

Relaxation Study at Microwave Frequency Using Time Domain Reflectometry

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Abstract-The dielectric relaxation study at microwave frequency gives information about solute(Methanol)-solvent (Balantkadha)-interaction and liquid structure of mixture. The objective of the present paper is to report the dielectric relaxation study of above system using Time Domain Reflectometry (TDR) in the temperature range 150C to 450C. The information related to the solute-solvent interaction has been carried out related to the static dielectric permittivity and relaxation time in the mixture of Ayurvedic Medicine-Balantkadha and Methanol. Dielectric relaxation study of Balantkadha used in Gynaec problems has been carried out at 150C, 250C, 350C and 450C in the frequency range 10 MHz to 20 GHz for 11 different concentrations of the system. Time Domain Reflectometry (TDR) Technique in reflection mode has been used to measure dielectric parameters viz. Dielectric loss (ϵ''), Static dielectric permittivity (ϵ') and relaxation Time (τ). Further, Fourier transforms and least square fit method has been used to obtain dielectric parameters. With change in concentration and temperature, the systematic changes in dielectric parameters are observed.

Index Terms — Dielectric loss, Permittivity, Relaxation time, Time domain Reflectometry.

I. EXPERIMENTAL MATERIAL

Balantkadha No.1 (Sandu pharmaceutical Ltd., Kolkata) and Methanol (Changshu Yangyan Chemical, China) were obtained commercially and used without further purification. The solutions were prepared at different volume percentage of Balantkadha no.1 in Methanol at 11 concentrations

II. EXPERIMENTAL METHOD

The dielectric 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 1.52 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 $\pm 1^\circ\text{C}$. 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.

III. DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz. Using Fourier Transformation as,

$$\rho^*(\omega) = (c/j\omega [p(\omega)/ q(\omega)]) \quad (1)$$

Where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t)-R_x(t)]$ and $[R_1(t) + R_x(t)]$ respectively, c is velocity of light, ω is angular frequency, d is effective pin length and the complex permittivity spectra $\epsilon^*(\omega)$ were $j = \sqrt{-1}$ obtained from reflection coefficient $\rho^*(\omega)$ spectra by applying a bilinear calibration method⁸. The example of $\rho^*(\omega)$ and $\epsilon^*(\omega)$ spectra are shown in Fig. 1(a) and (b) respectively.

The experimental value of ϵ^* are fitted with the Debye equation,

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 - j\omega\tau]} \quad (2)$$

With ϵ_0 and τ as fitting parameters. In Eq.2, ϵ_0 is the static permittivity, τ is the relaxation time and ϵ_∞ is the permittivity at high frequency. The value of ϵ_∞ is taken to be 3.0 for all the system studied, as for the frequency range considered here, the ϵ^* is not sensitive with respect to ϵ_∞ . A non-linear Least-Squares fit method used to determine the values of dielectric parameters.

The Frequency dependent complex permittivity spectra $\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega)$, in frequency range of 10 MHz to 20 GHz, for mixture of Balantkadha No.1 and Methanol is presented in this section.

Balantkadha No. 1 (Sandu pharmaceutical Ltd.) and Methanol (Qualigens fine chemicals) were obtained commercially and used without further purification. The solutions were prepared at different volume percentage of Balantkadha No. 1 in Methanol in steps of 10% vol., within 0.01% error limit. The experiment is performed for 11 concentrations, at 15°C , 25°C , 35°C and 45°C temperatures. The relative change in dielectric parameters with increasing concentrations of solute and temperature are presented in this section. The bilinear calibration method is used to obtain complex permittivity $\epsilon^*(\omega)$ from complex reflection coefficient $\rho^*(\omega)$. Reflection coefficient spectra $\rho^*(\omega)$ for pure

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Methanol is used to correct $\rho^*(\omega)$ of entire concentrations range at each temperature. The corrected data for each mixture is fitted to Debye equation to obtain static permittivity (ϵ_0) and relaxation time (τ). As the frequency range of dielectric investigation in present work is from 10 MHz to 20 GHz, the value of (ϵ_0) obtained is just fitting parameter. This value does not correspond to real value of permittivity which one gets after completion of dispersion processes related to vibration and electronic motions in liquid. It is found reasonably satisfactory procedure to keep value (ϵ_∞) fix. In the present work value of (ϵ_∞) is kept fix to 3.00.

