Temperature Invariance of NaCl Solubility in Water: Inferences from Salt–Water Cluster Behavior of NaCl, KCl, and NH₄Cl

Pankaj Bharmoria, Hariom Gupta, V. P. Mohandas, Pushpito K. Ghosh,* and Arvind Kumar*

Central Salt and Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar 364 002, Gujarat, India

Supporting Information

ABSTRACT: The growth and stability of salt–water clusters have been experimentally studied in aqueous solutions of NaCl, KCl, and NH₄Cl from dilute to near-saturation conditions employing dynamic light scattering and zeta potential measurements. In order to examine cluster stability, the changes in the cluster sizes were monitored as a function of temperature. Compared to the other cases, the average size of NaCl–water clusters remained almost constant over the studied temperature range of 20−70 °C. Information obtained from the temperature-dependent solution compressibility (determined from speed of sound and density measurements), multinuclear NMR (¹H, ¹⁷O, ³⁵Cl NMR), and FTIR were utilized to explain the cluster behavior. Comparison of NMR chemical shifts of saturated salt solutions with solid-state NMR data of pure salts, and evaluation of spectral modifications in the OH stretch region of saturated salt solutions as compared to that of pure water, provided important clues on ion pair–water interactions and water structure in the clusters. The high stability and temperature independence of the cluster sizes in aqueous NaCl shed light on the temperature invariance of its solubility.

INTRODUCTION

The characteristics of aqueous salt solutions and their structures (existence of free ions, solvated ions, ion pair, and higher order clusters) have been investigated employing different experimental methods which include thermodynamic,¹ spectroscopic (IR absorption, Raman, or NMR),² neutron and X-ray diffraction,³ dynamic light scattering,⁴ and zeta potential measurements.⁵

Ultrafast infrared spectroscopy²⁵,²⁶a and ultrafast optical Kerr effect study⁶b,c which shed light on low-frequency modes of aqueous alkali halide solutions, and molecular dynamics calculations⁷ have revealed the dynamical character of aqueous ion solvation. Along with the experimental studies, a large number of theories have been developed to explain the ionic associations and higher order cluster formation in the electrolyte solutions.⁸ The temperature invariance of NaCl solubility in water is an intriguing phenomenon of considerable basic and applied research interest.⁹ This temperature invariance is exploited, for example, for the separation of KCl from a solid mixture of KCl/NaCl by the “hot leaching” process.¹⁰ Surprisingly, there is scant information on the subject, and we report here our experimental studies of salt–water clusters to shed light on the phenomenon.

The presence of large clusters in unsaturated aqueous salt solutions under ambient conditions was detected by Georgalis et al. from dynamic light scattering experiments (DLS).⁴ However, important issues such as the growth of clusters with increase in concentration of salt, the nature of interactions involved in cluster formation, the temperature stability of clusters, and how the solubility of salts may be correlated with cluster size and stability have not been addressed. We have performed concentration- and temperature-dependent DLS and zeta potential measurements in aqueous solutions of NaCl, KCl, and NH₄Cl, and have examined the growth and temperature stability of clusters. It has been shown through separate studies that the adiabatic compressibility determined from complementary measurements of density and speed of sound provides important information on structural changes of water as a consequence of addition of electrolytes.¹¹ We have therefore conducted accurate measurements of speed of sound and density for the above saturated salt solutions as a function of temperature and derived information on their adiabatic compressibility.

Water is a structured liquid with distinct local structures that vary with temperature.¹² Such variations in water structure can be explicitly involved in solubility limits of different salts. Besides temperature, dissolved electrolytes too affect the water hydrogen bonding. In the aqueous electrolyte solutions there exist (i) hydrating water (water in the interior of cluster surrounding ions/ion pairs and water on the surface of cluster) and (ii) bulk water.² Although the nature of chemical environments of the former do not alter significantly with the changes in electrolyte concentration or other physical parameters such as solution temperature and pressure, the proportions of the different forms of water and detectable changes in the equilibrium structure of the “bulk” water are
observed as a consequence of changes in hydrogen bond strength. Ionic charge densities govern water/ion interactions and define the relative importance of both water structure electrostatics, i.e., ion–water dipole interactions, and the extent of hydrogen bonding between water molecules. Due to enhanced electrostatic ordering, ions with higher charge density perturb the bulk hydrogen bonding to a greater extent than larger ions with lower charge density. The water that is on the surface of clusters mediates between the “bulk” water and the hydrated ion pairs, and communicates these small shifts to the ion nuclei. Through FTIR and NMR, which are sensitive and noninvasive techniques, it is possible to detect the changes in the hydrogen-bonding environment of water and also small shifts in ion nuclei. We therefore recorded temperature-dependent FTIR and NMR spectra of sodium chloride, unlike in the case of KCl and NH₄Cl.

