Dielectric relaxation studies of aqueous sucrose in ethanol mixtures using time domain reflectometry

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Abstract. Time domain reflectometry method has been used in the frequency range of 10 MHz to 10 GHz to determine dielectric properties of aqueous sucrose in ethanol. The dielectric parameters, i.e., static dielectric constant and relaxation time were obtained from the complex permittivity spectra using the non-linear least squares fit method. The Luzar theory is applied to compute the cross-correlation terms for the mixtures. It adequately reproduces the experimental values of static dielectric constants. The Bruggeman model for the non-linear case has been fitted to the dielectric data for mixtures.

Keywords. Dielectric permittivity; time domain reflectometry; Kirkwood factor.

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1. Introduction

Alcohols are compounds in which hydroxyl (−OH) group is attached to saturated hydrogen atom. The hydroxyl group is a functional group of alcohols. Their general formula is R−OH and these are classified as monohydric, dihydric, trihydric, and polyhydric alcohols. The O−H bond in alcohol is highly polar, because oxygen is highly electronegative. The oxygen carries partial negative charge ($\delta-$) and the hydrogen carries partial positive charge ($\delta+$). The polarity of O−H bond gives rise to attraction of partially positive hydrogen atom of other molecules. Due to this, hydrogen bonding requires a great deal of energy in the form of heat to overcome these attractive forces, and hence the boiling point of alcohols is on the higher side.

Ethanol is the simplest alcohol of this class. It is the prime constituent of all types of beverages. It is traditionally prepared from starchy materials such as potatoes, maize, barley etc. by fermentation (fervre-to boil) by enzyme known as yeast, which is a single-celled living plant. It is also prepared from glucose, fructose, and sucrose, by catalytic action of enzymes molasses.

Water has a permanent dipole moment, that is, its electrical properties might be simulated to first order as arising from a fixed positive charge and a fixed negative charge, separated by a certain distance. The molecule also possesses a polarizability, that is, an additional dipole is induced by an electric field, and is proportional to its magnitude. The water molecule is non-linear, and the mean HOH angle is known from the infra-red absorption spectrum [1] to be 104.474°; the mean O–H distances are each 0.95718 Å, but these free molecule values are not maintained in the liquid. The oxygen atom is considered to be more electronegative than the hydrogen atom. When they are bonded, dipole moment will exist with the negative oxygen. From symmetry considerations, it would appear probable that the dipole moment vector bisects the HOH angle, and points from negative oxygen atom to the positive region between the hydrogen atoms. A number of point charge models of the water dipole have been constructed; but to attempt to reproduce the observed permanent dipole moment by a wave function which completely describes the electron density is also important [2–8].

For the water dipole to be able to undergo considerable rotation about one of its hydrogen bonds, the breakage of its other bonds is necessary. Unbounded molecules, or molecules making only one bond, can rotate without breakage, whilst molecules bonded to three or four neighbours require more than one bond. If the 'two bonded' molecules which reorient with the breakage and remaking of one only, and which because the activation enthalpy is of this order, can be regarded as playing the dominant role in the principle relaxation process. Continued bond breakage replenishes this species from other species. The faster bond-breaking processes make slower (high-energy) processes very rare, so that the three and four bonded species do not contribute any appreciable relaxation, even though they are present in large proportions [2–8]. The dipolar properties of water molecules affect the interaction between water and other molecules that dissolve in water. Water is the most important liquid of the biosphere because it is a major component of living system, and it interacts with many biomolecules [2–8]. The dielectric study has extensively been done on alcohol–water mixture [9–19] because this system has interesting behaviour with reference to hydrogen bonding. Mashimo *et al* [13] gave dielectric relaxation parameters of mixtures of water and primary alcohols over a frequency range of 10 MHz to 15 GHz using time domain reflectometry (TDR) technique at 25°C in the concentration range 0–1 mole fraction of water. Bertolini *et al* [14] have reported dielectric properties of ethanol in water using coaxial resonator spectrometer in the frequency range 0.47 to 4 GHz at temperatures from $-43°C$ to 30°C, in the concentration range $0V$ to $0.5V$, where V is the mole fraction of water.

