Thermodynamic parameters of medicine with Ethanol

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Abstract— The information related to the solute-solvent interaction has been carried out related to thermodynamic properties like activation energy, conductivity, enthalpy entropy etc in the mixture of Ayurvedic Medicine-Dashmularishta and ethanol. Dielectric relaxation study of Dashmularishta used in gynaec problems has been carried out at 15^0C, 25^0C, 35^0C and 45^0C in the frequency range 10MHz to 20GHz for 11 different concentrations of the system. Time Domain Reflectometry (TDR) Technique in reflection mode has been used to measure Thermodynamic parameters viz activation energy, conductivity, enthalpy entropy etc.Further, Fourier transforms and least square fit method has been used to obtain Thermodynamic parameters. With change in concentration and temperature, the systematic changes in Thermodynamic parameters are observed.

Index Terms— Time Domain Reflectometry, Thermodynamic parameters ,Dielectric parameters,Dashmularishta,Activation energy

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1. INTRODUCTION

The dielectric relaxation study at microwave frequency gives information about solute- solvent interaction and liquid structure of mixture. In this study, Ayurvedic medicine- **Dashmularishta** has been used as solvent and ethanol as solute. The Time Domain Reflectometry in reflection mode has been used to obtain thermodynamics parameter. The objective of the present paper is to report the dielectric relaxation study of above system using TDR in the temperature range 15^0C to 45^0C.

2. EXPERIMENTAL MATERIAL

Dashmularishta (Shree BaidyanathAyurvedicBhavan Pvt. Ltd. Kolkata) and Methanol (ChangshuYangyuan Chemicals, China) were obtained commercially and used without further purification. The solutions were prepared at different volume percentage of **Dashmularishta** in Methanol at 11 concentrations.

2.1Apparatus

The Thermodynamic parameters were obtained by using the Time Domain Reflectometry method. The Hewlett Packard HP54750 sampling oscilloscope with HP 54754A TDR plug in-module has been used. A fast rising step voltage pulse of about 200 mV amplitude and 43.8486 ns rise time with repetition frequency of 12.4 GHz is generated and is propagated through a coaxial transmission line. The sample is placed at the end of the coaxial transmission line in a standard Military application (SMA) coaxial cell. The SMA cell used for this work had 3.5 mm outer diameter and 1.33 mm effective pin length. The step pulse generated by tunnel diode and the pulse which is reflected from the sample cell were sampled by a sampling oscilloscope in the time window of 1.3 ns. The reflected pulse without sample $R_1(t)$ and with sample R_x (t) averaged 64 times and digitized with 1024 points in oscilloscope memory and transferred to PC through a 1.44 floppy diskette drive.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of ± 1 ^{0}C. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using temperature controller system is circulated. The temperature at the cell is checked using the thermometer.

3. DATA ANALYSIS

3.1Thermodynamic parameters

Kauzmann has given an extensive analysis of dipole orientation as a rate phenomenon. Eyring[14] considered that dipole orientation involves passage over a potential energy barrier with a certain probability of jumping from one orientation to another. He obtained the polarization P(t), as a function of time as

$$P(t) = P_0\, e^{-k_o t}$$

(1)

where, P_0 is orientation polarization at t = 0;

k_0 is the rate constant for the activation of dipole, i.e. mean number of jumps made by a dipole in unit time.

When t is such that $k_0 t$ = 1, P(t) must have decayed to P_0/e. This value of t is a relaxation time, which may be defined as $\tau = 1/k_0$. (2)

The process of molecular orientation requires an activation energy sufficient to overcome the energy barrier separating the two mean equilibrium positions. The number of times such a rotation will occur per second is given by the rate expression -

$$k_0 = 2\pi \tau = \frac{kT}{h} \ e^{-\Delta F/RT}$$

(3)

where   h is Plank's constant;

ΔF is molar free energy of activation for dipole relaxation.

Since $\Delta F = \Delta H - T\Delta S$,   (3.a)

$$\tau = \frac{h}{kT} \ e^{\Delta H/RT} \ e^{-\Delta S/R}$$

(4)

where ΔH is the enthalpy(heat) of activation for dipole relaxation and

ΔS is the entropy of activation for dipole relaxation.