The combination of DLS and compressibility data, together with temperature-dependent FT-IR and NMR results, have enabled us to account for the negligible influence of temperature on the solubility of sodium chloride, unlike in the case of KCl and NH₄Cl.

**EXPERIMENTAL SECTION**

**Materials and Methods.** NaCl, KCl, and NH₄Cl (>99.5% by mol) were obtained from SD Fine Chemicals (Mumbai). Salts were used after drying in an oven at 70 °C without further purification. Aqueous salt solutions were prepared by weight, using an analytical balance with a precision of ±0.0001 g (Denver Instrument APX-200) in Millipore grade water. Solubility of different salts at 20 °C was determined gravimetrically by taking excess salt and dissolving to the saturation limit, taking care to ensure that some solid salt remains undissolved. Stirring was carried out for at least 3 h at working temperature. Saturated solutions were filtered, water was evaporated, and the left solids were oven-dried and weighed. Solubility of salts was also confirmed by withdrawing the solutions periodically and analyzing the chloride content by volumetric method using standard AgNO₃ solution.

**Dynamic Light Scattering.** Cluster size and solution zeta potential measurements were performed at varying temperature from 20 to 70 °C on a Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, U.K.) with a He–Ne laser (633 nm, 4 M₀). Salt solutions were filtered directly into quartz cell using a membrane filter of 0.45 μm pore size. Prior to measurements the cell was rinsed several times with filtered water and then filled with filtered sample solutions. For zeta potential, the system employs electrophoretic light scattering method to measure electrophoretic velocities of colloidal clusters in an applied electric field. Temperature of the measurements was controlled with an accuracy of ±0.1 K.

**Densimetry.** The density (ρ) of the salt solutions at different temperatures was measured with an Anton Paar (Model DMA 4500) vibrating-tube densimeter with a resolution of 5 × 10⁻² kg m⁻³. The temperature of the apparatus was controlled to within ±0.03 K by a built-in Peltier device. Reproducibility of the results was confirmed by performing at least three measurements for each sample.

**Ultrasonics.** The speed of sound (c) in the salt solutions at varying temperatures was measured at 51 600 Hz using a concentration analyzer (Model 87, SCM Laboratory Sonic Composition Monitor) based on the sing-around technique with a single transducer cell, immersed in a water bath with temperature controlled to ±0.01 K. The analyzer was calibrated by measurements of speeds of sound in water as a reference, and the error was estimated to be less than ±0.1 m s⁻¹. Measurements were carried out in a specially designed sample jar of low volume capacity. Sample jars were provided with an airtight Teflon covering to keep the samples moisture free during measurements. Not less than three experiments were performed at each temperature to check the reproducibility of the results.

**FT-IR Measurements.** FT-IR measurements of saturated aqueous salt solutions were carried out at room temperature using Nicolet 6700 FT-IR spectrometer. For recording spectra, a cell with BaF₂ windows and a Teflon spacer was used; the optical path length was 0.02 mm. For each spectrum, 132 scans were made with a selected resolution of 4 cm⁻¹. Temperature-dependent FTIR spectra were recorded on a JIR Prestige-21 (Shimadzu) machine.

**Multi-Nuclear Magnetic Resonance (NMR) Measurements.** The ¹H, ¹⁷O, and ³⁵Cl NMR spectra of various saturated aqueous salt solutions were recorded using a Bruker 500 spectrometer. The proton and oxygen chemical shifts were referenced with respect to D₂O. ¹⁷O spectra were obtained at 67.79 MHz. ³⁵Cl spectra of various saturated aqueous salt solutions were recorded corresponding to a salt solution of 0.1 m concentration at 49 MHz. At least 32, 2000–3000, and 256 scans were made for proton, oxygen and chlorine NMR respectively. Temperature-dependent measurements were carried out with an accuracy of ±0.1 K using an inbuilt variable-temperature control unit.

