Conductance studies of $Ca(NO_3)_2.4H_2O$ in water and glucose-water mixtures by TDR technique

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Equivalent conductivity (Λ) of $Ca(NO_3)_2.4H_2O$ has been determined in water and glucose-water mixtures by time domain reflectometry (TDR). Λ_0 has been computed by a non-linear least squares treatment of Λ against the square root of concentration of the electrolyte. In an aqueous solution, the variation of Λ_0 with temperature (0-50°C) obeys the relation $\Lambda_0 = 2.5 T + 70.0$. In the case of glucose-water mixtures (0-2 M glucose), Λ_0 decreases with increase in molarity of glucose, and increases with increase in temperature. The Walden product $\Lambda_0\eta$ is not constant for all the mixtures, but the constancy is exhibited by a function $\Lambda_0\eta^{0.7}$. The degree of dissociation (α) of the electrolyte does not change with glucose percentage.

Dielectric spectroscopy is being successfully used to determine the time of relaxation of electrolytes in solution[1,2]. Time domain reflectometry (TDR) technique is being adopted to measure static conductivity of electrolytic solution[2]. We have used the TDR to measure conductance of calcium nitrate in water and glucose-water mixtures. Calcium ion was selected because of its biological importance[3], and its established role in the formation of kidney stones, contaract and blood coagulation[4]. Nitrate salt of calcium ion was preferred because of its good solubility in water.

Experimental

Chemicals like $Ca(NO_3)_2.4H_2O$ and glucose were from Aldrich (AR grade). Conductivity water (conductance 5 μmhos cm^{-1}) was used throughout the work.

Ostwald viscometers (typically three) were used for each viscosity measurements. The time period for a flow was between 300-400 s at 30°C. Estimated error in viscosity was of the order of 0.0006 cp. The kinetic energy correction was found to be negligible.

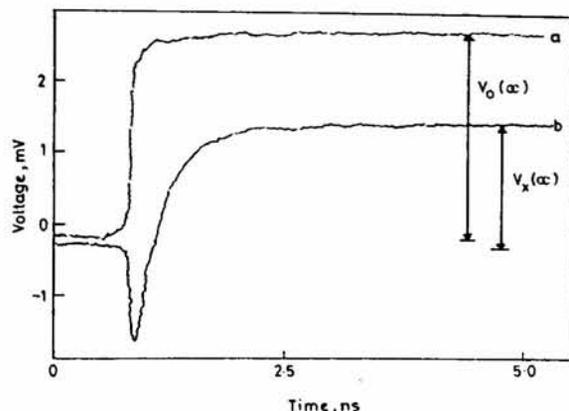The tektronix 7854 TDR unit has been used

Fig. 1—Plot of the reflected voltages (mV) (a) without and (b) with sample against time (ns).

for the measurement. The details regarding the working of the instrument was given earlier[5]. The nature of the pulse with and without sample is as shown in Fig. 1.

The conductivity of the sample is computed using the expression[6] (1)

$$\sigma_0 = \frac{d}{c} \frac{V_0(\infty) - V_x(\infty)}{V_0(\infty) + V_x(\infty)} \qquad \dots (1)$$

where $V_0(\infty)$ and $V_x(\infty)$ are values of reflected pulses at time $t = \infty$ without and with sample, respectively, d, the effective pin length and c is the velocity of light. Since the relaxation times for the samples reported in the paper are of the order of few hundred picoseconds, the reflected pulses get constant after a few nanoseconds. The time window of 5 ns was found to be satisfactory for our experiments.

Determination of base lines became difficult due to reflections from the connectors and fluctuations due to drift in electronic circuits of the oscilloscope. All electronic systems were switched on, three hours before recording actual data. The statistical average of 50 to 100 points were taken to determine the base line values of $V_0(\infty)$ and $V_x(\infty)$. The error in the measurements is estimated to be about $\pm 0.01\%$.

Results and discussion

The σ_0 values (ohm^{-1} cm^{-1}) derived from the experimental data were converted to equivalent conductivities. Accuracy of the present estimation
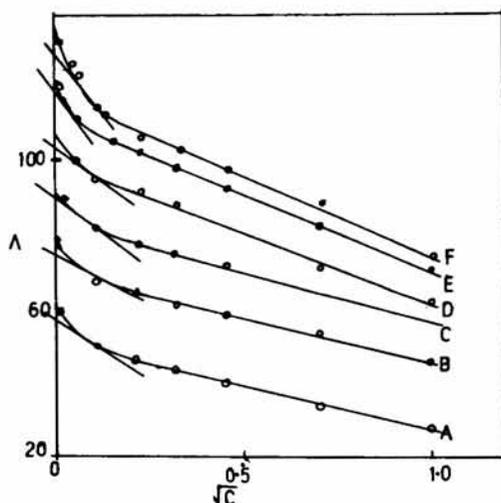
Fig. 2—Plot of Λ against $\sqrt{C}$ of $Ca(NO_3)_2.4H_2O$ in glucose-water mixtures at 25°C. Concentration of glucose: A−2.0M, B−1.5M, C−1.0M, D−0.5M, E−0.1M, F−0.0M.