The entropy of activation ΔS may be calculated since ΔF is now known from eq. (3.a), and ΔH is obtained from the slope of the curve for $\ln(\tau T)$ plotted against 1/T.

Eq. (4) can be rewritten as -

$$\ln(\tau T) = \frac{\Delta H}{RT} + A$$

(5)

where

$$A = \ln\left(\frac{h}{k}\right) - \left(\frac{\Delta S}{R}\right)$$

In eq. (4), $\Delta H/R$, is the slope of $\ln(\tau T)$ v/s 1/T. If ΔH and ΔS are independent of temperature, then plot of $\ln(\tau T)$ v/s 1/T is linear. The slope $\Delta H/R$ gives the height of potential barrier. Differentiating eq. (3.a) gives -

$$\Delta H = \ R \ \frac{d\left[\ln(\tau T)\right]}{d\left[1/T\right]} \ - RT$$

(6)

Thermodynamic properties may be used to access the dipole under the influence of applied field. The activation energy for every compound increases as the temperature increases, whereas the relaxation time decreases. This may be due to decreased viscosity of medium . With increase in temperature the thermal agitation increases and dipole requires more energy in order to attain the equilibrium with the applied field. The molar free energy of activation is greater than the molar enthalpy of activation, which results into negative values of enthalpy. This indicates that the activated state is more ordered than the normal state, which is true as in the activated state, and the dipoles try to align with the applied field.

Dispersion in conductivity

The complex thermodynamics constant, $\varepsilon^* = \varepsilon' - i\varepsilon''$, which is dimensionless quantity. The die-

lectric loss ε'', however, is a parameter which describes the motion of the charge i.e. conduction. Certain thermodynamicss are found to display conduction because of charge transport i.e. ionic conduction in electrolytes. This conduction normally be described by a volume conductivity σ (mho/m). It is additive to dielectric loss, ε'', so that-

$$\varepsilon'' = \varepsilon''_{dielectric} + \frac{\sigma}{\omega\varepsilon_0}$$

(6)

The frequency variation of thermodynamics loss is given by -

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}$$

$$= \frac{\sigma}{\varepsilon_0 \, \omega}$$

so that -

$$\sigma = \frac{(\varepsilon_s - \varepsilon_\infty)\omega^2\tau\varepsilon_0}{1 + \omega^2\tau^2}$$

(7)

If σ_∞ is conductivity at high frequency given by - $\sigma_\infty = (\varepsilon_s - \varepsilon_\infty)/\tau$, we obtain -

$$\sigma = \frac{\sigma_\infty \, \omega^2 \, \tau^2}{1 + \omega^2 \, \tau^2}$$

(8)

This equation describes the elevation of dielectric conductivity from its zero value at zero frequency to a value σ_∞ at infinite frequency. The form of this elevation is similar to the form of the fall of the real part of the thermodynamics constant. If a static conductivity term σ_s is added, we get -

$$\sigma = \sigma_s \ + \ \frac{(\sigma_\infty - \sigma_s)\omega^2 \, \tau^2}{1 + \omega^2 \, \tau^2}$$

(9)

Experiments designed to measure high frequency conductivity for bio-molecular solutions, confirms this relationship.
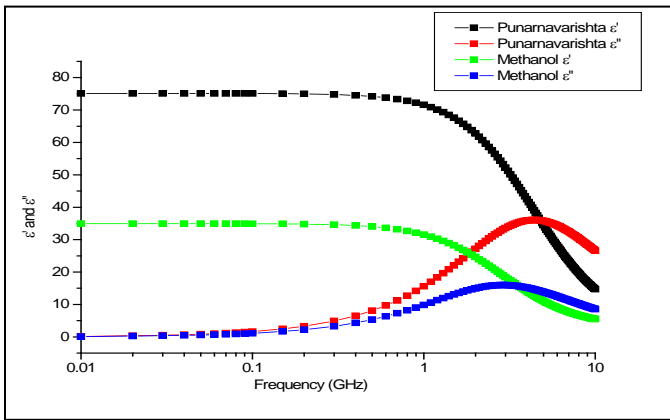
ture