**RESULTS**

The aqueous solubility (molal) of the studied salts as a function of temperature is shown in Figure 1. The investigated salts had varying solubility with temperature, with the highest increase for NH₄Cl followed by KCl and nearly constant solubility in the case of NaCl. Temperature invariance of solubility of NaCl was probed by examining the solution structures of NaCl, KCl, and NH₄Cl.
and NH₄Cl prepared at 20 °C. DLS measurements of salt solutions (from very dilute to saturated) showed a bimodal size distribution, i.e., a small component corresponding to solvated ions (∼5 Å) and a large component corresponding to bigger size clusters. A typical plot of the apparent hydrodynamic diameter ($D_h$) (calculated from the CONTIN method) versus concentration (Figure 2) showed distinct growth pattern of clusters in different salt solutions. The smallest cluster sizes observed at very low concentrations (∼1 × 10⁻⁶ m) were 240, 222, and 168 nm for NaCl, KCl, and NH₄Cl solution, respectively, at 20 °C. In the case of KCl solutions the size of the cluster grew linearly until saturation and acquired a maximum average size of ∼450 nm. In NaCl solutions the cluster size grew linearly up to a concentration of ∼4 m and then became almost constant (∼560 nm) until saturation. A peculiar behavior of cluster growth was observed in aqueous NH₄Cl solutions wherein clusters grew very slowly until a concentration of ∼4 m, and an exponential growth was observed thereafter (∼380 nm at saturation). Temperature-dependent DLS measurements were performed to investigate the temperature stability of different salt clusters at saturation concentrations. Plots of apparent hydrodynamic diameter ($D_h$) versus intensity of scattered light in the saturated salt solutions as a function of temperature showing the large component are provided in Figure 3a–c. With the increase in temperature from 20 to 70 °C, the size of the cluster reduced by 20, 140, and 200 nm for NaCl, KCl, and NH₄Cl, respectively (Figure 3d), indicating that clusters formed in NaCl solutions were temperature stable whereas those in aqueous KCl and NH₄Cl shrank to a sizable extent. The stability of different salt clusters was probed through the measurements of zeta potential (the effective surface potential at the hydrodynamic “shear surface” close to the cluster—bulk water interface), a key parameter governing the electrokinetic behavior of particles in solution. This parameter determines the electrophoretic mobility of the particles within an external electric field, as well as the electrostatic repulsion between particles (or between a particle and a bounding surface) that acts to prevent or promote particle attraction and adhesion. Very high negative zeta

Figure 2. Cluster growth pattern in the studied salt solutions plotted against concentration at 20 °C.

Figure 3. Hydrodynamic diameter $D_h$ distributions plotted against % intensity normalized to unity at different temperatures of (a) NaCl, (b) KCl, and (c) NH₄Cl. Panels d and e show the plots of size distribution and zeta potential, respectively, for various salt solutions at different temperatures.
Precise measurements of density and speed of sound (Table S1 in the Supporting Information) allow determination of solution compressibility ($k_s$) by using the Newton–Laplace equation ($k_s = 1/u^2\rho$), where $u$ is the speed of sound and $\rho$ is the solution density. Figure 4a shows the bar diagram indicating change in compressibility with temperature for water and the three saturated salt solutions, and plots of $k_s$ versus $T$ for the salt solutions are shown in Figure 4b. Saturated solution of NaCl was found to be the least compressible with a marginal rise in $k_s$ with temperature, whereas in the case of pure water and saturated KCl and NH4Cl solutions, there was a drop in $k_s$ with $T$, the trend being H2O > NH4Cl > KCl.