The corrected spectra $\epsilon^*(\omega)=\epsilon'(\omega)-j\epsilon''(\omega)$ for mixtures of Balantkadha No. 1 - Methanol system for different concentrations at 35°C is shown in fig..A. Gradual decrease in permittivity and dielectric loss with increasing volume fraction of Methanol can be observed from this fig. The fall in permittivity starts at low frequency for Balantkadha No. 1 rich region but this point shifts to higher frequency in Methanol rich region. This indicates small change in alignment of molecular dipoles with addition of Methanol in Balantkadha No. 1.

The Cole - Cole plot for Balantkadha No. 1 and Methanol system at 35°C is shown in fig..B. The Cole Cole plot follows the Debye semicircle, which indicates that relaxation process in Balantkadha No. 1 -Methanol system can be explained with single relaxation time.

Static permittivity and relaxation time

The Values of static permittivity (ϵ_0) and relaxation time (τ) of Balantkadha No.1 –Methanol system for 11 different concentrations at four temperatures are listed in table .1A and 1B. The Variation in static permittivity (ϵ_0) with increasing volume fraction of Methanol is shown in fig C. Static permittivity of mixture decreases linearly with increasing volume fraction of Methanol. Decrease in permittivity with increasing temperature is also observed for all concentrations. This fall in permittivity with increasing amount of solute indicates linear increase in effective dipole moment of the system.

The variation in relaxation time (τ) with increasing volume fraction of Methanol is shown in fig..D. Relaxation time increases with increasing volume of Methanol in solution. Raise in relaxation time (τ) is slow up to 50% Balantkadha No. 1 - Methanol solution. With increase in volume fraction of Methanol above 50%, relaxation time rises fast. Gradual decrease in relaxation time with increasing temperature is also observed for all concentrations. Fast increase in relaxation time in Methanol rich region shows that there is significant change in size of molecular structures in this region. The slow increase in relaxation time indicates decrease in density of larger molecular structures in solutions. This increase in relaxation time indicates increase in amount of hydrogen bonding between solute and solvent molecules, which leads to smaller molecular structures rotating fast.

Excess permittivity (ϵ^E) and excess inverse relaxation time ($1/\tau^E$)

The structural changes in binary mixture can explored by determining excess properties. The plot of excess

permittivity (ϵ^E) and excess inverse relaxation time ($1/\tau^E$) with change in volume fraction of Methanol is shown in fig .E & .F. The values of ($1/\tau^E$) and (ϵ^E) are fitted to Redlich - Kister equation The values of excess permittivity are positive for all concentrations and at all temperature. The positive values of excess permittivity in mixture indicate increase in effective dipole moments, in proportion to their vol. fraction, in pure liquids. This increase in effective dipole moment can be attributed to formation of new smaller structures, may be due to hydrogen bonding, with dipole moment more than addition of dipole moments of constituting molecules. The decrease in relaxation time from value of pure Methanol to 100% Balantkadha No. 1 can be explained with breaking of hydrogen bonds in mixture. Further increase in volume fraction of Balantkadha No. 1 increases density of comparatively smaller molecules, which leads to decrease in relaxation time. It must be noted that this decrease in relaxation time is rapid which shows formation of smaller structures.

The excess inverse relaxation time ($1/\tau^E$) reveals speed of rotation of molecular structure. The value of ($1/\tau^E$) gives us frequency at which dielectric loss is maximum. Positive value of ($1/\tau^E$) shows increase in frequency at which peak value of dielectric loss occurs.

IV. BRUGGEMAN FACTOR

The experimental values together with ideal and theoretical values of Bruggeman of (f_B), plotted against change in volume fraction of Methanol are shown in fig..G. The values of Bruggeman factor (f_B) of Balantkadha No. 1 - Methanol system for 11 different concentrations at four-temperature are listed in table 2A and 2B The Bruggeman mixture formulae state linear relationship between (f_B) and volume fraction of solvent by assuming that there is no interaction between solute and solvent. Modified Bruggeman mixture formula can be used if two components in binary mixture interact. The experimental value of (f_B) for Balantkadha No. 1 –Methanol is fitted to modify Bruggeman mixture formula. When value of numerical fitting parameter “a” is unity, modified Bruggeman mixture formula reduces to original Bruggeman mixture formula. Decrease in value of “a” below unity shows increase in effective volume fraction of solvent in mixture. The small values of “a” indicates significant expansion in effective volume of solvent as well as weak interaction between solute and solvent. Furthermore values of “a” changes remarkably with change in temperature, which shows temperature dependent nature of molecular interactions.

