Studies on Ion-solvent Interactions of Electrolyte Solutions – Part 2: Variation of Relative Permitivity with Temperature

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ABSTRACT

This paper is the continuation of part-1,of the similar title appeared in the same journal.earlier & the data of our studies on the variation of Dielectric constant with temperature using the new precise technique ,with Operational amplifiers for permitivity determinations with an additional temperature determining device developed at GIET,Rajahmundry, A.P.,INDIA.is communicated herein.Ion -Solvent interactions are responsible for the deviations between the theory and experiment, of chosen liquid systems. Temperature variation of relative permitivity of Methanol, Benzene,Nitrobenzene and Water,are obtained . Theoretical data is evaluated using an equation from literature.Comparison of theory and experiment is done and thevalues obtained through the above technicare found to show a reasonably good agreement as well as with the dataalready available in the literature .the deviations are explained on the basis of Ion pair formation mechanism , for which evidences are cited from literature .

Keywords: Dielectric constant, AN685 Temparature Sensor, Operational amplifier, Eigens Ion pair mechanism, operational amplifier techniques ,NRTL model, Redlich and Kister Polynomial, protic & aprotic solvents, Steinhart-Hart equation, Sargent Oscillometer technique

1. INTRODUCTION

An accurate representation [1] of demixing in mixed-solvent electrolyte solutions remains one of the challenging research areas in chemical engineering. Further the Binary and Ternary solvent systems involving electrolytic solutions is still an unexplored area, more so because still we have to understand several unknown dynamic features of established mechanisms like the Ion-pair formation mechanism [2] much in detail. The simulation and design of industrial extraction processes involving electrolytes depends heavily on the availability of models that can describe the influence of ions on the phase behaviour is being pursued rigorously with NRTL Model [3] developed by Chen et.al., L.S. Belvèze [36] concludes that NRTL model works very well in modelling activity coefficients of quaternary ammonium salts in water at 25°C. This simple model is not able to treat micelle formation in the solution, and it is expected that the fundamental hypothesis of complete dissociation of the salt breaks down at higher concentrations, or in an organic solvent. This leads to the below interesting question:

1.1 What would happen to a binary aqueous solvent mixture when an ionic species is added to it?

Several attempts, to know this, are already in progress. A multicomponent version [37] of NRTL model by Chen and Evans attempted to treat the problem of incomplete dissociation. Such a model designed for solutions containing several solvents and solutes should allow us to treat a single solvent, single solute but not completely dissociated system by considering the non-dissociated salt as a second solvent in the solution. In that case, the equilibrium constant of dissociation of the salt is considered as an adjustable parameter. Recently, Keyan Li et.al. [38] developed a new model in which the solvent effect is incorporated into the born effective radius. They have proposed an electronegativity scale of metal ions in aqueous solution with the most common oxidation states and hydration coordination numbers in terms of the effective ionic electrostatic potential. It was established by them that the metal ions in aqueous solution are poorer electron acceptors compared to those in the gas phase. This solution-phase electronegativity scale shows its efficiency in predicting some important properties of metal ions in aqueous solution such as the aqueous acidities of the metal ions, the stability constants of metal complexes, and the solubility product constants of the metal hydroxides.

However (apparently) we fail to notice that a suitable interpretation that takes into account the short and long range interactions responsible in these systems, between ions and solvents still remains to be the missing link. In addition to the molecular interactions explained by Redlich and Kister [4], J. Barthel et. al., R. Buchner et.al. [5] and others, in their work on High frequency permittivity of non-aqueous electrolyte solutions and their solvents, (discussed with the help of their evaluated Dielectric Relaxation data on the basis of models presupposing one or more relaxation processes)the depression of relative permittivity of the solution(when solute is added) and systematic variations observed in the other different measurable traits of the solvent-solute systems, like acoustic velocity & absorption, density, viscosity, refractive index, surface tension and related thermodynamic parameters

are getting investigated at several centres of première research, to understand the solute-solvent, and solvent-solvent interactions. With regard to actual theories underlying these phenomena, information is obtained [5] on structural and dynamical properties of classes of electrolyte solutions based on protic , H-bonding, dipolar aprotic and low permittivity solvents and mixtures of solvents . Reported data on studies on high frequency permittivity of protic and aprotic solvents and their electrolyte solutions indicates a sharp disagreement namely, in some cases it shows no ionic relaxation processes, in several other cases [6-14] records discrete ionic relaxation processes [15-22]. This points out that the permittivity is another parameter that requires a detailed study. These studies conclude that the influence of ions on the phase behaviour still requires a comprehensive model for the explanation of the experimental findings.

