Analytical modelling of electrical impedance based adulterant sensor for aqueous sucrose solutions

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ABSTRACT

An analytical model is developed to describe the dielectric behaviour of pure DI water-sucrose solution in which sodium carbonate (Na_2CO_3) is added as an adulterant. Relative impact of constituent dipoles has been emphasized and multi-body dipolar interactions have been explicitly considered for a comprehensive analysis of such a system in thermal equilibrium. The theoretical model is verified with experimental data obtained from the impedance and capacitance based spectroscopic measurements. The impedance and capacitance of DI water-sucrose solution are observed to vary in a quasi-oscillatory nature with different sucrose content in it. However, such variation shows a decreasing trend and linear nature for a minimum of 1% adulterant content. The system impedance decreases and capacitance increases with increasing adulterant wt% for a given sucrose concentration. For the 0% of adulterant in the solution with varying sucrose content, the impedance and capacitance have varied from 140.12 kΩ to 236.17 kΩ and 40.7 pF to 44.2 pF, respectively. However, such values change from 111 Ω to 157 kΩ and 42.5 pF to 72 μF for the adulterant content up to 5%.

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1. Introduction

The dielectric analysis of carbohydrates in different solutions has attracted a great deal of interest among the global research community since several decades and has emerged as a potential domain for both the academic and industrial world [1–4]. Sucrose, a naturally occurring carbohydrate in trees and plants, has immense impact on human physiology and therefore, research is being carried out around the globe to explore salient properties of sucrose solutions [1]. Among various approaches, the electrical analysis of sucrose solutions by impedimetric and capacitive studies has been a very promising method, finding enormous applications with a truly large variation, from genomic studies to rapid food quality monitoring [3,4]. Food adulteration is a serious issue in the present world and is a matter of major concern among the consumers. There is a growing tendency among the unscrupulous traders all over the world to incorporate several chemicals into natural food stuffs for their monetary profit [5]. Adulteration of sugar by chemical compounds such as chalk powder ($CaCO_3$) and soda wash (Na_2CO_3) has become quite a regular issue over some time causing serious health hazards, which mainly includes severe stomach disorders [6]. Rapid detection of such hazardous adulterants by electrical measurements has become a truly important area of research in recent days due to the deliberate threat over the public health security [5].

Sucrose is a disaccharide with pyranose and furanose skeletons linked via a glycocidic linkage and also it is polar in nature due to the arrangement of its constituent hydrogen and oxygen atoms, leading to an uneven distribution of electrons around the entire molecule [7]. As a consequence, sucrose in different base solutions exhibits very interesting electrical behaviour for its particular structure and polarization effect. Such electrical properties are functions of the polarity of base solvents as well as the compositional concentration of sucrose in the solution. The centres of positive and negative charges of water molecules do not coincide, thereby, make it a polar molecule and therefore the aqueous solution of sucrose exhibits different electrical properties compared to a pure ionic solution. Now, on addition of ionic adulterants, such behaviour of pure polar solution gets altered.

Several theoretical models have been proposed to describe the electrical behaviour of carbohydrate molecules in a solution. The Clausius-Mosotti equation is generally used to describe the effective dielectric behaviour of the solutions with non-polar solutes [8]. However, this is not sufficient enough to analyse the similar behaviour for the solutions which contain both the polar and ionic components. Debye gave a theory on the effective dielectric constant of a solution with polar molecules. Afterwards, Onsager and then Kirkwood founded their models on the basis of Debye theory with the concept considering the molecule to be surrounded by a continuous medium [4,8–10].

A sucrose molecule is a combination of glucose and fructose molecules. Hydrolysis is a phenomenon that breaks the glycocidic bond between these two monosaccharides and releases them in the solution. However, the process is very slow at room temperature and merely happens in absence of any mediator [11]. There are following three types of dipole interactions present in the system of a purely aqueous solution of sucrose: the water-water, water-sucrose and sucrose-sucrose interactions [12]. Addition of ionic compounds in this scenario would include interactions of ionic dipoles into the system [9]. Therefore, the net polarization must be a function of the compositional concentration of both sucrose and the adulterant in the system. In most of the theoretical models, the multi-body dipole correlations have not been adequately addressed which includes polar-polar, polar-ionic and ionic-ionic dipolar interactions. Therefore to develop a thorough understanding on the nature of dielectric behaviour of a polar-ionic mixed solution, a more generalised model is needed, considering all possible dipolar interactions.

In this work, a theoretical model is developed for describing the dielectric nature of pure DI water-sucrose solution in which sodium carbonate is mixed as an adulterant. Impact of ionic dipoles has been emphasized and inter-dipolar interactions have been explicitly considered for a detailed analysis of such a system in thermal equilibrium. The analytical model has been verified with the experimental results of impedance and capacitance measured by employing impedance and capacitance spectroscopy of the DI water-sucrose solution with sodium carbonate as adulterant.

2. Material and methods

2.1. Sample preparation

Sucrose stock solutions were prepared by using electronic grade deionised (DI) water (Millipore™) and sucrose powder (Merck) for five different concentrations of sucrose ranging from 13.72 °Bx to 68.6 °Bx. Sucrose concentrations under investigation were 13.72, 27.44, 41.15, 54.87 and 68.6 °Bx and the equivalent volume fractions of sucrose with respect to DI water in the solution are 0.1, 0.2, 0.3, 0.4 and 0.5 respectively. Sodium carbonate (Sigma-Aldrich), which was added as an adulterant in these stock solutions, is taken in different weight percentages with respect to sucrose, ranging from 0.0075 to 5%. The samples were kept in glass beakers at room temperature throughout the experiment.

