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Effect of Inorganic Salts in Sugar- Aqueous System

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A B S T R A C T

In the present study the preferential salvation of salts in sugar- aqueous system has been considered. It is carried out by using conductometric observation of analytical grade sugar and plantation white sugar aqueous system with salts viz. $CaCl_2$, $MgCl_2$, KCl, NaCl. It shows that the conductivity is in linear relationship with the electrolytes and non-sugar present in both analytical grade sugar and plantation white sugar over a range of 5 to 25 W/V percent. The optimum range of concentration found to be for both the sugars is about 20%. Encouraging results could be obtained in the determination of sugars i.e. non electrolytes and electrolytes in aqueous sugar solution products. The present study shows valid technological interest to understand Maillard reaction due to adoption of $MgCl_2$ salt in place of sulphite. These sugars–salts complexes are responsible for the formation of molasses which leads to substantial loss of sugar of around ten percent of the total sugar present in cane.

Key words: Conductivity, Electrolytes, Non sugars, Analytical grade sugar, Plantation white sugar, Salts

Assessment of sugar quality is carried out by using conventional parameters like Brix, Pol, and Purity. These conventional parameters are calibrated in terms of pure sucrose solution, ignoring non sugars substances having importance during cane sugar manufacture. Apart from these parameters, conductivity has a direct bearing on the quantity of non-sugars (Kumar *et al*. 2009, 2010, Ferreia *et al*. 2009). A lower conducting sugar has a more saleable appeal than one which is higher conductivity due to inclusion of impurities in the form of mineral constituent's, organic non sugars and insoluble impurities present in cane juice (Table 1), or may form during sugar processing like carbonation, phosphotation, sulphitation (Prasad and Singh 2005). In India, plantation white sugar is directly produced from cane juice having many impurities. These impurities like inorganic salts do affect solubility, crystallization rate of sucrose and change of shape of sucrose crystal (Mantovani and Fagioli 1965). The complexities of interactions between water, sugar and eventually impurities in supersaturated solutions have been demonstrated earlier (Mathlouthi and Genotelle 1989, Mathlouthi *et al*. 1986). The literature suggests that crystal growth occur due to transfer of molecules from the medium to the crystal surface where they are incorporated into the crystal lattice. The relative contribution of each may be considerably moderated by impurities which also modify the crystal form when they interface the surface reaction. Such impurities need to be detected instead of sugar part in the system for better control (Van Hook 1981). Knowledge of composition regarding these non-sugars as impurities with special reference to selected salts ($CaCl_2$, $MgCl_2$, KCl, NaCl) are used in this study through conductivity method, because they affect important properties of sugar manufacturing process, including browning development from Maillard reaction, sucrose hydrolysis & sugar crystallization (Santagapita and Buera 2006, 2008, Longinotti *et al*. 2002). The development of new approach for inhibiting the Maillard reaction employing additive such as $MgCl_2$ in sucrose in place of sulphite has a valid technological interest. The effect of cations which is produced from $CaCl_2$, $MgCl_2$, KCl, NaCl, can be analyzed through their impact on modification of solid–water interaction, which modulate the kinetic of Maillard reaction (Acevodo *et al.* 2006).

In recent years, Nuclear Magnetic Resonance is one of the useful techniques for analyzing the water mobility in food products (Schmidt *et al*. 2007). NMR techniques

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require lots of technical skill. Initially the mobility of water in sucrose solution used to be checked by conductivity method (Lindenbaum 1970). The study of interaction of salts with sucrose solution by the proposed conductivity method are explained on the basis of ion–solvent, solvent–solvent, and ion–ion interaction, present in solution (Vishnu and Singh 1978). Study concludes that both ion–solvent and electrolyte non-electrolytes are predominant in such system (Vishnu and Singh 1977). It is also worth mentioning that ions and hydrogen bonding tendencies of sucrose and water does play an effective role in such type of interactions. The above salts definitely affect the aqueous sugar system for their protective behavior.