Sucrose is a disaccharide and commonly known as carbohydrate, moreover it is ordinary table sugar. It is obtained from sugar cane juice and sugar beets. It is composed of α-D glucose unit and β-D fructose unit. These units are joined by α, β-glycosidic linkage between C-1 of the glucose unit and C-2 of the fructose unit. Carbohydrates constitute most of the organic matter in the biosphere and

contribute to almost all forms of life on the Earth. Carbohydrate solutions are most interesting in basic research and have large applications in biochemical and biophysical research [20–22]. Carbohydrate serves as a main energy source, used to maintain the structural and functional properties of the cells. Hence carbohydrates play diverse roles in biology as metabolic intermediates, as important components of nucleic acids, glycoproteins, and glycolipids, and as prime polymeric contributors to the structure and function of the extra cellular matrix. Recently, attention has been paid, in particular, to the rich conformational variety of carbohydrates [20–22]. The ability of carbohydrates to substitute water in the hydrogen network is essential for their role in bimolecular stabilization and protection [20]. The hydration properties of carbohydrates are thus a key feature in determining their structural and functional properties [20–22]. Fuchs and Kaatze [22] had studied some saccharides in aqueous solutions using dielectric relaxation technique. The dielectric spectra showed unusual characteristics as compared to other molecules [22].

We have reported the dielectric properties of aqueous sucrose in ethanol solutions using TDR technique in the frequency range 10 MHz to 10 GHz and the temperature range of 15°C to 45°C.

2. Experimental

2.1 *Materials*

Sucrose and ethanol were obtained commercially and used without further purification. The mixtures of various compositions were prepared by dissolving sugars in de-ionised glass distilled water. The complex permittivity spectra were studied using time domain reflectometry method [17–19]. Tektronix 7854 sampling oscilloscope with 7S12 TDR unit was used. A fast rising step voltage pulse of 25 psec-rise time generated by a tunnel diode was propagated through a coaxial line system. The sample cell was placed at the end of coaxial line in a standard military application (SMA) coaxial cell of 3.5 mm outer diameter. All measurements were done under open load condition. The sampling oscilloscope monitored the change in the pulse after reflection from the sample placed in the cell. The reflected pulses without sample and with the sample were digitized in 1024 sampling points in the window of 5 ns. For the experiment, a SMA cell with 1.35 mm effective pin length was used. The reflected pulses were transferred to PC/XT system for Fourier transformation as well as data processing [17–19]. The processing of the data was carried out to yield complex reflection coefficient spectra $\rho^*(\omega)$ over a frequency range from 10 MHz to 10 GHz [17–19]. The complex permittivity spectra $\varepsilon^*(\omega)$ was obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying the least squares fit method [23] as described in our earlier publications [17–19].

3. Results and discussions

The values of static dielectric constant (ε_0) and relaxation time (τ) at different temperatures have been determined by fitting the complex permittivity spectra

$[\varepsilon^*(\omega)]$ with the Havriliak–Negami equation [24],

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[(1 + j\omega\tau)^{1-\alpha}]^\beta}, \tag{1}$$

with $\varepsilon_0, \varepsilon_\infty, \tau, \alpha$ and β as fitting parameters in eq. (1). The Havriliak–Negami function includes the Cole-Cole ($\beta = 1$), the Davidson Cole ($\alpha = 0$) and the Debye ($\alpha = 0$ and $\beta = 1$). For the systems studied here, the values of α and β are found to be 0 and 1 respectively within the experimental error. The dielectric parameters of aqueous sucrose at various mole fraction of ethanol are also reported in table 1. It can be seen from table 1 that the static permittivity decreases with increasing mole fraction of ethanol in aqueous sucrose, whereas the relaxation time increases with increasing mole fraction of ethanol in aqueous sucrose. Thus, the decrease in static dielectric constant indicates complete association of large amount of sucrose solution. The change in the variation of relaxation time provides information regarding hydrophilic character of the solute particle.

To understand the significance of association effect due to the hydrogen bonding, it is useful to compute the values of the Kirkwood correlation factor g and it can be expressed as [8]

$$\sum_{i=1,2} \frac{4\pi N \mu_i^2 \rho_i}{9kTM_i} \, g_i = \frac{(\varepsilon_{0i} - \varepsilon_{\infty i})(2\varepsilon_{0i} - \varepsilon_{\infty i})}{\varepsilon_{0i}(\varepsilon_{\infty i} + 2)^2}, \tag{2}$$

where $i = 1, 2$ represents water and ethanol respectively, μ_i is the dipole moment in gas phase, M_i is the molecular weight, ρ_i is the density, k is the Boltzmann constant, N is the Avogadro's number, ε_{0i} and $\varepsilon_{\infty i}$ are the static dielectric constant and dielectric constant at high frequency, respectively and g_i is the correlation factor.