2.2. Theoretical modelling

A mixture of aqueous solution of sucrose and sodium carbonate has been considered in the present work, where the bulk sucrose solution is purely polar and sodium carbonate is ionic in nature. To describe the dielectric behaviour of such solution, the system is considered to be constituted of pure polar dipoles relevant to sucrose molecules and ionic dipoles generated by sodium and carbonate ions. The schematic representation of such a solution is shown in Fig. 1. The mixture is first considered to be a bulk solution with n number of dipoles per unit volume and a resultant dipole moment $\boldsymbol{p}$. Without the application of an external field $\boldsymbol{E}$, thermal agitation keeps all the dipoles randomly oriented, resulting in a net zero dipole moment. On application of the electric field the system tends to line up along the field direction in the least energy configuration and consequently, giving rise to an average polarization $\boldsymbol{P}$. For the calculation of $\boldsymbol{P}$, it is noted that the Hamiltonian of the system is given by,

$$H = H_0 - \boldsymbol{p} \cdot \boldsymbol{E} \tag{1}$$

where, H_0 stands for a coordinate depending function of the molecule. The Boltzmann factor for classical systems is given as $f(H) = e^{\frac{-H}{kT}}$, k and T being the Boltzmann constant and the temperature of the system
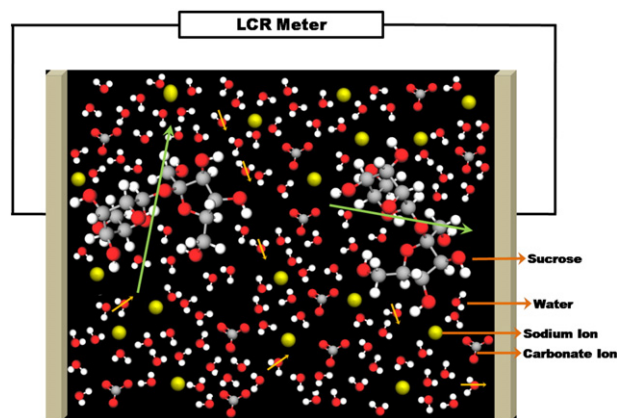

Fig. 1. Schematic representation of a system consisting of water and sucrose dipoles along with sodium and carbonate ions under the effect of an external electric field.

respectively. Using the Boltzmann factor, which is proportional to the number of dipoles per unit volume per unit solid angle with the direction of electric field, the net contribution from the dipoles to the polarization can be written as [13], where, θ is the angle between the vectors relevant to dipole moment and applied electric field. Generally, pE/kT is less than unity (except at very low temperature) and therefore, expanding the exponentials one obtains, $\overrightarrow{P} = \frac{np^2}{3kT}\overrightarrow{E}$. Again, Gauss's theorem of dielectrics leads to expression for polarization as, $\overrightarrow{P} = (\varepsilon - \varepsilon_0)\overrightarrow{E}$. Comparing the above relations, we can write,

$$\overrightarrow{P} = np \frac{\int_0^\pi e^{pE\cos\theta/kT}\sin\theta\cos\theta d\theta}{\int_0^\pi e^{pE\cos\theta/kT}\sin\theta d\theta} \tag{2}$$

$$\frac{\varepsilon}{\varepsilon_0} = \frac{np^2}{3kT\varepsilon_0} + 1 \tag{3}$$

The solution of DI water and sucrose is pure polar in nature and will have three different types of interactions at the molecular level, including the water-water, sucrose-sucrose and water-sucrose dipoles which finally determine the overall dielectric behaviour of the solution [14]. Considering the fact that the dipoles are randomly oriented in reference to the applied electric field and also with each other, the effective net dielectric constant (DC) of the system can be expressed as [4]:

$$\varepsilon_{eff} = \frac{\varepsilon}{\varepsilon_0} = \left[\sum_{i=1}^{N_W} (p_{Wi}\cos\theta_{Wi})^2 + \sum_{i=1}^{N_S} (p_{Si}\cos\theta_{Si})^2 \right. \tag{4}$$

$$\left. + 2\sum_{i=1}^{N_{Sol}} p_{Wi}p_{Si}\cos\theta_{Wi}\cos\theta_{Si}\cos\varphi_i \right] + 1$$

where, p_S and p_W correspond to the dipole moments of sucrose and water, respectively, θ_W and θ_S represent the angles between the dipoles and applied field for water and sucrose, respectively, and φ is the angle between the resultant dipole moments for water and sucrose molecules in the system. N_W, N_S and N_{Sol} are the numbers of elementary volumes relevant to water, sucrose and entire solution within the measuring cell, respectively. Thus, (N_S/N_W) is equivalent to the volume fraction of sucrose with respect to DI water in the solution.

Now, the addition of ionic compound such as sodium carbonate (Na_2CO_3) will alter the dielectric behaviour of such solution. The effective dielectric constant will then be a function of the number density and polarization of the constituents of the system and their interactions at the molecular level, including polar-polar, polar-ionic and ionic-ionic dipoles.