V. THERMODYNAMIC PARAMETERS

Arrhenius plot i.e. plot of $\log(\tau T)$ verses $1000/T$ for Balantkadha No. 1 – Methanol system is shown in the fig L. The nature of plot is almost linear. The values of molar enthalpy of activation (ΔH) in KJ/Mole, and Entropy (ΔS) in $J/0^0$ Kmole, obtained from Eyring's equation are given in table 3A. The values of (ΔH) and (ΔS) decreases with increases in a volume fraction of Balantkadha No. 1 in Methanol. The value of activation enthalpy gives an idea about nature of compactness in molecules of liquid. The smaller value

of (ΔH) shows weaker hydrogen bonding in solute and solvent with decrease in Balantkadha No. 1 concentration in mixture. The plot of change in enthalpy and entropy with variation in vol. fraction of Methanol is shown in fig. I and fig.J. The variation in free energy of activation with volume fraction of Methanol in solution is shown in fig.K. The variation of conductivity for Balantkadha No. 1 with volume fraction of Ethanol is shown in fig.H.

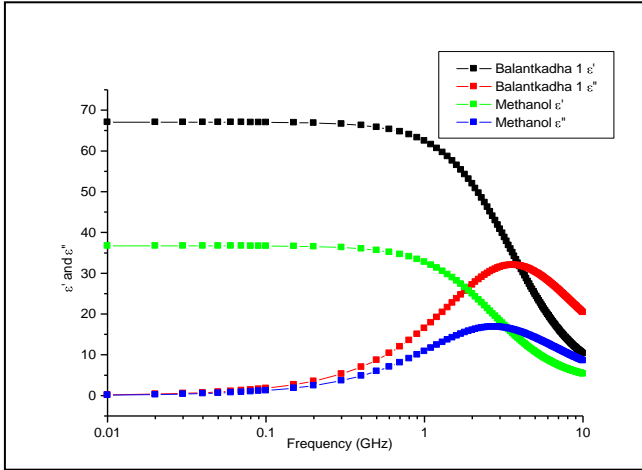


Figure.A: Corrected data for Balantkadha No. 1 + Methanol mixture at 35^oC.

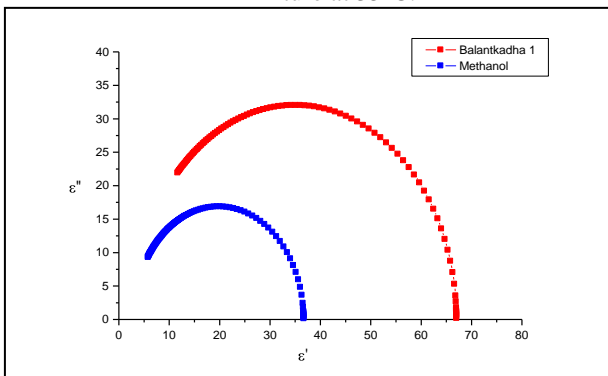


Figure.B: Cole -Cole plot for Balantkadha No. 1 + Methanol.

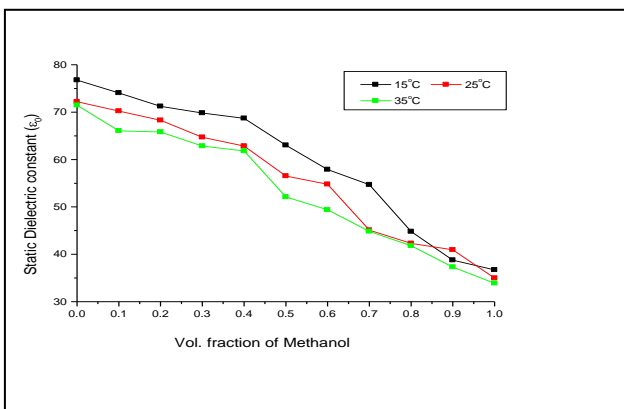


Figure C: Variation of permittivity (ϵ_0) with vol. fraction of Methanol at various temperatures for Balantkadha No. 1