To understand such interaction a simple mechanism may be cited as under (Eggleston *et al*. 1996).

$$A\,(H_2O)\,n^{Z+} \longleftrightarrow A\,(H_20)_{(n-1)}\,(OH)^{(Z-1)+} + H^+$$

The salt cation of Z^+ charge in water molecules interacts to form a complex as hydrated–salt cation and a proton (H^+) ion. The protons are then available to protonate the glycoside linkage of the sucrose molecules and catalyze sucrose hydrolysis. It is evident that more the Z^+ charge of salt cation causes more catalysis of sucrose hydrolysis (Eggleston and Amorim 2006). Multivalent electrolytes in aqueous sugar solution constitute an almost unexplored field. So, the conductivity analysis of these inorganic non sugar electrolytes in analytical grade sugar as well as plantation white sugar have been carried out by taking 5 to 25% w/v concentration.

The aim of present investigation to find out the actual concentration of both analytical grade sugar as well as plantation white sugar where deviation in linearity occur in presence of selected salts. Study reveals that deviation in linearity for conductivity values occurs at around 22.5% w/v of sugar solution.

MATERIALS AND METHODS

This study has been taken up initially in pure sugar i.e. analytical grade sugar in comparison with plantation white sugar (PWS) as obtained directly from sugar factories with different ICUMSA color values and of different sizes. The Analytical grade sugar used in the investigation was obtained from BDH. In the present investigation, the conductance of Analytical grade sugar, Plantation White Sugar and the effect of various salts as found in cane juice composition like salts of sodium, calcium, magnesium and potassium have been carried out. The weighments of sugar and salts were carried out by using Shimadzu AW 320 balance.

For the conductivity measurements (μS/cm) a glass cell with platinized platinum electrode was employed. The resistance, R, of the solution was measured with an A.C. bridge (Wayne Kerr 6425) in the frequency range ω=500 Hz-5 Hz and true resistance were obtained by extrapolation of R vs. ω-1 at infinite frequency. The volume of the cell was 30 $cm^{3.}$ One set of experiment was performed under isothermal condition at 298.15K. In A second set sugar concentration varied and with an experimental temperature (from 298.15K to 373.15K). A thermostatic ethylene water bath was used to control the temperature of the super cooled solution within ±0.05K. and a kerosene/oil bath was used to control the temperature for the measurement at 298.15Kwith in ±0. 02K. The cell constant was determined as function of temperature employing the reported electrical conductivity of solution of known concentration, aqueous KCl as temperature above 273.15K and ethanol solution of KI for temperature below 273.15K. The cell constant varied from $0.1002cm^{-1}$ at 248K, down to $0.0957cm^{-1}$ at 323K, and the value at 298.15K was 0.0968 ±0.0006 cm^{-1}. Solution was prepared with demonized water free of CO_2 and nitrogen was bubbled into the solution to minimize CO_2 solubilization prior to the measurement. In all cases specific conductivity of pure sugar in water was determined to correct the measure electrical conductivity by the contribution of ionic impurities of the disaccharide or residual CO_2. The experiment results were given as the mean of five parallel trail and measurement. Analysis of variance and Duncans multiple range test were employed to statistically analyze all results. A statistical data analysis software system (Stat Soft, Inc. version 6.2001) was used for analysis. P value, <0.05 were regarded as significant.

RESULTS AND DISCUSSION

The effect of various impurities on sucrose crystallization has been investigated by many authors but could not draw a meaningful conclusion. Impurities like invert sugar, dextran, raffinose, salts and color have been investigated in last six decades. However little information is available in literature on the mechanism of impurity transfer during crystallization. In the first series of experiments, the blank value i.e. the solution containing the same concentration of salts (0.01M) as in the above experiment and with no sugar was observed. The variations of concentration of salts were, however, limited by the solubility of the salt under examination. However, it was in the range of 0.0025–0.01 molar concentration. (Fig 1) shows the percent rise in conductivity values of NaCl and KCl is around 73 percent, whereas in case of $CaCl_{2,}$ $MgCl_2$ it is to be 76 percent.