The presence of charged species in a mixed-solvent solution dramatically influences the phase distribution of a solute between the liquid phases. The analysis led to the result that the assumption of a single relaxation processes Peter Debye equation with a single relaxation time generally does not reproduce high frequency permittivity within frequency regions large enough for the reliable interpretation of physical effects, is naïve and incomplete. Possibly the happenings in the ion atmosphere pointed out by Glueckauff [34], are needed to be impregnated into the various equations and models, to ensure the correction for the theories. With this as the theme of pursuit, the dielectric constant measurement and its systematic application to the different models and equations involving measurements and estimations of basic parameters like acoustic velocity, viscosity, density, conductance, surface tension, refractive index , and their related thermodynamic parameters was taken up in our laboratories at Andhra University, Visakhapatnam, A.P.,(India); G.I.E.T., Rajahmundry, A.P.,(India) and at MGNIRSA (a Research wing of D. Swaminathan Research Foundation at Hyderabad, A.P., (India)). Already the first part [35] of this work was accepted for publication in IJST, U.K. and the present paper reports our findings on the set up developed in our laboratories for precise determination of temperature, used to determine the variation of the dielectric constant of Methyl alcohol, Benzene, Nitrobenzene and water, and its comparison with similar values available in literature.

The remaining circuits and details of equipment in regard to the basic set up for the determination of Dielectric constant are already communicated [35].Here below the extension of the set up for temperature variation studies of the relative permittivity characteristic of the chosen set of solvents. All our values are compared with the standard values given in IUPAC (Physical Chemistry Division).Recommended Reference Materials for Realization of Physiochemical Properties [39] and the cross references cited therein [40-45]. Our data is found to be in very good agreement, with literature. However the deviation becomes conspicuous at higher temperatures, which requires more detailed analysis.

## 2. EXPERIMENTAL SETUP FOR PRECISE TEMPERATURE DETERMINATION

Neeta Sarma et.al, [46]., in their studies used an electronically controlled temperature bath with an accuracy of 0.002 K. Our equipment has the ability to determine the temperature at the place of interaction. The thermistor is placed inside the inner test tube of the capacitance measuring cell. The connections from thermistor are suitably connected to insulated platinum leads (of negligible resistance), covered with non-conducting sleeves. They are connected to a digital micro ammeter externally. This set up enables the temperature measurement by the thermistor to an accuracy of 0.0001K. The resistance measurement, is related to the temperature on a logarithmic scale (as can be seen from the below mathematical details). Since the thermistor is held in the very close proximity of the place of interaction, the temperature measurement is very precise.

2.1 Accurate Temperature Determination

The temperature is determined from the calibration chart shown below. Our evaluation of temperature uses the accurate Steinhart -Hart equation.

$$T = 1/(A_O + A_1 ln(R_T) + A_3 ln(R_T^3)) \text{, in which } \{ln(R_T) = B_0 + [B_1/T] + [B_3/T^3]\},$$