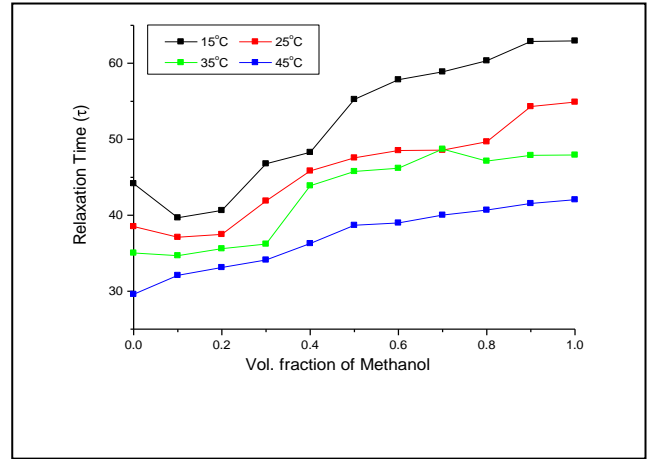


Figure.D: Variation of relaxation time (τ) with vol. fraction of Methanol at various temperature for Balantkadha No. 1

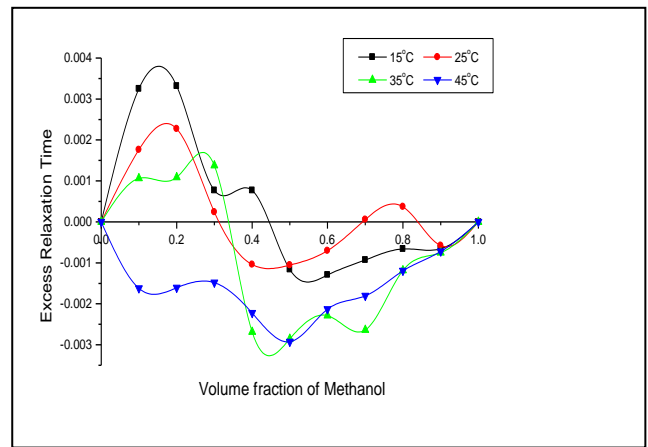


Figure.E: Variation of excess permittivity (ϵ^E) with vol. fraction of Methanol in Balantkadha No. 1 at various temperatures

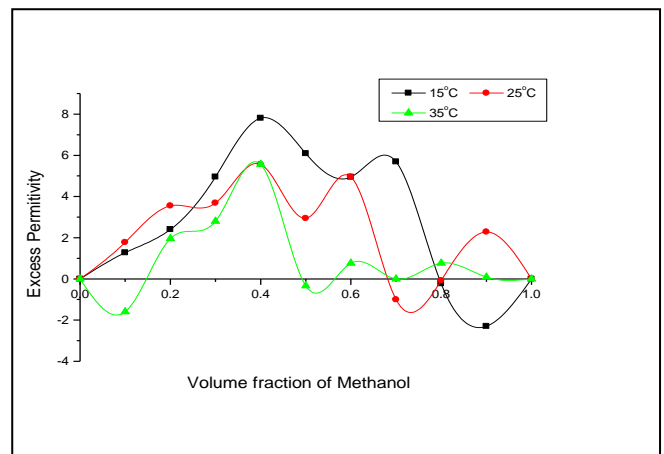


Figure.F: Variation of excess inverse relaxation time ($(1/\tau)^E$) with vol. fraction of Methanol at various temperatures for Balantkadha No. 1

Table2A. Bruggeman factor for Balantkadha No. 1- Methanol mixture

| Vol. fraction of Methanol | Ideal value for F_b | 15 °C, a=1.100 | | 25 °C, a=1.120 | |
|---------------------------|-----------------------|----------------|--------|----------------|--------|
| | | Expt. | Theor. | Expt. | Theor. |
| 0.0 | 1.0 | 1.000 | 1.000 | 1.000 | 1.000 |
| 0.1 | 0.9 | 0.9433 | 0.891 | 0.9563 | 0.889 |
| 0.2 | 0.8 | 0.8822 | 0.784 | 0.9120 | 0.780 |
| 0.3 | 0.7 | 0.8514 | 0.679 | 0.8286 | 0.674 |
| 0.4 | 0.6 | 0.8269 | 0.576 | 0.7847 | 0.571 |
| 0.5 | 0.5 | 0.6980 | 0.475 | 0.6283 | 0.47 |
| 0.6 | 0.4 | 0.5764 | 0.376 | 0.5842 | 0.371 |
| 0.7 | 0.3 | 0.4965 | 0.279 | 0.3193 | 0.274 |
| 0.8 | 0.2 | 0.2324 | 0.184 | 0.2364 | 0.180 |
| 0.9 | 0.1 | 0.0529 | 0.091 | 0.1949 | 0.089 |
| 1.0 | 0.0 | 0.000 | 0.000 | 0.000 | 0.000 |