Fig. 3—Plot of Λ_0 against temperature (T°C) for $Ca(NO_3)_2.4H_2O$ in water. ○—Our values; ●—Literature values.

Table 1—Λ_0 of $Ca(NO_3)_2.4H_2O$ at different temperatures in glucose-water mixtures

Conc. of glucose (moles/litre)	Λ_0 (ohm^{-1} cm^2 equiv^{-1}) at			
	5°	15°	25°	35°C
0.1	84.70	99.65	124.56	148.22
0.5	73.59	87.65	108.22	132.04
1.0	56.62	76.71	91.32	112.81
1.5	38.13	61.02	76.26	95.33
2.0	24.95	36.22	58.25	73.44

was noted by taking conductivity measurements of calcium nitrate at 25°C in a very dilute region $(2-64) \times 10^{-4}$ M, only in water. The variation of Λ versus $\sqrt{C}$ over the entire range (0.0002-1.0M), was found to be non-linear (Fig. 2). The asymptotic nature of the curves commenced beyond 0.01 M.

A non-linear least squares method[5] was used to fit the experimental data to the expression[6].

$$\Lambda = \Lambda_0 - \frac{A\sqrt{C}}{1+B\sqrt{C}} + DC \qquad \ldots (2)$$

with Λ_0, A, B, and D as fitting parameters.

Λ_0 computed for calcium nitrate in water at 25°C was 130.62 ohm^{-1} cm^2 equiv^{-1} which is in very good agreement with the literature values 131.0 (ref. 7). Substituting the values of A, B, D and Λ_0 in Eq. (2), Λ values at different concentrations were calculated. The agreement between the calculated and experimental values is good over the entire concentration range, the maximum difference being never larger than 0.3. The values of Λ_0 at 5, 15, 25 and 35°C were also computed similarly and all these values were compared with the literature values wherever available. Variation of Λ_0 with temperature is linear (Fig. 3) satisfying the equation $\Lambda_0 = 2.5$ T + 70.0, the intercept being Λ_0 at 0°C.

Λ_0 values in several glucose-water mixtures were obtained by following the procedure of Stokes et al.[8] Plots of Λ versus $\sqrt{C}$ for different glucose-water mixtures are presented in Fig. 2. The slopes of these, were obtained from the line-
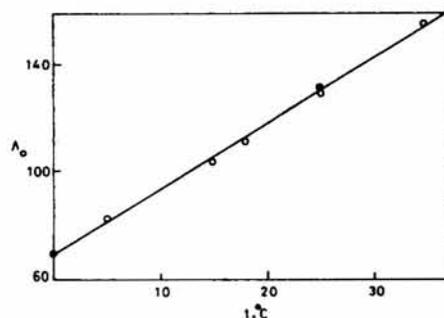
ar variation in a very dilute range. These are 160, 150, 110, 100, 70 and 60 (all values negative) for the lines corresponding to 0.0, 0.1, 0.5, 1.0, 1.5 and 2.0 M glucose respectively. The Λ_0 values thus derived are given in Table 1. These values decrease with increase in molarity of glucose and increase with increase in temperature. The variation with glucose concentration is linear and the slopes of these plots are 0.68, 0.64, 0.60, 0.54, 0.50 and 0.40 for 0.0, 0.1, 0.5, 1.0, 1.5 and 2.0 M glucose respectively. $\delta\Lambda_0/\delta T$ varies linearly with molarity of glucose. The influence of temperature, is less effective at higher percentages of glucose.

The magnitude of $(\Lambda\sqrt{C}/(1+B\sqrt{C}))$ and $(-D)$ parameters for glucose-water mixtures are presented in Table 2. Both the quantities decrease with an increase in glucose molarity. Moreover, for any glucose concentration, these increase with increase in temperature, and the rise seems to be less for solutions more concentrated in glucose.