Table 1 Mineral concentration of cations in cane juice

Constituents (cationic)	Salts	Concentration (% Brix)	Molar concentration
K_2O	KCl	0.77-1.31	0.5616
Na_2O	NaCl	0.01-0.04	0.0078
CaO	$CaCl_2$	0.24-0.48	0.2016
MgO	$MgCl_2$	0.10-0.39	0.096

However, in practice the molar concentration ranges of these salts in cane juice is within 0.09 to 0.5 shown against indicated brixes, as in (Table 1), and in that case the trend of graph shall remain same.

In the second series of experiments, the effect of inorganic salts on electrical conductivity of analytical grade sugar as well as plantation white sugars was carried out. For this purpose, standard solutions of mentioned salts were prepared for making molar concentration of salts. It may be pointed out that all the inorganic salts examined viz. $CaCl_2$, $MgCl_2$, KCl, NaCl were found as inhibiting the electrical conductivity of sucrose solution. For a known concentration of sugar, the influence of salts on the electrical conductivity shows an increasing trend in both the case i.e. analytical reagent as well as plantation white sugar. A comparative study of the electrical conductivity producing ability of various alkaline earth metals in distilled water is summarized in (Fig 1). Only $CaCl_2$ was found to generate sufficient amount of electrical conductivity to be monitored by electrical conductivity meter of 0.01 molar concentration ranges in analytical grade sugar as well as plantation white sugar at room temperature. The electrical conductivity generation potential of $CaCl_2$ was comparable to well-known electrical conducting salts like $MgCl_2$ (Fig 2). Further, to this, from (Fig 2), one can get the following series indicating the effect of inorganic salt components on the electrical conductivity of sugars i.e. $Ca^{++} > Mg^{++}$.