Figure.A: Corrected data for Dashmularishta + Methanol mixture at 35⁰
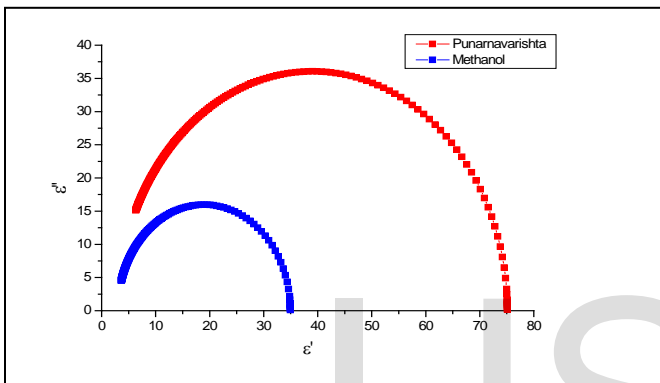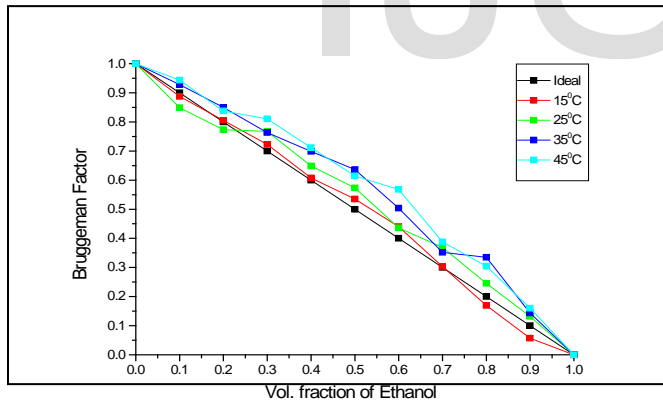

Figure.B: Cole –Cole plot for Dashmularishta + Methanol.
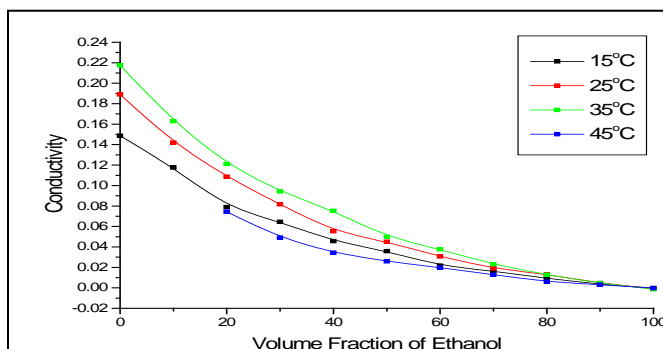

Figure C : Variation of Bruggeman factor

Figure D:Variation for Dashmularishta for vol

Table1.1: Bruggeman factor for Ashokarishta-Ethanol mix-

Vol. fraction of Ethanol	Ideal value for F_b	15 ^{0}C,0.630		25 ^{0}C,0.658	
		Expt.	Theor.	Expt.	Theor.
0.0	1.0	1.000	1.000	1.000	1.000
0.1	0.9	0.8873	0.933	0.8486	0.930
0.2	0.8	0.8053	0.859	0.7736	0.854
0.3	0.7	0.7228	0.777	0.7674	0.771
0.4	0.6	0.6077	0.688	0.6485	0.682
0.5	0.5	0.5349	0.592	0.5733	0.585
0.6	0.4	0.4402	0.488	0.4364	0.482
0.7	0.3	0.3033	0.377	0.3688	0.371
0.8	0.2	0.1695	0.259	0.2457	0.254
0.9	0.1	0.0568	0.133	0.1317	0.130
1.0	0.0	0.000	0.000	0.000	0.000
Vol. fraction of Ethanol	Ideal value for F_b	35 ^{0}C,0.576	35 ^{0}C,0.576	45 ^{0}C,0.695	45 ^{0}C,0.695
		Expt.	Theor.	Expt.	Theor.
0.0	1.0	1.000	1.000	1.000	1.000
0.1	0.9	0.9282	0.938	0.9437	0.927
0.2	0.8	0.8499	0.867	0.8374	0.848
0.3	0.7	0.7634	0.789	0.8105	0.764
0.4	0.6	0.6985	0.701	0.7114	0.673
0.5	0.5	0.6362	0.606	0.6147	0.576
0.6	0.4	0.5038	0.501	0.5680	0.473
0.7	0.3	0.3520	0.389	0.3878	0.364
0.8	0.2	0.3348	0.267	0.3041	0.248
0.9	0.1	0.1437	0.138	0.1603	0.127
1.0	0.0	0.000	0.000	0.000	0.000

