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Molecular dynamics simulations of K^+–Cl^- ion pair in polar mixtures of acetone and water: Preferential solvation and structural studies

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ABSTRACT

Molecular dynamics simulation studies have been performed for a series of polar mixtures of acetone and water containing a K^+–Cl^- ion pair. We have obtained the potentials of mean force (PMFs) for 15 mixtures spanning the whole composition range from 0% to 100% acetone. The PMFs indicate the presence of a stable contact ion pair (CIP), a solvent assisted ion pair (SAIP) and a solvent separated ion pair (SSIP) in all the compositions with acetone mole fraction ($x_{acetone}$) ≤ 0.50. However, for $x_{acetone}$ > 0.50 and $x_{acetone}$ ≤ 0.90, PMFs suggest the presence of only a stable CIP and SAIP. For $x_{acetone}$ > 0.90, PMFs show the existence of only a stable CIP. While the stability of CIPs in mixtures increases with $x_{acetone}$, the reverse trend is observed for SAIPs. The determination of thermodynamic properties suggests that entropy favours the CIPs and SAIPs in all the mixtures. The analysis of radial distribution functions using Kirkwood–Buff (KB) integrals explains the preferential solvation of the ion pair. We observed that in all the mixtures, K^+–Cl^- ion pair is preferentially solvated by water. Running coordination numbers of solvent molecules around the ion pair and preferential binding parameters also support the above observations. The dynamical aspects have been explored by calculating self-diffusion constants and hydrogen bond dynamics.

1. Introduction

Several studies have been undertaken to understand the solvation structures and dynamics of ion pairs in solvents/mixed solvents [1–14]. Ion pairs play a significant role in variety of chemical and biochemical processes such as ionic reactions in various solvents, macromolecular catalysis, biochemical hydrolysis and stability of proteins [15–16]. Molecular liquid systems such as binary mixtures of both aqueous and non-aqueous solutions show unusual properties in relation with the properties of respective pure components. The non-ideality is reflected in number of physical properties such as viscosity, density, dielectric constants, and translational and rotational diffusion constants [17–19]. Alkali halides, for example, lithium iodide (LiI), sodium iodide (NaI) and potassium chloride (KCl) are electrolytes of particular interest because of wide range of their applications in chemistry and their biological significance [20–22]. Acetone is a dipolar aprotic liquid largely used as a solvent in chemistry and is soluble in water in all proportions [23–24]. In the laboratory, it is used as a polar aprotic solvent in variety of organic reactions such as SN^2 reactions. The study of solvation structures and dynamics assists in understanding the mechanisms of such reactions.

The theoretical/computational and experimental structural studies of molecular liquid systems have been the subject matter of studies for several years. The potentials of mean force (PMFs) obtained using constrained molecular dynamics (MD) simulations provide an insight into the solvations of ions and ion pairs that influence the nature of reactions in solution media. Gordon and Kim [25] calculated interaction potentials of alkali and alkaline earth halide ion pairs using their own model and compared the predicted properties such as bond energies and bond lengths with the experimental values. Patey and Carnie [26] applied the linearized hypernetted (LHNC) theory to calculate ion–ion potentials of mean force and the solute dependent dielectric constants at infinite dilution limit in the temperature range from 25 °C to 300 °C. Pettitt and Rossky [27] in their work obtained correlation functions and interionic PMFs at infinite dilution for a set of models representing alkali halides in water using extended RISM formalism. Their results indicated that certain thermodynamic properties such as mean activity coefficients and osmotic pressures are quite sensitive to the details potential model. Kecki et al. [28] employed spectroscopic technique to study the influence of molecular local order on the non-coincidence shifts (NCE) in the Raman Spectra of methanol in binary mixtures with water, acetonitrile and carbon tetrachloride. They observed opposite effects for methanol with polar and non-polar co-solvents. Gaiduk and co-workers [29] studied the dependence of electric conductivity of NaCl–water and KCl–water on the microwave and far-infrared frequencies. Venables and Schmuttenmaer [30] used molecular dynamics (MD) simulations for the studies of binary mixtures of acetone–methanol, acetone–acetonitrile and methanol–acetonitrile over the entire composition range. They reproduce much of the experimental spectra using effective pair potentials of neat liquids. They also

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calculated autocorrelation functions and analysed radial and spatial distribution functions for all the mixtures.