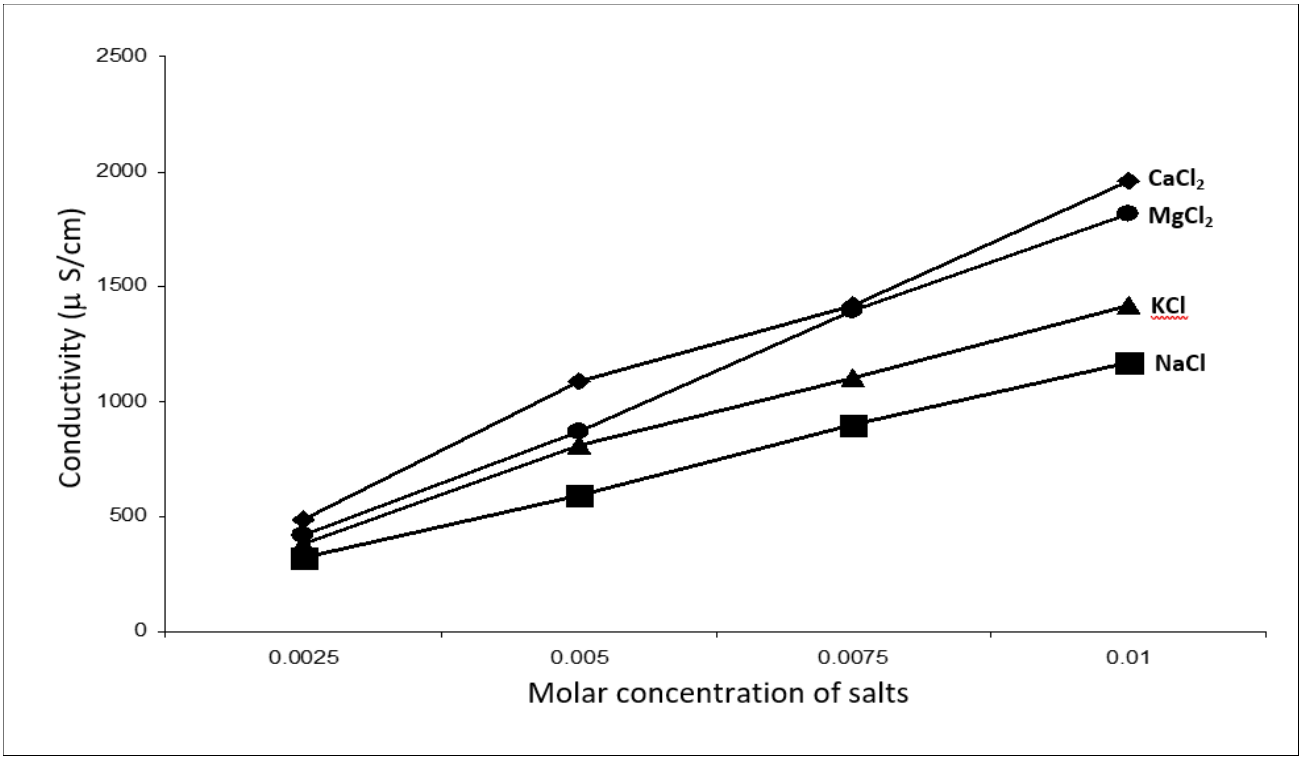

Fig 1 Conductivity Vs molar concentration of salts

Further, from (Fig 3) it is evident that the series indicates the effect of inorganic salt components on the electrical conductivity of analytical grade sugar solution as $K^+ > Na^+$. Similar data were obtained at same concentration of plantation white sugar solution having slightly higher values than analytical grade sugar due to more impurities adhering in plantation white sugars. The observation for KCl and NaCl are represented graphically in (Fig 3). On the other hand, the complex formed between sugar and univalent metallic salts like KCl and NaCl etc. are unimolecular type. This is of marked importance and suggests that in mixture of a sugar and univalent metallic salts complex formation takes place as a result of one molecule of sugar and one molecule of salt. The complexes may be represented as $C_{12}H_{22}O_{11}KCl$ and $C_{12}H_{22}O_{11}NaCl$ etc. in accord with the data obtained in crystallization and phase rule studies.

Exact measurement of inorganic salts as impurity are mentioned at known concentration of sugar solution in present analysis by conductivity method to specify the salts generating higher effect on crystal growth as found in the order of $Ca^{++} > Mg^{++} > K^+ > Na^+$.

Further to this, (Fig 2-3) shows that the deviation in linearity of conductivity values of both the sugars occurs at 20 gram/volume concentration, whereas at higher concentration than 20% gram/volume linearity deviates. It is due to that in sugar–salts system a micellar colloid is formed and volatiles substances are entrapped. By observing electrical conductivity of sugar solution, it suggests that the micellar colloid beyond this concentration forms at maximum degree hence our observation for 22.5% w/v proves to be appropriate. So, the analysis would be helpful within this concentration. The observed results are having good agreement of previous work (Gillett 1949, Sanyal *et al*. 2004). Similar work on calcium chloride, affecting the sugar crystal growth is already mentioned in literature (Ferreia *et al*. 2009) showing that impurity act on the properties of the solution is controlled by conductivity measurement.

