the critical micelle concentration (CMC) values, “loss of selectivity” explains the increase in the ionic surfactants CMC’s with increase in urea concentration.

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1. Introduction

The mechanism of protein denaturation, and association colloid disruption, by urea has been debated for more than sixty years. Two limiting proposals, attributing urea effects on the solvent or,

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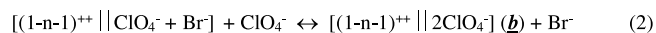
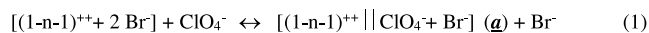
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alternatively, to urea colloid interaction, are currently considered [1–3]. In the indirect limit urea interferes exclusively with the three dimensional water structure leading to structure breaking of the solvent. In the direct limit urea interacts preferentially with the macromolecules or aggregates. Alternatively, we presented evidences suggesting that aqueous urea solutions are more polar than pure water and that this polarity difference is the driving force for structural destabilization of colloidal aggregates [4]. Here we report clear and critical evidences that favor the increased polarity of urea water mixtures by examining ion pair formation and the resulting caotropic effect [4].

Surfactant species are very suited to study the hydrophobic effect once the polar and non-polar parts of these compounds are “easy” to discriminate. Consider, for example, typical surfactants such as sodium dodecyl sulfate (SDS), where the polar moiety is the anionic head group and the dodecyl group the non-polar part. The addition of SDS to water leads to interfacial tension decrease and micelle formation [4,7]. In simple words, one can say that the polar head of the surfactant sticks to the water and the apolar tail away from it, that is the surfactant is said to act as “glue” between the two non-miscible parts. What urea does to this phenomenon? Using the more polar water-urea mixes, the answer is simple: as the polar medium increases its polarity, more surfactant, or more “glue”, will be necessary to transform an emulsion into a micro emulsion. In other words the effect is centered in the aqueous phase. Notice that water and urea are completely soluble one in the other and vice-versa, as well the solubility of urea in the organic media [5,6] is practically none. With the above rationale it is clear to grasp the difference of urea being either a hydrophilic agent or a hydrophobic additive. Our understanding is on the waterside, that is the “Hydrophilic Effect of Urea” (HEU). In other words HEU is the main force that drives association colloids to disrupt and also to macromolecules to disentangle their three-dimensional structure [7].

In this context, and leaving aside details of electrostatic interactions at the interfacial level, as well further details such as steric hindrances, on macromolecules and association colloids, let us consider the effect of urea solely within the hydrophilic medium [7]. For this goal Ion Association is the selected scenario and Ion Pair formation the title of the present play [8–10]. Ion solvation expresses the nature of ion/solvent interactions. Considering water as the solvent, the hydration of the ions involves all the forces that minimize the energy of the system, that is, the Coulombic term that reflects the electrostatic interactions of free ions or sticky ones (mostly an enthalpic contribution), plus the entropic term that keeps the ions apart. Here the concept of ion pair formation represents a situation where the pair can be visualized as solvent separated ion pair, solvent shared ion pair and contact ion pair [11].

The aim of the present study is to describe ion pair formation between Gemini Bolaform ammonium (1-n-1) and or tetramethylammonium (TMA) ions with bromide and perchlorate counterions with or without added urea. Perchlorate binds so strongly to ammonium groups as exemplified by symmetrical ammonium derivatives with this anion [9] that this effect can be used to “titrate” the ion pair. As expected, depending on concentration and temperature, perchlorate-ammonium derivative salts easily precipitate from aqueous solutions [9]. For the present study temperature was fixed at 25°C and concentrations were varied. In most experiments sodium perchlorate was added to ammonium bromide solutions as the titration equilibria depicted in Scheme 1, which includes the strong association of the mono and dications by added ClO₄⁻ (left to right in Scheme 1). Following urea was introduced and its effect evaluated. These cations are also models for the interfacial regions of micelles composed of single chain alkyltrimethylammonium bromide surfactants and some



Scheme 1. Equilibrium association reactions of ClO₄⁻ with salts of bola salt dications (n = 2–4) in water and urea/water mixtures. Species labeled as **a** and **b** represent one and two ClO₄⁻ substitution of the Br⁻ counterions. For TMAB only one step will occur.

twin chain, gemini, dialkylbis(dimethyl)- α,ω -alkanediammonium dibromides, s-n-s 2Br (e.g., s = 8–16, n = 2–4) surfactants [4,11].

In these equations a two-step association between the bola salt and perchlorate anions is represented. The strong association of perchlorate to alkylammonium renders the species having 1:1 Br⁻:ClO₄⁻ and 2 ClO₄⁻ partially soluble or insoluble, respectively depending on the size of the methylene spacer groups (see below). In concentrated salt solutions, e.g., Scheme 1, and in the absence of macromolecules and surfactant aggregates, only association between anions and cations is significant [9,10]. Tight or contact ion-pairs as well as water separated, and water shared ion-pairs may be formed [9,10] and we focus on ion-pairing versus free ions in our discussion [8–10]. The aim of these experiments was thus to characterize ion pair formation between bromide and perchlorate and dicationic gemini salts with 2–4 methylene spacers and monocationic TMA⁺ in the presence and absence of urea.

2. Materials and methods

Urea came from two sources: a) from Herga (Brazil); it was recrystallized from hot methanol. Conductance of a 10 mol x l⁻¹ was less than 6 $\mu\text{S}\cdot\text{cm}^{-1}$ ensuring the absence of ionic contaminants or urea degradation. b) Sigma Ultra (Sigma/Aldrich USA) and gave the same low conductance values, this urea was used without further purification.

Bromides of bolaform salts 1–2–1, 1–3–1 and 1–4–1 ((1-n-1)Br₂) were prepared by a published procedure [12] and tetramethylammonium bromide (used as received) (TMAB) grade (ACS \geq 99%) (Sigma Aldrich,) was used for comparisons. All salts were stored in desiccators and vacuum-dried overnight to constant weight before use. Solutions were prepared daily and kept in well-closed vials and tubes.

All other reagents were analytical grade or better and used without further purification. Water was bidistilled and further purified through a Milli-Q system (Millipore, Inc.).

Solubility measurements of (1-n-1)Br₂ and TMA salts and determination of solubility product constants (K_{sp}) is exemplified below with TMA measurements (Scheme 2). An aqueous solution having concentrations of 0.06 mol x l⁻¹ of TMAB and 0.06 mol x l⁻¹ NaClO₄ in a 2 mL flask was prepared, this solution is clear. Increase the salts concentration to 0.07 mol x l⁻¹ TMAB and 0.07 mol x l⁻¹ NaClO₄ produced a faint precipitate. The amount of precipitate increased with higher salt concentrations of 0.08, 0.09, and, 0.1, respectively. The molar ratio between TMAB and NaClO₄ was kept at 1:1, while the molar ratio between (1-n-1)Br₂ and NaClO₄ were 1: 2. In separate assays, aqueous urea stock solutions were added to the volumetric flasks to make 2 or 5 mol x l⁻¹ urea solutions. Water was added to all flasks to complete 2 mL and each flask was shaken, left for ca. 60 min at room temperature and inspected for precipitate. Mixtures were then warmed to obtain a transparent solution, cooled down to room temperature and re-inspected for precipitate.

Measurement of the ⁷⁹Br NMR linewidth (L_w) were conducted in a Varian VNMR5 500 MHz (Rutgers, NMR Facility) using a [13] C probe carefully tuned to the ⁷⁹Br frequency (all solutions contained

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