Many applications of electrolytes, potassium chloride (KCl), for example, depend on their solvation structures in different media [31–32]. Degreve and Vieira [33] carried out MD simulations of concentrated aqueous KCl solution to study the influence of concentration on the hydration structure of ions and ion cluster formation. They found the hydration structures of ions to be almost independent of concentration whereas the ion clustering was found to be concentration dependent. Matsumiya and Takagi [34] investigated the electric properties of molten quarternary systems (Li, Na, K, Cs) Cl at different temperatures by MD simulations for various compositions. They concluded that the electric conductivities of Li, Na, K and Cs with reference to Cl show similar tendencies for each composition. Grossfield et al. [35] performed thermodynamic measurements of the solvation of salts and electrolytes using molecular dynamics simulations with the AMOEBA polarizable force field and perturbation techniques. The results obtained were compared with experimental values and found to be matching.

Aqueous solutions of acetone are good examples of mixed solvent systems/binary mixtures. The properties of these binary mixtures depend on the relative concentrations of the individual components. The aqueous solutions of acetone exhibit non-ideal behaviour. Perera and Sokolic [36] in their studies on acetone–water mixtures using different models concluded that most of the experimental data such as enthalpies, pressure and densities can be reproduced by all the models. However, their study could not conclude any one model as a 'single good' model. Further, Perera and co-workers [37] calculated Kirkwood–Buff (KB) integrals of acetone–water mixtures using experimental techniques and compared with earlier reported values. The variations in the results were attributed to micro-inhomogeneity of the aqueous solutions.

Soper and co-workers [38] studied ion solvation and water structure of potassium halide aqueous solutions using the combined techniques of neutron diffraction with hydrogen isotope substitution. Their studies showed that the water structure is strongly perturbed in the first hydration shells of both anion and cation whereas it is mild outside. Soper and Weckstrom [39] in another similar work showed that hydration shell of K^+ is orientationally more disordered than that of Cl^- ion. Also, Liu et al. [40] investigated the hydration structure and coordination of K^+ solvation in water at 300 and 450 K using *ab initio* Car–Parrinello molecular dynamics. The K^+–oxygen radial distribution function obtained indicated that the perturbation of K^+ on the water structure is strong in the first hydration shells, while it is mild outside of this region in normal liquid. Luzar and co-workers [41] investigated the structure of acetone and dimethyl sulphoxide in liquid state using the combination of neutron diffraction measurements and empirical potential structure refinement (EPSR) modelling. Their studies helped in understanding the alignment/orientation of dipoles in both the liquids. Perera and co-workers [42] carried out MD simulations to obtained density and energy distribution functions for neat water, methanol and acetone. They analysed the functions so obtained to elucidate the peculiarities of each system with respect to the influence of the local hydrogen bonding on the micro-heterogeneity of the system.

Klasczyk and Knecht [43] used the Kirkwood–Buff theory to develop force fields for Li^+, K^+, Rb^+, and Cs^+ in SPC water to reproduce experimental data on respective aqueous alkali chloride solutions (LiCl, KCl, Rb–Cl, CsCl). The force field developed by them reproduced many of the known properties of alkali metal chlorides solutions. They suggested that the derived force field will be useful for modelling physiological conditions and ion-specific phenomena for bio-molecular systems. Pereyra and co-workers [44] in their work emphasised on the use of many body terms force field (to account for polarization of acetone) in MD simulations to reproduce the experimental data for the excess enthalpy. Their work was to explain the role of acetone dipole moment in acetone water mixtures. However, Perera and co-workers [45] in their comparative molecular dynamics study of water–methanol and acetone–methanol mixtures using non-polarizable model for acetone and methanol showed that besides thermodynamic properties, the structural properties using KB integral can also be reliably calculated taking into consideration the micro-heterogeneity of the system.