Table2B.: Bruggeman factor for Balantkadha No. 1- Methanol mixture

| Vol. fraction of Methanol | Ideal value for F_b | 35 °C, a=0.824 | | 45 °C, a=1.035 | |
|---------------------------|-----------------------|----------------|--------|----------------|--------|
| | | Expt. | Theor. | Expt. | Theor. |
| 0.0 | 1.0 | 1.000 | 1.000 | 1.000 | 1.000 |
| 0.1 | 0.9 | 0.944 | 0.915 | 0.926 | 0.896 |
| 0.2 | 0.8 | 0.868 | 0.828 | 0.853 | 0.794 |
| 0.3 | 0.7 | 0.781 | 0.736 | 0.795 | 0.692 |
| 0.4 | 0.6 | 0.680 | 0.642 | 0.692 | 0.591 |
| 0.5 | 0.5 | 0.565 | 0.544 | 0.583 | 0.491 |
| 0.6 | 0.4 | 0.456 | 0.442 | 0.481 | 0.391 |
| 0.7 | 0.3 | 0.343 | 0.336 | 0.362 | 0.292 |
| 0.8 | 0.2 | 0.229 | 0.228 | 0.254 | 0.194 |
| 0.9 | 0.1 | 0.117 | 0.115 | 0.156 | 0.096 |
| 1.0 | 0.0 | 0.000 | 0.000 | 0.000 | 0.000 |

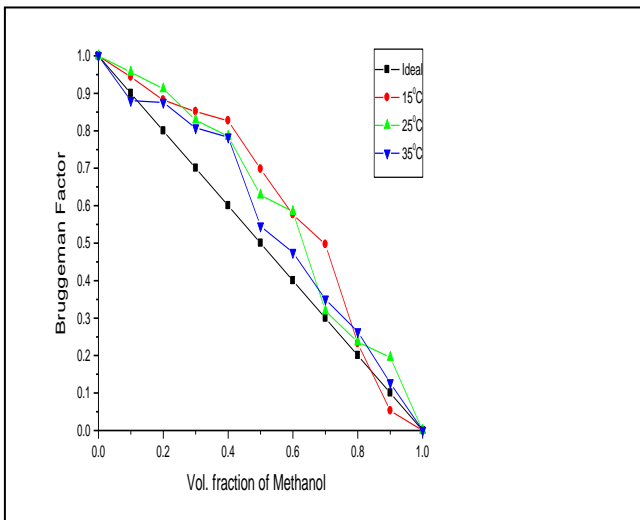


Figure.G : Variation of Bruggeman factor (F_b) with vol. fraction of Methanol in Balantkadha No. 1 at various temperatures

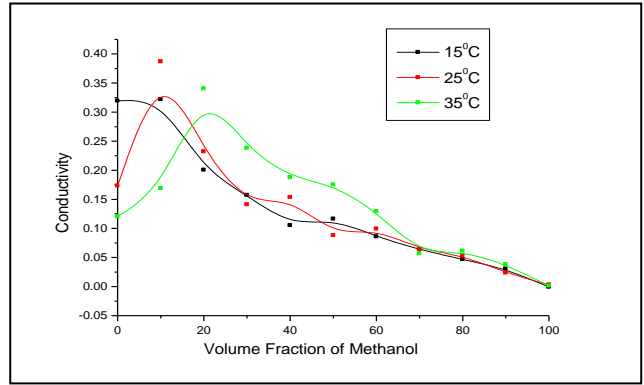


Figure.H : Variation of conductivity for Balantkadha No. 1 with vol. fraction of Methanol at various temperatures.

