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Chemistry of ice: Migration of ions and gases by directional freezing of water

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Abstract Redistribution of anions and cations creates an electrical imbalance in ice grown from electrolyte solutions. Movement of acidic and basic ions in cooling solutions can permanently change the pH of frozen and unfrozen parts of the system, largely. The extent of pH change associated with freezing is determined by solute concentration and the extent of cooling. In the present work, redistribution of hydrogen, hydroxyl, carbonate, and bicarbonate ions was studied during directional freezing in batch aqueous systems. Controlled freezing was employed vertically as well as radially in acidic and basic solutions. In each case, the ions substantially migrated along with moving freezing front. Conductometry and pH-metry were employed to monitor the moving ions. Besides, some other experiments were carried out with molecular gases, such as oxygen, carbon dioxide, and chlorine and an azeotropic mixture like water–ethanol. Findings can be used to understand possible changes that can occur in preserving materials by freezing.

1. Introduction

In winter, when oceans freeze up (usually at −1.9 °C), the ice at the top contains much less salt than water underneath the surface. This is because of the buildup of ice crystals by pure water leaving the dissolved salts in liquid phase. The increased density of seawater beneath the ice causes it to sink towards the bottom. The process results in ocean currents forming to transport water away from the pole. Freezing of contaminated water represents a practicable application of the phenomenon of solute rejection during the solidification of multi-component systems. The phenomenon has been thoroughly studied at

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different freezing conditions i.e., rate of cooling (Kammerer and Lee, 1969; Parker and Collins, 1999) and effect of stirring (Gay et al., 2003). Several workers employed this process for desalination of water (Himes et al., 1959), food processing, such as concentration of milk and fruit juices (Lorain et al., 2001) and elimination of organic contaminants in refinery effluents (Gao et al., 2009). The effect of rejecting foreign bodies by freezing water is equally valid for soluble salts, organic compounds, and suspended materials.

Various chemical, biological, and environmental processes take place at the interface of ice (Robinson et al., 2006). Reports on the unlike evolution of nitrous acid from assorted high-latitude snowpacks point to place-reliant acidities (Chen et al., 2004; Davis et al., 2001). Freeze-induced pH changes are concerned with food, drugs, and tissues during cryogenic storage (Baicu and Taylor, 2002; Cao et al., 2003; Elford and Walter, 1972; Eriksson et al., 2003; Yamamoto and Harris, 2001). However, pre-freeze treatments (removal of water) can help to reduce the damaging phenomena of loss of shape and texture decline of fruits during thawing (Huxsoll, 1982). Hanley and Rao (1982) studied the migration of moisture and ions in freezing soil and inferred that at the freezing front, cations are preferentially rejected from the frozen region into the unfrozen portion. Li et al. (2007) measured pH and electrical conductivity of polar ice cores to rebuild the history of air pollution. Similar studies were carried out on the Tibetan plateau (Sheng and Yao, 1996; Yao and Sheng, 1993), Tianshan Mountains (Hou et al., 1999; Li et al., 2006) and other regions (Goto-Azuma et al., 2002, 1995, 1993). It was found that pH and electrical conductivity values were high in spring (April and May) and early summer (June) but low in late summer (August and September).

The theory of solute redistribution during freezing of water has been the subject of extensive study in recent years. The present work includes study of migrating H^+, OH^-, CO_3^{-2} and HCO_3^- ions as well as molecular gases both by vertical and radial freezing. Transfer of ions was noted in gradually frozen solutions under controlled conditions by measuring pH and conductance. The acquired information can be helpful in studying migration of these ions during the preservation of foods and pathological samples at low temperatures.

2. Materials and methods

2.1. Reagents and chemicals

All the chemicals and reagents used during the study were of high purity, availed from Sigma–Aldrich, Inc., were used as such (by dissolving appropriate quantity in deionized water). Acetic acid, citric acid, formic acid, sulfuric acid, hydrochloric acid, nitric acid, oxalic acid, and tartaric acid were among acids, while sodium hydroxide, potassium hydroxide, sodium carbonate, and bicarbonate were the bases that were selected for studying ion migration.

2.2. Unidirectional downward freezing

To carry out unidirectional downward freezing, a 2 mm thick polyvinyl chloride pipe with an inner diameter of 2 cm and a height of 30 cm was used. Insulation with polystyrene was

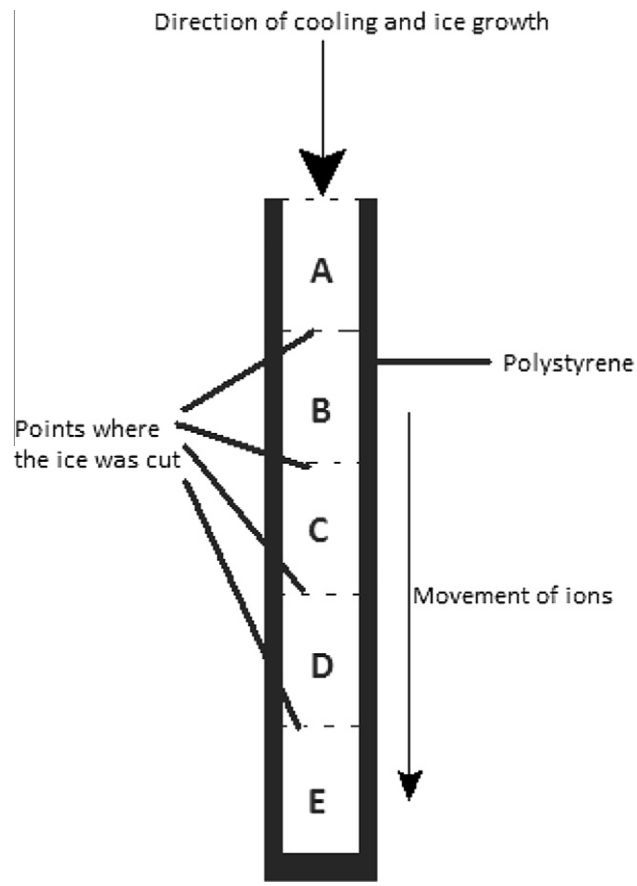

Figure 1 Gradual cooling in PVC pipe that pushed ions (H^+, OH^-, CO_3^{2-} and HCO_3^-) towards bottom.

applied at bottom and outer surfaces of the pipe to ensure gradual cooling in the downward direction. Ice crystals, propagating in the downward direction have pushed the ions towards the bottom of the pipe. After continuous freezing for 20 h, the frozen mass was taken out of the pipe and cut into small pieces of equal length (3 cm), melted and analyzed.

2.3. Radial freezing

To perform radial freezing, a circular glass tank with an inner diameter of 30 cm and height of 15 cm was used. Opening (top) and bottom were insulated with thick polystyrene cover (1–2 in.). Protection was applied to ensure cooling from the sides through the glass. Under such conditions, ice crystals started to develop from the sides towards the center radially and consequently ions would migrate to the center. After continuous freezing for 20 h, the frozen mass was taken out of the tank. To record the effect of freezing on the movement of ions, ice samples were collected by assorted positions, thawed, and analyzed to measure the concentration of ions at that specific position by measuring pH and conductance.

3. Results and discussion

The present work represents results in terms of pH and conductance for solutions carrying H^+, OH^-, CO_3^{2-}, and HCO_3^-