It is impossible to determine g_1 and g_2 from a single value of the static dielectric constant without some assumption. We have considered that the mixture can be represented by one correlation factor g^{eff} as [18]

$$\frac{4\pi N}{9KT} \left(\frac{\mu_e^2 \rho_e (1 - V)}{M_e} + \frac{\mu_w^2 \rho_w V}{M_w} \right) g^{\text{eff}} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} - \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2}, \tag{3}$$

where μ_e and μ_w are the dipole moments of ethanol and water respectively and ρ_e and ρ_w are their corresponding densities, V is the volume fraction of water and m indicates the binary mixture. To calculate g^{eff} values, we have taken dipole moments of ethanol and water as 1.69D and 1.84D, respectively. The high values of g^{eff} indicate parallel orientation of electric dipoles in a molecule [8]. It can be seen that, as water is added in ethanol at regular steps in the mixture, the values of g^{eff} increase. The increase of correlation in ethanol and ethanol–water mixtures may be due to association effects.

In the above model, no cross-correlation terms were included. Luzar and coworkers have suggested a model in which the cross-correlation terms have been taken into account [25–27]. The correlation factor g_1 and g_2, were computed in the mean field approximation. We have used the same model to explain the static permittivity of the mixture. The different parameters required in the Luzar model are dipole moments, polarizabilities, energies, ethalpies, and possible number of hydrogen bonding.

Table 1. Temperature-dependent dielectric parameters for aqueous sucrose in ethanol mixtures.

Mole fraction of ethanol	15°C		25°C		35°C		45°C	
	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)	ε_s	τ (ps)
Water								
0.000	83.9	10.7	79.5	8.8	75.9	6.5	71.3	5.5
0.072	71.8	18.9	70.1	15.7	68.0	12.7	65.8	10.4
0.173	63.3	26.9	59.5	24.1	53.2	20.3	49.2	15.6
0.318	50.2	42.7	48.1	35.0	45.8	28.2	42.5	20.8
0.2 M Sucrose								
0.000	82.6	17.6	77.5	15.3	73.8	14.4	70.6	13.1
0.072	72.0	27.1	71.2	22.3	68.7	17.4	66.5	12.5
0.173	64.6	40.9	61.2	32.4	55.2	28.0	51.4	22.6
0.318	50.7	54.9	48.9	47.8	46.8	40.7	44.3	32.6
0.4 M Sucrose								
0.000	78.2	19.8	74.8	17.6	71.5	16.1	68.7	14.2
0.072	73.5	33.4	72.3	26.5	70.2	20.9	67.6	17.7
0.173	66.9	43.1	63.8	35.3	57.6	30.5	54.5	26.0
0.318	51.3	58.0	50.2	53.5	48.5	45.4	46.5	38.3
0.6 M Sucrose								
0.000	76.3	21.3	73.1	18.9	69.4	17.2	66.9	15.5
0.072	69.7	35.3	73.5	29.2	71.5	23.5	68.2	21.1
0.173	68.4	49.1	65.9	40.3	61.4	33.4	56.5	30.1
0.318	51.8	65.9	51.0	58.4	50.6	48.3	48.4	40.0
0.8 M Sucrose								
0.000	75.2	26.3	72.0	22.5	68.2	19.6	65.0	18.0
0.072	79.8	38.3	67.8	31.1	65.2	26.2	61.4	23.5
0.173	64.5	51.3	61.6	43.8	57.3	37.7	53.6	33.8
0.318	48.7	72.5	47.2	63.7	46.4	52.6	44.8	45.7
Sucrose								
0.000	74.7	30.4	71.6	25.8	67.8	23.1	64.7	21.1
0.072	68.2	42.2	64.5	34.5	61.8	29.5	57.9	25.3
0.173	61.2	55.4	51.8	47.9	53.5	41.2	51.8	37.5
0.318	46.8	82.5	45.0	74.7	44.2	60.2	43.5	52.0

In our analysis, the best possible values of the above molecular parameters for which experimental and theoretical static permittivity values give reasonably satisfactory agreement are as follows:

Dipole moment of water = 2.14D
Dipole moment of ethanol = 3.04D
Polarizability of water = $1.96 A^{03}$
Polarizability of ethanol = $5.1 A^{03}$
Bonding energy for water–water pair = −13.4 kJ/mol
Bonding energy for water–ethanol pair = −15.5 kJ/mol

Statistical volume ratio for the water–water pair $= 28A^{03}$
Statistical volume ratio for the water–ethanol pair $= 46A^{03}$
Number of ethanol molecule interacting with water $= 2$
Average direction cosine angles between dipoles $= 1/3$

The values of permittivity obtained from Luzar model using the above parameters are given in table 2 along with the experimental values. It can be seen from table 2 that the theoretical values are in reasonable agreement with experimental values. It should also be noted that the values of dipole moments of water and ethanol molecule are taken to be 14% and 10 % higher than the corresponding values of dipole moments in the gas phase. The values of g^{eff}, g_1 and g_2 are also given in table 3.

The static permittivity of the mixtures can be related using Bruggeman's mixture formula, with volume fraction V of water. The Bruggeman mixture formula is given by the expression [28]

$$f_{\text{B}} = \left(\frac{\varepsilon_{0\text{m}} - \varepsilon_{0\text{w}}}{\varepsilon_{0\text{e}} - \varepsilon_{0\text{w}}} \right) \left(\frac{\varepsilon_{0\text{e}}}{\varepsilon_{0\text{m}}} \right)^{1/3} = 1 - V, \tag{4}$$

where f_{B} is the Bruggeman dielectric factor. $\varepsilon_{0\text{m}}$, $\varepsilon_{0\text{e}}$ and $\varepsilon_{0\text{w}}$ are the values of static dielectric constant corresponding to mixture, ethanol and water respectively, and V is the volume fraction of the solvent. The experimental values of f_{B} vs. volume fraction is shown in figure 1. The Bruggeman equation predicted a linear relationship between f_{B} and volume fraction V of water, whereas it can be seen from figure 1, the experimental values of f_{B} shows non-linear behaviour. Therefore, the Bruggeman equation is modified by assuming non-linear behaviour as equation

$$f_{\text{B}} = \frac{\varepsilon_{0\text{m}} - \varepsilon_{0\text{w}}}{\varepsilon_{0\text{e}} - \varepsilon_{0\text{w}}} (\varepsilon_{0\text{e}}/\varepsilon_{0\text{m}})^{1/3} = 1 - [a - (a-1)V]V. \tag{5}$$

Table 2. Comparison of experimental values of static dielectric constant with theoretical values obtained from Luzar model.

Volume fraction of water	0°C		10°C		25°C		40°C	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
0.0	26.70	27.14	26.31	26.22	24.95	24.96	22.41	23.81
0.1	32.16	35.61	30.53	34.29	29.27	32.41	25.13	30.67
0.2	37.86	42.80	36.85	41.13	35.42	38.78	32.00	36.81
0.3	49.19	49.55	45.99	47.56	41.15	44.73	40.51	42.02
0.4	52.10	55.89	52.86	53.59	47.56	50.31	45.36	47.17
0.5	61.04	61.93	60.08	59.34	55.07	55.62	46.57	52.05
0.6	66.17	67.75	64.41	64.86	59.67	60.73	47.88	56.73
0.7	68.26	73.37	66.49	70.20	66.08	65.66	59.48	61.25
0.8	73.09	78.84	71.04	75.40	70.23	70.46	66.96	65.54
0.9	76.19	84.17	74.60	80.46	73.73	75.13	67.26	69.92
1.0	86.20	89.38	85.60	85.41	79.50	79.70	70.50	74.09

Table 3. Temperature-dependent Kirkwood factor for ethanol–water mixture.