FT-IR spectroscopy has been used to study the structure of water under the influence of salts. Curve fitting of water vibrational spectrum into four deconvoluted bands is often used to describe the structure of liquid water by the continuum model proposed by Walrafen and subsequently developed by others. The most prominent bands are around 3250 and 3420 cm$^{-1}$ corresponding to the strongly H-bonded patches of molecules with strongly and weakly H-bonded molecules, respectively. The component bands at 3550 and 3620 cm$^{-1}$ are attributed to the coupling of OH asymmetric stretching vibrational modes and the dangling OH stretching modes from 3- and 2-coordinate water molecules, respectively. The deconvoluted FT-IR spectra of water and the three salt solutions are shown in Figure 5a–d. In the case of NH4Cl–water solution, the vibrational bands of NH$_4^+$ and OH stretching of water were deconvoluted according to literature procedure and only the bands of OH were considered (Figure 5d). The band area ratio (BAR) of strongly bound to the band area of the weakly H-bonded water molecules [i.e., A$_{3250}$/A$_{3420}$] provided important information about the changes in hydrogen-bonding network of water with the addition of salts. Temperature dependence of FTIR spectra of saturated NaCl solution and BAR of strongly bound to all the weakly H-bonded water molecules are shown in Figure 6a, and b, respectively. Only a small reduction in spectral intensity was observed with the rise in solution temperature from 25 to 70 °C, and the value of BAR hardly changed with temperature.

The extent of interactions of ion pairs of various salts with water molecules in the vicinity can be well understood from the NMR of various nuclei. Figure 7 shows the NMR spectra of $^1$H, $^17$O, and $^{35}$Cl for the three saturated salt solutions as a function of temperature. $^1$H shifts were found to decrease only slightly for both NaCl and KCl, while an increase in $^{17}$O shifts were observed for both the cases. The $^{35}$Cl resonance appeared markedly downfield in saturated NH4Cl, whereas it was least downfield in the case of saturated NaCl. To obtain better insight on the Cl--H--O--H bond strengths in different salt–water clusters, the solid-state $^{35}$Cl spectra of the various studied salts were compared with those of the corresponding saturated aqueous solutions (Figure 8). The chemical shifts in solid state for NH4Cl, KCl, and NaCl were 75.2, 4.41, and $-44.8$ ppm, respectively (very close to literature values and the corresponding values for the solutions were 17.99, 6.5, and 4.04 ppm, respectively. For the solid-state spectra, the shifts in the chemical shift values were 49 and 2 ppm downfield for NaCl and KCl, respectively, while it was 57 ppm upfield for NH4Cl.

**DISCUSSION**

Temperature-dependent DLS (Figure 3d) and zeta potential (Figure 3e) measurements indicated that the clusters in the saturated salt solutions were highly stable. A combination of factors such as electrostatic interactions among oppositely charged ions, hydrophobic interactions among ions caused by exclusion of ions by water, and bridging of water molecules by anions and/or cations is reported to be responsible for the cluster stability. In the saturated salt solutions (particularly for the salts having high solubility), there are only a few water molecules available per ion which will necessarily be involved in the first solvation shell of the ions, and most of the salt molecules will be existing in the form of contact ion pairs (CIP) or solvent-separated ion pairs (SSIP) with the overlapping hydration shells. SSIP species are reported to be thermodynamically predominant in the larger clusters. These ion pairs will influence the water hydrogen bonding strongly and also enhance the water dipole moment. Under such conditions, the force constants for the OH---Cl$^-$ bonds are even larger than for the OH---O (water–water) H-bond. It is further reported that, when the hydration shell of an anion is shared by a cation forming a Y'OH---X' structure (in the present case Y = Na, K, NH4, X = Cl), the cation modifies the properties of the associated anion–water H-bond. As the charge on the cation
increases, the effect becomes more pronounced, with increasing polarization leading to stronger H-bonds. Therefore, the arrangement of water molecules around the ion pairs/contact ion pairs of Na\(^{+}\) with Cl\(^{-}\) would have stronger order in the hydration shells with respect to the ion pairs/contact ion pairs K\(^{+}\) or NH\(_4\)^{+} with Cl\(^{-}\). Consequently, the water molecules would be most strongly anchored in NaCl–water clusters. The solubility of the three salts in water as a function of temperature (Figure 1) could be correlated to the temperature stability of the corresponding salt–water clusters (Figure 3a–d). In NaCl clusters, the dipoles resulting from this local alignment of solvated water may grow large enough, slowing down the equilibrium of bulk and solvated water, thus minimizing the hydration of additional amounts of NaCl even with the rise in temperature. On the other hand, solvated water molecules available in the outer hydration shell were released from KCl–water and NH\(_4\)Cl–water clusters with the rise in temperature as evident from the observed reduction in the cluster sizes (Figure 3d). The released water was utilized for the dissolution of more salt.