Table:1.2 Activation Enthalpy and Entropy of Dashmular-ishta –Ethanol

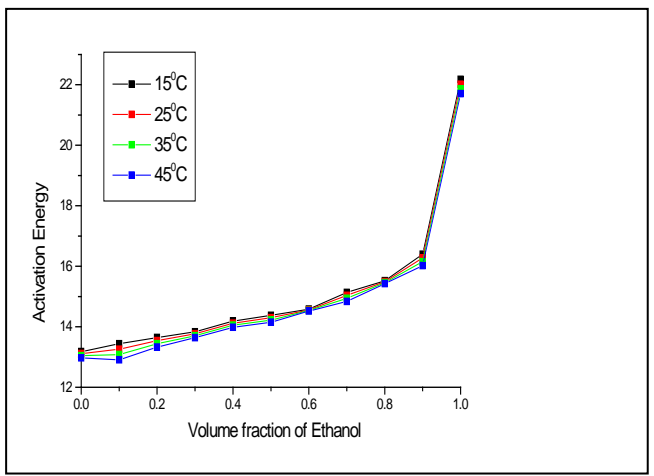| Vol. fraction of Ethanol	Entropy (ΔS) J/^{O}Kmole	Enthalpy(ΔH) KJ/Kmole
0.0	-0.006878	10.993
0.1	-0.0178	7.7768
0.2	-0.010495	10.307
0.3	-0.006514	11.762
0.4	-0.006766	12.035
0.5	-0.007575	11.966
0.6	-0.0021512	13.897
0.7	-0.009829	12.008
0.8	-0.00309	14.537
0.9	-0.0125	12.423
1.0	-0.01564	17.201

Figure G: Variation of free energy of activation for Dashmularishta + Ethanol
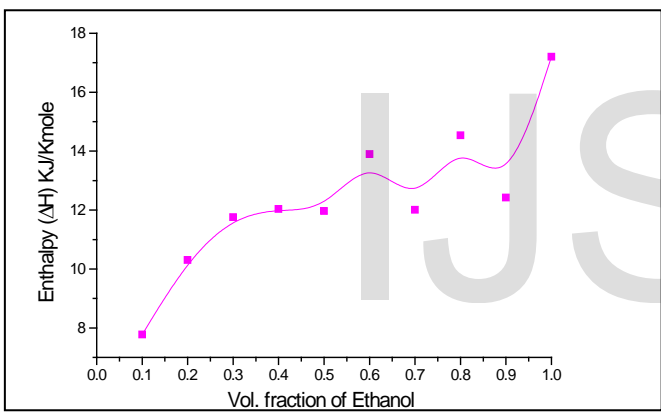