Fig 2 Conductivity vs sugar salts solution of 0.01 molar concentrations

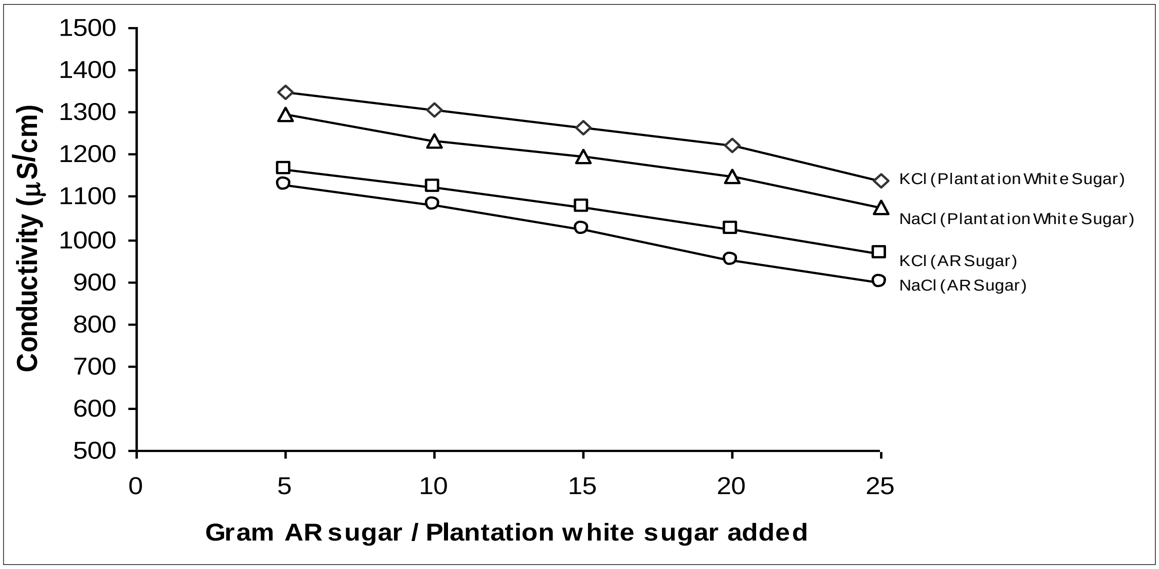

Fig 3 Conductivity vs sugar salts solution of 0.01 molar concentrations

Impurity measurement in sugar solution during batch crystallization, conductivity analysis would be helpful. Conductivity technique was used in detriments of others because of its possibility to be implemented online avoiding problems of sample collection and more importantly the pH which is practically ignored in this analysis due to some obvious reason as mentioned earlier (Kumar *et al*. 2009, 2010). Literature also reveals that the conductivity of solution depends upon several variables such as ash content, crystal content, brix and temperature. In such case the conductivity (K), of sucrose solution at temperature (35°C) can be assumed as a function of impurity concentration ($C_{impurity}$) and sucrose concentration ($C_{sucrose}$):

$$K = f\,(C_{impurity}, C_{sucrose}). \text{ ----------------- } (1)$$

The pH influence on K measurement was also studied and was found to be negligible. The elucidating part of this study reveals that the complex formation occurs between sugar and inorganic salts causes a dip in electrical conductivity value. The charge transfer reaction occurs in sugar–water–salts system. Finally, a similar picture of ion–water interactions has been reached by a quite different approach. Method from self-diffusion measurements the average time that a water molecule spends in the immediate vicinity of ion by calculation was done in past (Samoilov 1957). This can be more or less than the exchange time for molecules in pure water. Values of this ratio for the above analyzed salts are given in (Table 2).

Moreover, it is based on study that the ion association would be minimum in the salts of alkali metals with univalent anions, and this generally true; there is no evidence of ion paring in the halides of sodium and potassium hence record lesser conductivity value in comparison with alkaline earth metals i.e. calcium and magnesium. Here the metal of higher atomic number shows more ion pairing, as in the halide. It is interesting to note that ion pairing is directly proportional to atomic radius. Data is available in literature for the group II metals, and with the increase in cationic charges the formation of ion pairs in dilute solution becomes the rule rather than the exceptions (Table 2).

Table 2 Time spends by the water molecule in the immediate vicinity of ions and hydration number of ions

Constituents (cationic)	Average time	Hydration number
Na^+	1.46	7-9
K^+	0.65	4
Mg^{++}	86.3	12-14
Ca^{++}	2.16	9-12

The present study reveals that the conductivity parameter can be utilized to measure the impurity in sugar solution in terms of its concentration at around 20% W/V. The conductivity value can be assumed as a function of impurity concentration ($C_{impurity}$) and sucrose concentration ($C_{sucrose}$) as a similar finding is available in literature. The Maillard reaction due to adoption of magnesium chloride and not sulphite is another fact-finding interpretation of the present study.

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