| Volume fraction of water	0°C			10°C			25°C			40°C		
	g^{eff}	g_1	g_2	g^{eff}	g_1	g_2	g^{eff}	g_1	g_2	g^{eff}	g_1	g_2
0.0	2.96		1.00	3.02		1.00	3.02		1.00	2.82		1.00
0.1	2.83	1.97	1.13	2.78	1.95	1.13	2.80	1.94	1.12	2.51	1.96	1.12
0.2	2.77	2.05	1.20	2.79	2.04	1.20	2.82	2.01	1.19	2.67	2.02	1.21
0.3	3.10	2.10	1.26	3.00	2.08	1.26	2.82	2.05	1.25	2.92	2.05	1.24
0.4	2.88	2.13	1.31	3.03	2.12	1.30	2.87	2.09	1.29	2.87	2.08	1.29
0.5	3.02	2.16	1.34	3.08	2.14	1.34	2.97	2.11	1.33	2.63	2.10	1.32
0.6	2.97	2.18	1.37	3.00	2.16	1.37	2.92	2.13	1.36	2.45	2.11	1.35
0.7	2.80	2.20	1.40	2.83	2.18	1.39	2.92	2.15	1.38	2.80	2.13	1.37
0.8	2.78	2.22	1.42	2.80	2.20	1.41	2.96	2.16	1.40	2.91	2.14	1.39
0.9	2.69	2.23	1.43	2.73	2.21	1.43	2.84	2.18	1.42	2.72	2.15	1.41
1.0	2.86	2.24		2.95	2.22		2.88	2.19		2.68	2.15	
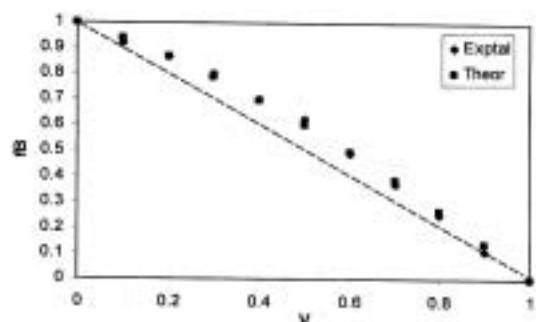
Figure 1. Bruggeman dielectric factor (f_{B}) vs. volume fraction (V) of water in ethanol at 25°C. Dashed line represents theoretical curve according to the Bruggman model (eq. (5)).

The value of a equal to 1 corresponds to an ideal mixture with no additional interaction between two liquids and leads to the Bruggeman equation (4). The modified Bruggeman equation fits the experimental values within 4%. The value of a has been found by least squares to be 0.5 in ethanol–water mixtures.

The thermodynamic parameters evaluated using Eyring equation are as follows [8]:

$$\tau = (h/kT)\exp(\Delta H/RT)\exp(-\Delta S/R), \tag{6}$$

where ΔS is the entropy of activation, ΔH is the activation energy in kJ/mol, respectively. τ is the relaxation time, T is the temperature in degree Kelvin and h is the Planck's constant. The temperature dependence of relaxation time, described by Arrhenius plot of log (τ) vs. $1000/T$, is shown in figure 2 for aqueous sucrose in ethanol.
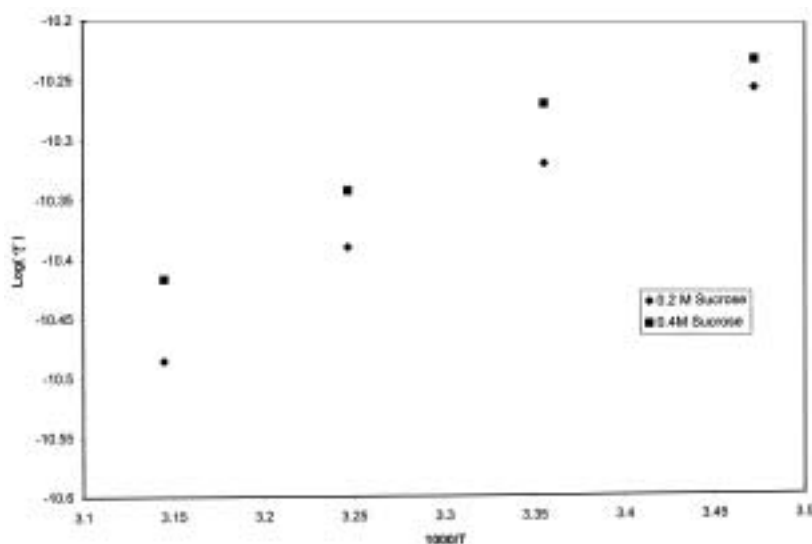
Figure 2. Temperature dependence of relaxation time for aqueous sucrose in 0.3 M ethanol.

4. Conclusions

The temperature-dependent dielectric parameters and the Kirkwood correlation factor have been reported in this paper. The Luzar model reproduces the static dielectric constants of the mixture. Luzar model is also used to calculate Kirkwood factors g_1 and g_2 in the mixture. A modification in the Bruggeman equation provides a better description of dielectric behaviour in the mixture.

Acknowledgements

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