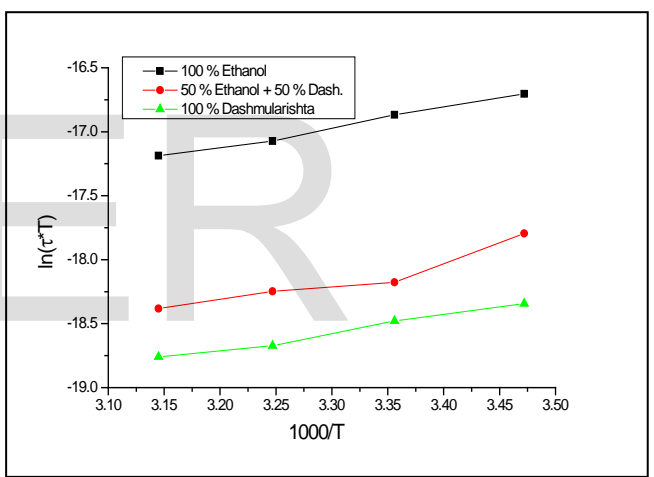Figure E: Variation of   Enthalpy for Dashmularishta + Ethanol

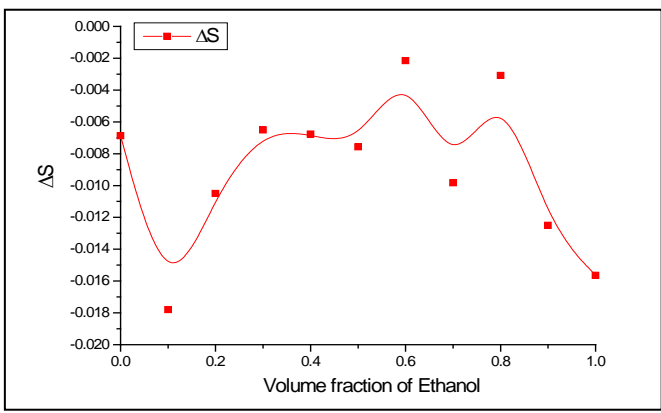Figure H:Arrehenius plot for Dashmularishta+Ethanol

Figure F: Variation of entropy for Dashmularishta+Entropy

4.CONCLUSIONS

Table : Summary of results for Dashmularista + Ethanol

Property	Dashmularishta + Ethanol
1) Bruggeman factor (F_b)	Experimental and theoretical values agree with each other.
The value of 'a' in modified Bruggeman mix-ture formula	0.630 at 15°C 0.658 at 25°C 0.576 at 35°C 0.695 at 45°C
2)Activation energy (ΔG)	Increases with addition of Etha-nol for all temperatures.
3)Conductivity (σ)	Decreases with addition of Etha-nol for all temperatures.

Bruggeman factor is used as first evidence of molecular interaction .This formula states the static permittivity ofthe mixtures which are related to volume fraction. The realationship between Bruggeman factor and V shows devaition which indicates molecular interact ion and can be observed practically. The values of Bruggeman factor shows repulsive force,attractive force and ideal situations.

Activation energy shows the dynamics of solute-solvent
 interaction,rotation of effective dipoles,etc.The activation energy for every compound increases as the temperature increases,whereas the relaxation time decreases. This is due to decreased viscosity of the medium,which also indicates the activated state is more ordered than the normal one ,as the dipoles try to align with the applied field. The dielectric loss is a parameter which describes the motion of charge,that is conductivity.

Certain dilelectrics are found to display conduction due to charge tranfer,i.e. volume conductivity.

REFERENCES

1. A.C. Kumbharkhane, S. M. Puranic and S. C. Mehro-tra, J. Solution Chemistry20 (1991)12.

2. M. T. Hosamani, R. H. Fattepur, D. K. Deshpande and S. C. Mehrotra, J.Chem.soc. Faraday Trans91 (4) (1995) 623.

3. C. E. Shannon, Proc.IRE, 37 (1949)10.

4. R. H. Cole, J. G. Berbarian,S. Mashimo, G. Chryssikos, A. Burns and E. Tombari, J.Appl.Phys.,66 (1989) 793.

5. P. Debye, polar molecules, Chemical catlog, New York (1929)

6. P.R. Bevington, Data reduction and error analysis for the physical sciences,Mc-Graw Hill, New York (1969)

7. U. R. Lahane ,Structural Molecular Study of Ayurve-dic Medicines Using Dielectric Relaxation Tech.- Ph.D. Thesis ,Feb.(2003)