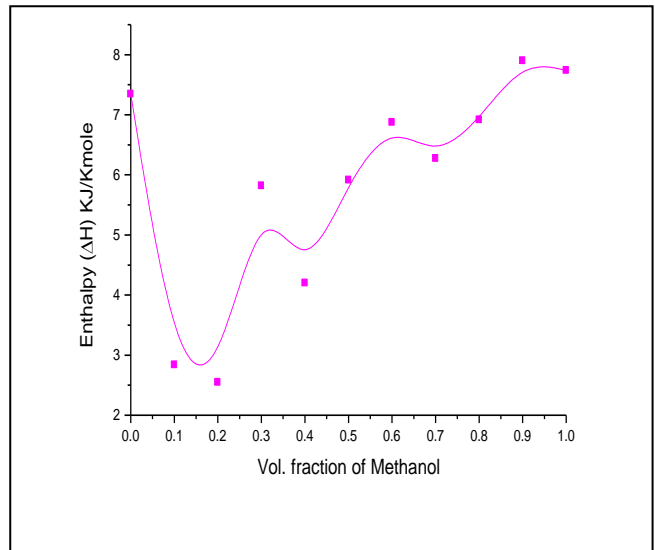


Figure.I Variation of Enthalpy for Balantkadha No. 1 + Methanol

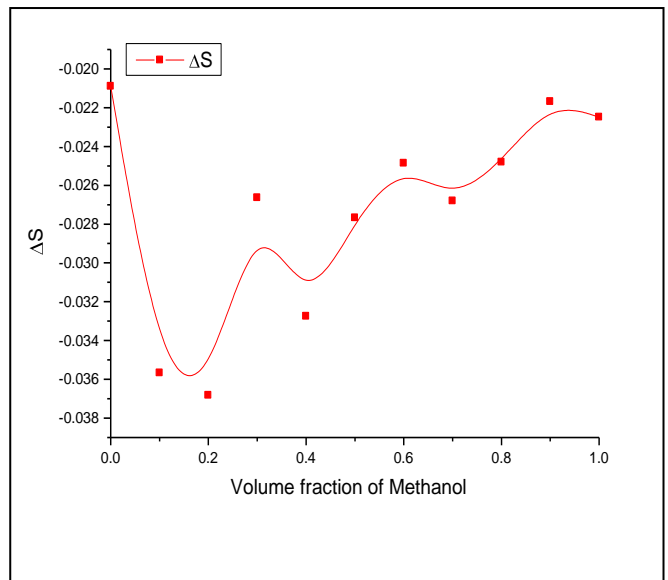


Figure.J Variation of Entropy for Balantkadha No. 1 + Methanol

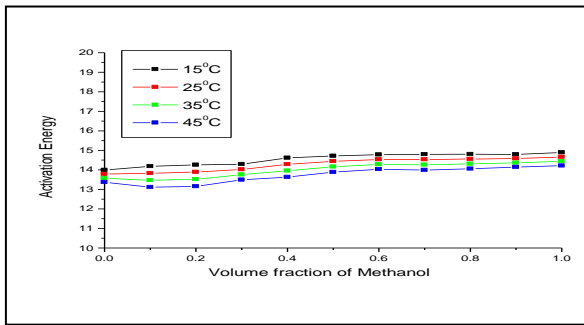


Figure.K Variation of free energy of activation for Balantkadha No. 1 + Methanol

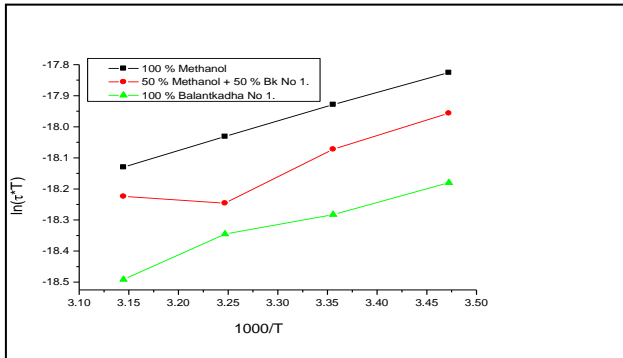


Figure.L Arrhenius plot of Balantkadha No. 1 + Methanol mixture

Table .1.A: Static Dielectric constant for Balantkadha at different temperatures

| Vol. fraction of Ethanol | Static Dielectric constant (ϵ_0) | | | |
|--------------------------|---|-------------------|-------------------|-------------------|
| | 15 ⁰ C | 25 ⁰ C | 35 ⁰ C | 45 ⁰ C |
| 0.0 | 74.67 | 72.71 | 71.37 | 69.29 |
| 0.1 | 70.47 | 69.28 | 68.13 | 64.90 |
| 0.2 | 68.24 | 65.21 | 63.78 | 60.68 |
| 0.3 | 62.48 | 60.51 | 58.98 | 57.43 |
| 0.4 | 57.72 | 54.56 | 53.66 | 51.86 |
| 0.5 | 52.83 | 50.58 | 47.92 | 46.25 |
| 0.6 | 47.08 | 44.76 | 42.81 | 41.35 |
| 0.7 | 41.74 | 39.44 | 37.84 | 35.98 |
| 0.8 | 36.27 | 34.69 | 33.19 | 31.49 |
| 0.9 | 31.88 | 29.57 | 28.99 | 27.72 |
| 1.0 | 28.12 | 26.24 | 24.94 | 22.30 |

Table .1.B: Relaxation Time (t) for Balantkadha at different temperatures

| Vol. fraction of Ethanol | Relaxation Time (τ) | | | |
|--------------------------|----------------------------|-------------------|-------------------|-------------------|
| | 15 ⁰ C | 25 ⁰ C | 35 ⁰ C | 45 ⁰ C |
| 0.0 | 15.0 | 25.0 | 35.0 | 45.0 |
| 0.0 | 31.91 | 28.51 | 26.68 | 24.49 |
| 0.1 | 36.67 | 32.85 | 30.56 | 26.22 |
| 0.2 | 44.62 | 36.73 | 33.63 | 28.84 |
| 0.3 | 50.33 | 40.31 | 37.13 | 32.66 |
| 0.4 | 57.67 | 43.61 | 38.26 | 35.35 |
| 0.5 | 63.69 | 49.81 | 44.25 | 37.13 |