There was also good correlation between the solubility differences among the three salts and the \(\kappa_S\) differences of their

---

**Figure 5.** Gaussian decomposition of the vibration FTIR spectra of (a) water, (b) saturated NaCl–water, (c) saturated KCl–water, and (d) saturated NH\(_4\)Cl–water.

**Figure 6.** (a) Temperature dependence of FTIR absorption spectra of saturated NaCl–water solution in the range 2500–4000 cm\(^{-1}\) and (b) band area ratio of strongly bound (icelike) to the band area of the fraction of all weakly H-bonded water molecules (liquidlike).
saturated solutions, the latter being influenced strongly by the perturbation of the water hydrogen-bonding network (Figure 4). Recently, it has been shown that the oxygen–oxygen structure is strongly dependent on the ionic concentration while it is almost independent of the cation. The hydrogen bonding is preserved at all concentrations and temperatures. The main effect of increasing the ionic concentration is the tendency of the water structure to assume the high-density

Figure 7. $^{35}$Cl, $^{17}$O, and $^1$H NMR spectra at variable temperature of aqueous (a) NaCl, (b) KCl, and (c) NH$_4$Cl solutions.

Figure 8. Comparison of $^{35}$Cl NMR spectra of aqueous salt saturated solutions with their corresponding solid salts.
liquid. Our $\kappa_s$ results though favor these results partially that high-density (less compressible) solutions are formed with increase in salt concentrations, but the influence of cation size and charge on water hydrogen bonding cannot be certainly ignored as is evident from different $\kappa_s$ values of salt solutions of similar concentrations (Figure 4b). The $\kappa_s$ differences could be explained on the basis of the partial molar volumes and charge densities of the respective salts. In the case of $\text{NH}_4\text{Cl}$, the ammonium and chloride ions both have partial molar volumes close to that of water ($\sim18 \text{ cm}^3 \text{ mol}^{-1}$), and these do not change appreciably with concentration. Hence the perturbation of the water structure is small. From the very low values of $\kappa_s$ for $\text{NaCl}$–water solution (Figure 4), we inferred that the sodium ion in had pronounced electrostrictive effect. Due to the high charge density and comparatively smaller size, the $\text{Na}^+$ perturbed the water hydrogen bonding to a greater extent. $\text{NaCl}$–water solutions were thus very rigid with greatly reduced free volume and, consequently, having little scope for further solubilization of salt.

The extent of hydrogen-bonding distortion in different saturated salt solutions is further evident from FTIR results (Figure 5). The electric field of the cation polarizes the $\text{O}--\text{H}$--$\text{O}$ and $\text{O}--\text{H}--\text{Cl}^-$ hydrogen bonds of water molecules adjacent to the cation. The strength of the hydrogen bonds increases with increasing polarization and alters $\text{O}--\text{H}$ stretch vibration of an $\text{H}_2\text{O}$ molecule solvating the anion. The small BAR value (0.38) for $\text{NaCl}$–water compared to that of pure water (1.07) obtained from Figure 5 indicated perturbation of hydrogen bonding network by sodium ions to a marked extent in line with the compressibility data. The temperature-dependent studies of BAR indicated that the ratio was virtually unaffected by temperature (Figure 6b). The BAR value of 0.71 in $\text{KCl}$–water revealed moderate perturbation of water hydrogen bonding network and, therefore, had some free volume to accommodate more KCl. In case of $\text{NH}_4\text{Cl}$–water, the value of BAR was even higher (1.33) than that of pure water. The high hydrophobic hydration and good compatibility of ammonium ions with water molecules meant that there is little reduction in free volume of solution. Thus, besides the factors such as high hydration energy and low lattice energy, the negligible perturbation of free volume allowed maximum solubilization of $\text{NH}_4\text{Cl}$ with the rise in temperature.