The approximate constancy of $\Lambda_0\eta$, known as Walden's product[9] was examined for calcium nitrate in glucose-water mixtures at 25°C. Constancy is shown by the first two mixtures i.e. upto 0.4 M glucose and departure is shown by the remaining concentrations of glucose. Thus, in 2.0 M solution

Table 2—Values of parameter $(-D)$ and $A\sqrt{C}/(1+B\sqrt{C})$ in parentheses for different glucose-water mixtures

Conc. of glucose (moles/litre)	5°	15°	25°	35°C
0.0	21.2	29.6	36.2	40.4
	(14.95)	(17.08)	(21.35)	(25.62)
0.1	20.4	26.4	30.0	36.2
	(12.88)	(15.44)	(18.33)	(22.60)
0.5	18.3	21.3	25.4	29.3
	(11.38)	(13.52)	(16.49)	(19.79)
1.0	13.4	17.6	21.2	25.3
	(8.67)	(10.15)	(12.38)	(14.86)
1.5	11.2	13.4	17.6	23.4
	(7.56)	(9.45)	(11.12)	(13.34)
2.0	8.0	10.8	14.0	18.6
	(7.20)	(9.08)	(11.08)	(13.29)

Table 3—Validity of Walden's product for $Ca(NO_3)_2.4H_2O$ in glucose-water mixtures at 25°C

Conc. of glucose (moles/litre)	Λ_0 (ohm^{-1} cm^2 equiv^{-1})	η (cp)	$\Lambda_0\eta$	$\Lambda_0\eta^{0.7}$
0.0	130.62	0.8240	116.78	120.82
0.1	124.56	0.9280	115.59	118.20
0.5	108.22	1.1578	114.48	119.04
1.0	91.32	1.4269	130.30	117.07
1.5	76.26	1.9087	149.37	119.52
2.0	58.25	2.7773	161.77	119.06

$\Lambda_0\eta$ is 1.5 times than its value in aqueous medium (Table 3). However, the corresponding values of the empirical function $\Lambda_0\eta^{0.7}$ are almost constant over an entire range, even for mixtures with viscosity 3 times that of water.

Non-electrolytes like glucose and sucrose enhance the viscosity of water, the enhancement is much larger at higher percentages of these. Viscosity of 1.7 M and 0.3 M sucrose are 0.4373 and 0.01179 poise[8] respectively at 25°C, thus the viscosity at 1.7 M is 38 times larger than 0.3 M solution. The variation in viscosity with sucrose concentration is linear up to 1.2 M, beyond which it exhibits a sharp rise. The situation with glucose is different. Here a linear variation is shown up to 2 M solution, viscosity at this molarity being 2.8 times larger than at 0.1 M. Lower molecular weight, hydration behaviour and smaller size of glucose, than sucrose, may possibly explain the viscosity difference between the two. The disso-

Table 4—α values of $Ca(NO_3)_2.4H_2O$ at 25°C in glucose-water mixtures

Conc. of glucose (moles/litre)	0.01	α at 0.1	$1.0 M [Ca^{2+}]$
0.0	0.810	0.278	0.126
0.1	0.804	0.282	0.124
1.0	0.828	0.266	0.117
2.0	0.818	0.272	0.125

Table 5—Conductance and fluidity ratio for glucose-water mixtures at 25°C

Glucose conc. (moles/litre)	R	r
0.1	0.953	0.963
0.5	0.828	0.802
1.0	0.699	0.626
1.5	0.584	0.468
2.0	0.445	0.320

ciation of calcium nitrate in glucose-water mixtures was examined by calculating the degree of dissociation parameter α which is concentration dependent. The experimental data was fitted to Eq. (3).

$$\Lambda = \Lambda_0 - S(\alpha \cdot C)^{1/2} \qquad \ldots (3)$$

α values for different glucose-water mixtures are presented in Table 4. It is apparent from the Table 4 that α is almost constant for a particular electrolytic solution. It decreases with increase in salt concentration as is expected from the ion-pair concept. The present observation leads to the conclusion that the degree of dissociation of calcium nitrate is not affected by the presence of glucose up to 2 M. Since the total conductance of an ion depends on its concentration, charge and mobility, the first two being constant, the third alone is changing with the glucose percentage. This obviously is the viscosity effect.

The ratios $R = \dfrac{\Lambda_{0(medium)}}{\Lambda_{0(water)}}$ and $r = \dfrac{fluidity_{(medium)}}{fluidity_{(water)}}$

$= \dfrac{\eta_{(water)}}{\eta_{(medium)}}$ at different glucose concentrations

are set out in Table 5. Both R and r decrease with increase in glucose concentration and the decrease in $r > R$. The data explain the importance of viscosity factor.

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