| 0.6 | 71.93 | 55.12 | 48.89 | 41.65 |
| 0.7 | 86.03 | 64.95 | 55.92 | 47.26 |
| 0.8 | 103.4 | 82.73 | 67.57 | 56.48 |
| 0.9 | 127.1 | 105.4 | 86.12 | 69.63 |
| 1.0 | 194.4 | 150.7 | 125.9 | 108.4 |

Table no 3A Activation Enthalpy and Entropy of Balantkadha No. 1 - Methanol

| Vol. fraction of Ethanol | Entropy (ΔS) J/ ⁰ Kmole | Enthalpy(ΔH) KJ/Kmole |
|--------------------------|--|---------------------------------|
| 0.0 | -0.02977 | 3.99 |
| 0.1 | -0.02527 | 5.469 |
| 0.2 | -0.01801 | 8.162 |
| 0.3 | -0.0194 | 8.019 |
| 0.4 | -0.01427 | 9.77 |
| 0.5 | -0.01227 | 10.65 |
| 0.6 | -0.01216 | 10.954 |
| 0.7 | -0.00872 | 12.374 |
| 0.8 | -0.0092 | 12.739 |
| 0.9 | -0.01097 | 12.759 |
| 1.0 | -0.01603 | 12.24 |

VI. CONCLUSIONS

| Property | Balantkadha No. 1 + Methanol |
|--|--|
| 1) Static permittivity (ϵ_0) | Decreases with addition of Methanol in Balantkadha No. 1. |
| 2) Relaxation time (τ) | Increases with addition of Methanol in Balantkadha No. 1. |
| 3) Excess permittivity (ϵ^E) | Almost all Positive values occur. Peak value at 40% of Methanol and 60% of Balantkadha No. 1. |
| 4) Excess inverse relaxation time ($(1/\tau)^E$) | Positive values upto 30% Ethanol and after that negative values occur with peak value at 20% of Methanol and 80% of Balantkadha No. 1. |
| 5) Bruggeman factor (F_b) | Experimental and theoretical values agree with each other. 1.1 at 15 ⁰ C 1.12 at 25 ⁰ C 1.0043 at 35 ⁰ C |
| The value of 'a' in modified Bruggeman mixture formula | Increases with addition of Methanol for all temperatures. |
| 6) Activation energy (ΔG^\ddagger) | Decreases with addition of Methanol for all temperatures. |
| 7) Conductivity (σ) | |

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