The changes in $^{35}\text{Cl}$ resonance also provided valuable clues on the nature of the interactions. The high downfield shift observed for the saturated aqueous $\text{NH}_4\text{Cl}$ solution with respect to very dilute standard solution (Figure 7c) was the consequence of larger deshielding of chlorine nucleus under the influence of more electropositive $\text{NH}_4^+$ cation. On the other hand, the large upfield $^{35}\text{Cl}$ shift with respect to solid state (Figure 8) and comparatively high $^{17}\text{O}$ shift (Figure 7c) were indicative of weak Cl--H and O--$\text{NH}_4^+$ bridging thereby forming weaker clusters, as was also indicated by DLS results which showed a significant reduction in the cluster size with the rise in temperature. The high $^{35}\text{Cl}$ downfield shift observed in the case of saturated aqueous NaCl solution with respect to solid state (Figure 8) suggested very strong Cl--H--O--H bonds whereas, in the case of KCl, the much smaller extent of downfield shift was indicative of moderate strength of Cl--H--O--H bonds. Therefore, it was concluded that strong Cl--H bridges as compared to the other cases were possibly responsible for the thermally stable large NaCl–water clusters detected. The strong connections between water oxygen and Na$^+$ ions and weakened water intermolecular hydrogen bonding (as inferred from very low $^{17}\text{O}$ and $^1\text{H}$ NMR chemical shifts in saturated NaCl solutions, Figure 7) also contributed to strengthening of the NaCl–water clusters. When we looked at changes in $^{35}\text{Cl}$ chemical field in saturated aqueous solution as a function of temperature (Figure 7), it went marginally upfield ($\sim3$ ppm), indicating some decrease in hydrogen-bonding strength between Cl$^-$ ions and water protons, which is also perhaps the cause of marginal rise of solution compressibility of saturated NaCl–water solution with the rise in temperature (Figure 4). However, as can be seen from the large downfield shift ($\sim49$ ppm) with respect to solid state (Figure 8), the decrease in hydrogen-bonding strength as a function of temperature was not enough to break the Cl--H--O--H contacts involved in the NaCl–water cluster and hence these remained quite stable in the investigated temperature range.

### CONCLUSIONS

The marked variations in the aqueous solubilities of NaCl, KCl, and $\text{NH}_4\text{Cl}$ as a function of temperature were correlated with their cluster stabilities. The nature of the clusters and their stabilities were probed by a combination of measurements including dynamic light scattering, compressibility, and IR/NMR spectroscopy. Slow exchange of solvated water molecules with bulk water as a consequence of formation of (i) stable NaCl–water clusters, (ii) highly perturbed water hydrogen bonding network with reduced capacity to solvate ions/ion pairs, and (iii) high rigidity of aqueous NaCl saturated solution—preventing penetration of sodium chloride further into the solution—is the probable reason behind the nearly constant solubility of sodium chloride as a function of temperature. As mentioned in the text, this phenomenon is of importance in practical processes such as the separation of KCl from KCl/NaCl solid mixture. Unravelling the phenomenon at a more fundamental level would be a logical extension of the above work. Additionally, the study of the temperature dependence of salt–water clusters on colligative properties may be of considerable importance.

### ASSOCIATED CONTENT

#### Supporting Information

Hydrodynamic diameter ($D_h$) distributions plotted against % intensity normalized to unity of NaCl–water clusters (Figures S1–S3), and density ($\rho$) and speed of sound ($u$) data as a function of temperature (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

#### Corresponding Author

*E-mail: arvind@csmcni.org (A.K.); pkghos@csmcni.org (P.K.G.).* Tel.: +91-278-2567039. Fax: +91-278-2567562.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We thank the reviewers for their critical review of the work and important suggestions which were incorporated in the revised manuscript. The authors are thankful to Prof. Nobuo Kimizuka and Dr. Tejwant Singh for temperature-dependent FTIR measurements. We also thank the Analytical Discipline and Centralized Instrumental Facility of our Institute for helpful assistance. CSIR India is gratefully acknowledged for supporting the research as part of an in-house project.
REFERENCES