Where T is the temperature of the thermistor in Kelvin& A_0, A_1, A_3, B_0, B_1, and B_3, are constants provided by the manufacturer[2] ,and R_T is the thermistor resistance at temperature, T. In precision temperature measurement of environments, the thermistor is used in a "zero power" condition. In this condition, the power consumption of the thermistor has a negligible effect on the elements resistance. The below graph of an NTC 10kW thermistor resistance-versus-temperature, clearly indicates the accuracy of the measurements.
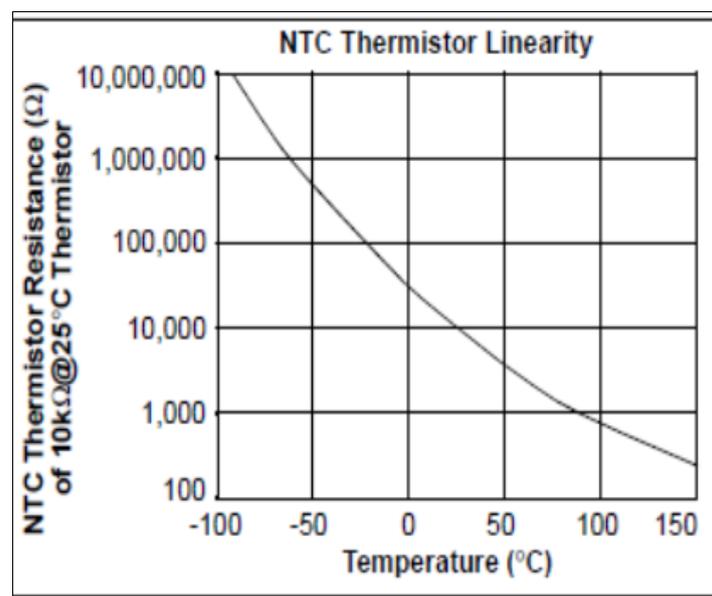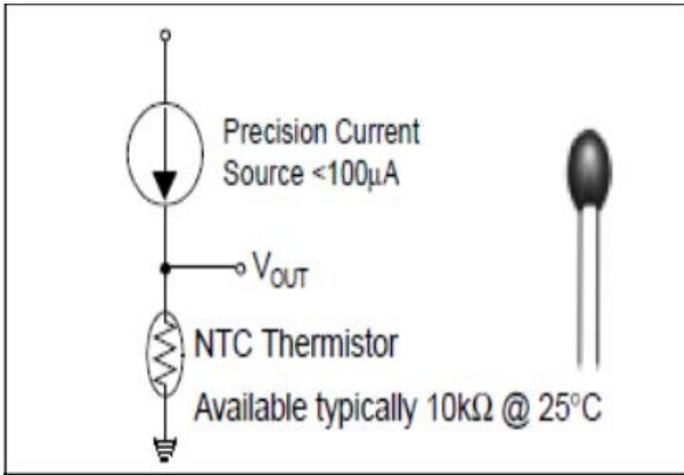
Fig 1: The Temperature VS Resistance Calibration Plot and the circuit element adopted for resistance measurement

The Thermistor is operated in the Temperature –Resistive mode. A separate current source is used to excite the sensing element for the temperature measurement .The lesser is the current source, the possibility of self-heating is better eliminated .The current source is determined depending upon the range of the temperatures involved. Several other details are available from cited references.

The advantages versus disadvantages of the thermistor are summarized in Table 1.

ADVANTAGES	DISADVANTAGES
Fast	Non-Linear
Small	Excitation Required
Two-Wire	Limited Temperature Range
Inexpensive	Self-Heating
	Fragile

Fig.2: Cell for Capacitance measurement with thermistor Inside the inner tube(details of size given in Ref [35])

Temp (°C)	R Value (Ω)	Temp (°C)	R Value (Ω)	Temp (°C)	R Value (Ω)
-80	7296874	0	32650.8	75	1480.12
-75	4713762	5	253985.5	80	1256.17
-70	3095611	10	19903.5	85	1070.58
-65	2064919	15	15714.0	90	916.11
-60	1397935	20	12493.7	95	786.99
-55	959789	25	10000	100	678.63
-50	667828	30	8056.0	105	587.31
-45	470609	35	6530.1	110	510.06
-40	335671	40	5324.9	115	44.48
-35	242195	45	4366.9	120	388.59
-30	176683	50	3601.0	125	340.82
-25	130243	55	2985.1	130	299.82
-20	96974	60	2487.1	135	264.54
-15	72895	65	2082.3	140	234.08
-10	55298	70	1751.6	145	207.70
-5	42314.6			150	184.79

TABLE 2: Resistive changes with temperature of a BetaTHERM, 10kΩ @ 25 °C (10K3A1) NTC Thermistor in its "zero power" mode.

Table 3: Theoretical and Experimental Dielectric Data of benzene, Methanol, Nitrobenzene and Water at Different Temperatures

Temp. (K)	BENZENE			METHANOL			NITROBENZENE			WATER		
	Dielectric Const.		Capacitance pF	Dielectric const.		Capacitance pF	Dielectric const.		Capacitance pF	Dielectric const.		Capacitance pF
	Theo. value	Exptl. value		Theo. value	Exptl. value		Theo. value	Exptl. value		Theo. value	Exptl. value	
288	2.2922	2.3252	34.1835	33.3727	33.4319	78.6392	36.7319	35.7635	79.1408	82.0147	82.1245	83.4491
293	2.2821	2.2957	33.9188	32.4853	32.5296	78.4277	35.7873	34.7728	78.9351	80.1379	80.1275	83.3618