Gallo and co-workers [46] studied the structural properties of aqueous solutions of NaCl, KCl and KF salts at ambient and super cooled conditions using MD simulations. They concluded that the hydrogen bonding is preserved at all concentrations and temperatures. Their work explored the concept of an ion as water structure maker or breaker taking into account the other ionic species, ionic concentration and thermodynamic conditions of the solutions. Further, they studied [47] structural properties of aqueous solutions of KCl and KF at ambient and super cooled conditions in the wide concentration range to substantiate their earlier findings.

Polok and co-workers [48] obtained a low frequency spectra of methanol/acetone mixtures from the Fourier transform of the time resolved optical Kerr effect (OKE) signal to investigate the effect of the mole fraction of acetone on the low frequency response. They also performed molecular dynamics simulations and suggested that the hydrogen bonding (HB) manifests itself at higher frequencies, which is mainly visible in the induced contribution to the low frequency response of methanol.

Fennell and co-workers [49] used classical molecular dynamics simulations to study ion–ion interactions in water. They studied the PMFs for the full set of alkali halide ion pairs employing different parameter sets for modelling of both, the water and the ions. They analysed the PMFs to explain the relative stabilities of different ion pairs in associated form.

Heyda et al. [50] studied the behaviour of HIV-1 protease in aqueous NaCl and KCl solutions using kinetic measurements and molecular dynamics simulations. They used MD simulations to explain ion-specific effects on the enzymatic activity as showed by experiments. Pezeshki et al. [51] employed all-atom molecular dynamics simulations to understand the ion conductance on a molecular level in Bacteria Porin OmpF, a major porin in the outer membrane of bacteria. The results obtained were confirmed with the experimental results on mutants.

In the earlier works done from our laboratory, constrained MD simulations have been performed to investigate the solvation structure and dynamics of ions/ion pairs in solvents/mixed solvents. Studies have been done to investigate the potential of mean force (PMF), the structure of the solvation shell around Na^+–Cl^- ion pair and the dynamics of Na^+–Cl^-, Na^+–Na^+ and Cl^-–Cl^- pairs in dimethyl sulphoxide (DMSO), DMSO–water and DMSO–methanol mixtures [7–8,10,52–53]. Studies have also been done for Mg^{2+}–Cl^- ion pair in water–ethanol mixtures [54].

Amongst other ion pairing studies reported by our group, we have also investigated solvation structures and dynamics of K^+–Cl^- ion pair in water–DMSO mixtures [55] with the mole fraction of DMSO (x_{DMSO}) varying from 0.0 to 1.0. The PMFs derived using MD simulations provided information about CIPs, SAIPs and SSIPs in all the compositions. The stability of CIP is found to increase with x_{DMSO} and the CIP is the most stable species in pure DMSO. In the case of pure water, the two species have almost the same stabilities with a low transition barrier. The values of association constants favour the association of the ions pair at higher x_{DMSO}. The analysis of radial distribution functions calculated for all x_{DMSO}, suggests preferential solvation of ion pair with water in all mixtures. In order to understand the solvation shell dynamics in these systems, we also calculated the diffusion constants of solvent molecules in the first solvation shell around K^+ and Cl^- ions in all x_{DMSO}. We obtained low values of the diffusion constants of the solvent molecules in the solvation shells of the mixtures particularly for $0.2 < x_{DMSO} < 0.5$.

There have been a few theoretical studies towards explaining the molecular structure and interactions of ion pairs in aqueous solutions of acetone with varying compositions [56–58].

Gupta and Chandra [56] performed molecular dynamics simulations of water–acetone mixtures containing either an ionic solute or a neutral hydrophobic solute to study the extent of nonideality in the dynamics of these solutes with variation of composition of the mixtures. They found