298	2.2722	2.2678	33.6659	31.6215	31.6017	78.1989	34.8671	33.6839	78.6964	78.3040	78.2141	83.2742
303	2.2622	2.2412	33.4225	30.7807	30.7128	77.9682	33.9706	32.9699	78.5322	76.5121	76.305	83.1826
308	2.2524	2.2216	33.2417	29.9623	29.8019	77.7190	33.097	31.8586	78.2635	74.7612	74.5512	83.0945
313	2.2425	2.2092	33.1267	29.1656	28.9112	77.4618	32.2460	30.5627	77.9281	73.0503	73.0091	83.0138
318	2.2327	2.1866	32.9159	28.3900	27.1238	76.9007	31.4168	29.4729	77.6256	71.3786	71.2975	82.9203
323	2.2229	2.1769	32.8249	27.6351	26.2596	76.6053	30.609	29.1102	77.5204	69.7452	69.6977	82.8289
328	2.2132	2.1676	32.7374	26.9	25.3987	76.2935	29.8219	28.0659	77.2043	68.1491	68.1286	82.7353
333	2.2036	2.1542	32.6108	26.1850	24.5015	75.9483	29.0551	27.1224	76.9002	66.5896	66.5777	82.6387
338	2.1939	2.1439	32.5131	25.4888	23.6785	75.6115	28.3080	26.2219	76.5920	65.0658	65.0950	82.5422
343	2.1843	2.1336	32.4150	24.8110	22.9762	75.3078	27.5801	25.3999	76.2939	63.5768	63.4992	82.4336

3. DISCUSSION OF RESULTS

A simple relationship between dielectric constant of mixed solvents with solvent composition and temperature was proposed by Abolghasem Jouybanl C:\Users\Administrator\Downloads\let.al. [48]. for pure liquids. O. Wear [49] reported a technique for Relative permittivity determination. The Sargent Oscillometer technique is good enough but not compatible for temperature controlled measurements. Even though J.O.Wear's method is a development for the Oscillometer method, its accuracy of measurement of temperature is restricted, mainly because a temperature bath is used to regulate the temperature by a liquid circulation technique.

In our technique we use a precise resistance tool kept at the same temperature as the medium, and determine the dielectric constant. This is possible because the small thermistor is held inside the dielectric cell .This makes the environment around the thermistor to be isothermal.

Up to now the dielectric properties of the ion conducting systems have been almost unexamined, in detail, despite their fundamental importance. Chemists are keen to obtain information on the structure of solutions which can be provided by permittivity measurements. Theoreticians hope to get more insight into the dynamic and transport Properties of electrolyte solutions from knowledge of relaxation times and dielectric decrements.

Theoretically [50] the equation for the temperature dependence can be given as:

$$\varepsilon = (\varepsilon_0)\, e^{-LT},$$

in which ε is the Dielectric constant , T is the absolute temperature , and L & ε_0 are constants for a given solvent .The theoretical value of the ' ε ', has been evaluated ,using this equation.
The values of the constants for the standard solvents are given in the table below:

Liquid	ε_0	$L \times 10^3$
Benzene	2.95	0.876
Methanol	157.6	5.39
Nitrobenzene	164.7	5.21
Water	311.17	4.63.

A similar method is [51] is used in literature for the water-ethanol system also. The water-methanol data of J.O.Wear's [2] records discrete departure between theory and experiment .This is expected , as per the observations of other prominent findings of different [52] techniques, like U-V visible spectrophotometry,Ion selective electrode potentiometry, Dielectric relaxation spectroscopy, and titration colorimetry. The electrochemical results must be explained by something other than bulk dielectric constant changes. Chandrika Akhilan, presented an explanation viable to the Ion pair formation of Manfred Eigen & Tamm[53], in her work of dielectric relaxation on copper sulphate solutions . She concluded after a detailed investigation that the presence of solvent-separated ion pairs was detected partially by UV-Vis spectrophotometry. A similar mechanism, due to hydrogen bonding or otherwise invokes modification to the simple mathematical relation between the dielectric constant and temperature.

Further her findings revealed the presence of three ion-pair types: double solvent-separated, solvent-shared and contact ion pairs. This is confirmed in our work [54]. If the Ion pair formation is to be considered it becomes necessary, for a term or two to be added to the basic equations for the parameters determined to interpret the happenings, responsible to record the deviations observed between the theory and experiment .This becomes conspicuous in the case of several fundamental thermodynamic parameters, information about whom would follow in the succeeding parts of our communications, with the same common title appearing in literature soon.

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